

# JOURNAL OF THE CHEMICAL SOCIETY.

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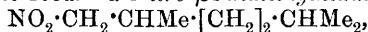
ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
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### PART I.

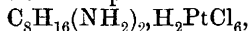
#### Organic Chemistry.

**Action of Nitric Acid on Saturated Hydrocarbons. Nitration of Saturated Hydrocarbons containing two *iso*Propyl Groups. XIV. & XV.** MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 109—123, 124—141. Compare Abstr., 1905, i, 764).— $\beta\epsilon$ -Dimethylhexane is best obtained from  $\beta$ -methyl-propyl bromide. When treated with nitric acid, the substances formed depend on: (1) the temperature; (2) whether the experiment is carried out in sealed tubes or in open vessels; (3) the sp. gr. of the nitric acid employed; (4) the duration of heating.

The mononitro- $\beta\epsilon$ -dimethylhexanes.—Under the most favourable conditions 83% of the  $\beta$ -nitro-compound and 17% of a mixture of the  $\alpha$ - and  $\gamma$ -derivatives were obtained.  $\beta$ -Nitro- $\beta\epsilon$ -dimethylhexane,  $\text{NO}_2\cdot\text{CMe}_2\cdot[\text{CH}_2]_2\cdot\text{CHMe}_2$ , is a colourless liquid, b. p. 200—201°/760 mm.,  $D_0^\circ$  0.9396,  $D_{20}^\circ$  0.9205,  $n_D^{15}$  1.43055. In an ethereal or benzene solution, sodium reacts violently with it, forming a characteristic metallic compound (*J. Russ. Phys. Chem. Soc.*, 1898, 30, ii, 234; 1902, 34, ii, 45). The corresponding amine, formed by reduction with tin and hydrochloric acid, b. p. about 744°(74.4°)/749 mm.,  $D_0^\circ$  0.7803,  $D_{20}^{22.3}$  0.7605 (in *Ber.*, 1895, 28, 1854, the same author gives b. p. 145°/746.5 mm.,  $n_D^{24.3}$  1.41655). The hydrochloride, m. p. 157—160°, the platinichloride,  $(\text{C}_8\text{H}_{17}\text{NH}_2)_2\text{H}_2\text{PtCl}_6$ , and the normal sulphate, m. p. about 235°, are described.  *$\alpha$ -Nitro- $\beta\epsilon$ -dimethylhexane,*

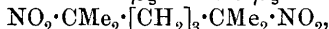


b. p. 100—105°/20 mm. The  $\gamma$ -nitro-compound,  $\text{CHMe}_2 \cdot \text{CH}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , forms a bromo-compound,  $\text{CHMe}_2 \cdot \text{CBr}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{CHMe}_2$ ,  $D_0^\circ$  1.3211,  $D_D^{20}$  1.3033, and  $n_D^{20}$  1.47857.  $\beta$ -Dinitro- $\beta$ -dimethylhexane,  $\text{NO}_2 \cdot \text{CMe}_2 \cdot [\text{CH}_2]_2 \cdot \text{CMe}_2 \cdot \text{NO}_2$ , crystallises from benzene in colourless, odourless scales resembling naphthalene, m. p. 124—125°, distils and decomposes under ordinary pressure. The formula is deduced: (1) from its insolubility in alkalis; (2) its formation from the corresponding  $\beta$ -mononitro-compound. Zinc dust and acetic acid, but not tin and hydrochloric acid, readily reduce it to the corresponding amine, a colourless liquid, b. p. 186°/753 mm.,  $D_0^\circ$  0.8580,  $D_D^{14.5}$  0.8485, and  $n_D^{14.5}$  1.45062. The following salts all decompose at their melting points: the *hydrochloride* and *hydrobromide*, above 300°; the *nitrate*, at 226°; the *picrate*, at 293°; the *oxalate*, at 269—270°; and the *aureibromide*, at 295—300°. The platinichloride,



and the *dibenzoyl* derivative,  $\text{C}_8\text{H}_{16}(\text{NH}\text{Bz})_2$ , m. p. 215°, were obtained.

$\beta\zeta$ -Dimethylheptane,  $\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CHMe}_2$ , b. p. 134—135°/747 mm.,  $D_0^\circ$  0.7265,  $D_D^{16}$  0.7144, and  $n_D^{16}$  1.40270 (compare Wurtz, *Jahresber.*, 1855, 575). It is conveniently nitrated at 120°, using nitric acid  $D$  1.075, the chief product of the reaction being the  $\beta$ -mononitro-derivative,  $\text{NO}_2 \cdot \text{CMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CHMe}_2$ , b. p. 113—115°/25 mm.,  $D_0^\circ$  0.9281,  $D_D^{18}$  0.9150, and  $n_D^{18}$  1.43256. Tin and hydrochloric acid reduce the nitro-compound, forming  $\beta$ -amino- $\beta\zeta$ -dimethylheptane, b. p. 165.5—166.5°/754 mm.,  $D_0^\circ$  0.7860,  $D_D^{20}$  0.7533, and  $n_D$  1.42455. The *hydrochloride*, *nitrate*, *sulphate*, and *picrate* are all well-defined, crystalline salts. The *platinichloride*,  $(\text{C}_9\text{H}_{19}\text{NH}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , blackens at 200° and does not melt below 255°.  $\beta\zeta$ -Dinitro- $\beta\zeta$ -dimethylheptane,



crystallises in flat needles, m. p. 74—74.5°, and cannot be distilled unchanged. Zinc dust and acetic acid reduce it to  $\beta\zeta$ -diamino- $\beta\zeta$ -dimethylheptane, which does not solidify at -15°, and has b. p. 204—206°/749 mm.,  $D_0^\circ$  0.8544,  $D_D^{24.5}$  0.8388, and  $n_D^{24.5}$  1.4481. The *hydrochloride* does not melt even at 241°, but darkens at 195°. The *dibenzoyl* derivative,  $\text{C}_9\text{H}_{18}(\text{NH}\cdot\text{COPh})_2$ , m. p. 159—160°, distils without decomposition, but in the presence of ammonium chloride a new substance is formed.

$\beta\eta$ -Dimethyloctane,  $\text{CHMe}_2 \cdot [\text{CH}_2]_4 \cdot \text{CHMe}_2$ , can be nitrated both in closed and open vessels. The products obtained and the progress of the reaction depend on the same circumstances as in the case of the heptane hydrocarbon. When concentrated nitric acid is employed, vigorous oxidation is also noticeable. The process of nitration is greatly facilitated by the removal of the nitro-compounds as formed, and also by the use of nitric acid which has been used in previous experiments. Mercuric nitrate yields no nitro-derivatives when the experiment is performed in an open vessel, whilst aluminium and bismuth nitrates give chiefly  $\alpha$ - and  $\gamma$ -nitro-derivatives. In a sealed tube, aluminium nitrate reacts vigorously only when dry. An attempt to find a sharper reaction than Meyer's for identifying and separating  $\alpha$ - and  $\gamma$ -nitro-derivatives has not led to any conclusive results so far.

$\alpha$ -Nitro- $\beta\eta$ -dimethyloctane,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot [\text{CH}_2]_4 \cdot \text{CHMe}_2$ , is often

obtained almost pure by nitrating the hydrocarbon with concentrated nitric acid; b. p. 125—127°/17 mm., or 235—237°/760 mm., then decomposing;  $D_0^0$  0·94176,  $D_0^{21}$  0·9246, and  $n_D^{21}$  1·4426. Tin and hydrochloric acid reduce it, giving the corresponding *amine* and the *aldehyde*,  $\text{CHMe}_2 \cdot [\text{CH}_2]_4 \cdot \text{CHMe} \cdot \text{CHO}$ , which is also formed by the action of concentrated nitric acid on  $\beta\eta$ -dimethyloctane; it has b. p. 184·5—185°/744 mm.,  $D_0^0$  0·8356,  $D_0^{20}$  0·8204.  $\gamma$ -(or  $\delta$ )Nitro- $\beta\eta$ -dimethyloctane, obtained by treating the hydrocarbon with nitric acid,  $D$  1·075, has b. p. 129—132°,  $D_0^{20}$  0·9115. On reduction with tin and hydrochloric acid, it yields the corresponding amine, b. p. 190—192°,  $D_0^{20}$  0·7934; a small quantity of a *ketone*, b. p. 190—192°, is also formed.  $\beta$ -Nitro- $\beta\eta$ -dimethyloctane is a colourless liquid solidifying in a mixture of solid carbon dioxide and ether, b. p. 125°/22·5 mm., or 135—137°/749 mm., when it decomposes;  $D_4^{20}$  0·9092,  $n_D^{20}$  1·43570. It is reduced by tin and hydrochloric acid to the corresponding amine, b. p. 190°/758 mm.,  $D_0^{20}$  0·7815, and  $n_D$  1·42793. With sodium, the  $\beta$ -nitro-derivative reacts violently, forming a characteristic *sodium* derivative.  $\beta\eta$ -Dinitro- $\beta\eta$ -dimethyloctane, m. p. 101·5—102°; the heat of combustion is 1513·614 Cal. per gram mol. When its ethereal solution is heated with sodium in a sealed tube, a mixture of hydrocarbons is obtained, b. p. 165—170°, and having a composition which lies between  $\text{C}_{10}\text{H}_{20}$  and  $\text{C}_{10}\text{H}_{18}$ . These hydrocarbons are either similar to or identical with the substances obtained from the dry distillation of the hydrochloride of the diamine,  $\text{C}_{10}\text{H}_{20}(\text{NH}_2)_2$ . Zinc dust and acetic acid reduce the dinitro-derivative forming the corresponding diamine which forms crystals, m. p. 31°, b. p. 228·5°/747 mm.,  $D_0^{28}$  0·8344, and  $n_D^{28}$  1·4485. When exposed to air it absorbs carbon dioxide, forming a solid salt. The hydrochloride, m. p. 168—170°, the *hydrobromide*, m. p. 265°, the sulphate, m. p. above 300°, the *oxalate*, m. p. 292·5—293°, the *picrate*, m. p. 255—256°, and the *auribromide*, m. p. 220—222°, all decompose at their melting point. The platinichloride,  $\text{C}_{10}\text{H}_{20}(\text{NH}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , forms shiny, orange-yellow, prismatic crystals. The *benzoyl* derivative,  $\text{C}_{10}\text{H}_{20}(\text{NHBz})_2$ , m. p. 206·5—207°. Z. K.

**Constitution of the Acetylidene Compounds.** JAMES W. LAWRIE (*Amer. Chem. J.*, 1906, 36, 487—510).—An extension of Nef's views (*Abstr.*, 1898, i, 105, 114) as to the halogen-substituted derivatives of acetylene. The author considers that it is now proved that all the known mono- and di-halogen derivatives of acetylene belong to the acetylidene series, whilst the existence of corresponding compounds with the acetylene constitution is considered improbable.

When well-cooled dibromoacetylidene is added to aqueous hydriodic acid,  $D$  1·96, combination takes place with formation of dibromo-iodoethylene together with some dibromodi-iodoethylene. *Dibromo-iodoethylene*,  $\text{CBr}_2 \cdot \text{CHI}$ , is a sweet smelling oil, b. p. 91°/15 mm.,  $D^{24}$  2·952. The constitution of this substance was ascertained by the following experiments. When dibromoiodoethylene is treated with fuming nitric acid at  $-10^\circ$ , it is converted into dibromoacetic acid and iodine. Tribromoethylene undergoes a similar oxidation. The formation of dibromoacetic acid in these reactions is explained as follows. The dibromoiodoethylene or tribromoethylene is dissociated into

hydrogen iodide or bromide and dibromoacetylidene,  $\text{CBr}_2\cdot\text{C}$ ; the latter compound is oxidised to dibromoacetylidene oxide,  $\text{CBr}_2\cdot\text{CO}$ , and this absorbs water with production of dibromoacetic acid. In confirmation of this, it has been observed that tribromo- and tetrabromoethylene unite directly with oxygen at  $50^\circ$  with formation of dibromo- and tribromo-acetyl bromides respectively.

When dry oxygen is passed through a mixture of dibromoacetylidene and alcohol, carbon monoxide is evolved and tetrabromoethylene, oxalic acid, and dibromoacetic acid are produced. The reactions which take place are as follows: (1) the main reaction ( $78.4^\circ/\text{o}$ ),  $2\text{C}_2\text{Br}_2 + \text{O}_2 = \text{C}_2\text{Br}_4 + 2\text{CO}$  (including some  $\text{CO}_2$ ); (2) ( $15.54^\circ/\text{o}$ ),  $\text{C}_2\text{Br}_2 + \text{O}_2 = \text{COBr}\cdot\text{COBr}$ ; and (3) ( $6.06^\circ/\text{o}$ ),  $2\text{C}_2\text{Br}_2 + \text{O}_2 + 2\text{EtOH} = 2\text{CHBr}_2\cdot\text{CO}_2\text{Et}$ .

When dibromiodoethylene or tribromoethylene is treated with alcoholic sodium phenoxide, a large yield of phenyl dibromovinyl ether,  $\text{CBr}_2\cdot\text{CH}\cdot\text{OPh}$ , is obtained,  $D^{25} 1.799$ . If this ether is treated with fuming nitric acid at  $-10^\circ$ , it is converted into a mixture of isomeric dinitrophenyl dibromoacetates,  $\text{CHBr}_2\cdot\text{CO}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ . It is evident, therefore, that in dibromoacetylidene both the bromine atoms are attached to the same carbon atom. Further, since the dibromiodoethylene obtained by the action of iodine on dibromoacetylidene (Lemoult, *Abstr.*, 1903, i, 596) is identical with that obtained by Nef (*Abstr.*, 1898, i, 114) by the action of bromine on di-iodoacetylidene, it follows that di-iodoacetylidene must have the constitution  $\text{CI}_2\cdot\text{C}$ .

When phenyl dibromovinyl ether is heated at  $100^\circ$  in presence of alcohol, water, or acetic acid, it loses hydrogen bromide and is converted into phenol and bromoacetic acid or its ester. E. G.

**Bromine as a Differential Reagent for Isomeric Secondary and Tertiary Aliphatic Alcohols.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 424—435).—The action of bromine on the secondary and tertiary aliphatic alcohols containing from four to nine atoms of carbon has been investigated, and it is shown that the replacement by bromine of hydrogen attached to the carbon united to the hydroxyl group or, in the case of tertiary alcohols, the hydrogen attached to the carbon contiguous to this, takes place the less readily the more hydrogenated these groups are.

In general the secondary alcohols react energetically and even almost explosively with bromine at the ordinary temperature, and an intermediate compound appears to be formed, hydrogen bromide being evolved only at the end of the reaction. The tertiary alcohols, on the contrary, do not react immediately with bromine in the cold even on exposure to sunlight, but action takes place rapidly in most cases on warming, hydrogen bromide being evolved, however, only at the end of the reaction. The changes observed on the addition of bromine to a number of these alcohols are described in detail in the original, and it is pointed out that the tertiary alcohols do not all begin to react with bromine at the same temperature, and, similarly, when the reaction is carried out in the cold, the periods of time which elapse before action commences also differ. It is considered that bromine, like oxalic and

hydrochloric acids and acetyl chloride, may be used in the way indicated to distinguish between secondary and tertiary aliphatic alcohols, but it is only applicable in the cases of simple alcohols in which the alcoholic function is not modified by the previous introduction of other radicles.

T. A. H.

### Catalytic Reactions at High Temperatures and Pressures.

**X. Influence of Pressure.** WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 63—75. Compare Abstr., 1904, ii, 645).—At high pressures, the catalytic decomposition of alcohol with alumina as catalyst is considerably diminished, as shown (1) by the slowness of the reaction, (2) by its remaining at the first stage, for example,  $2\text{EtOH} \rightleftharpoons \text{OEt}_2 + \text{H}_2\text{O}$ . The apparatus previously employed has now been so modified that any quantity of gas can be forced into the reaction tube and its pressure determined, after which the tube can be disconnected from the gas supply and heated. At temperatures above  $450^\circ$  and pressures near to 26 atmos., hydrogen in presence of iron reduces the decomposition products of aldehyde, forming saturated hydrocarbons, but neither carbon dioxide up to 50 nor nitrogen up to 78 atmos. pressure has any influence on the course of the catalytic decomposition of alcohol. When the experiments were performed in iron tubes, the residual liquid contained undecomposed alcohol, aldehyde, and higher unsaturated hydrocarbons,  $\text{C}_n\text{H}_{2n}$ , formed by the polymerisation of ethylene. Ethylene very readily polymerises when heated in a sealed tube at  $400\text{--}450^\circ$  in the presence of iron or copper, but at very high temperatures much ethane, methane, and hydrogen are also obtained as by-products. In the presence of an excess of hydrogen more gaseous hydrocarbons, chiefly methane, are obtained. The reaction always tends to an equilibrium, after which further heating no longer produces any change in pressure or in the proportion of the substances formed. In the presence of reduced nickel as catalyst, ethane and methane are produced. Time and pressure curves are given for the polymerisation of ethylene at various temperatures, from which it is observed that  $(dp/dt)_{\text{max.}}$  varies considerably between  $400^\circ$  and  $450^\circ$ .

Z. K.

### Catalytic Reactions at High Temperatures and Pressures.

**XI. Reducing Catalysts.** WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 75—92. Compare preceding abstract).—In order to arrive at an explanation of the catalytic decomposition of the alcohols, it is possible either to heat alcohols with catalysts in sealed tubes, or to allow aldehydes or ketones to react with hydrogen in presence of catalysts. When acetaldehyde was heated with dry hydrogen in the presence of iron at  $400\text{--}450^\circ$  under 60 atmos. pressure, no variation in pressure occurred and only the ordinary products of its decomposition were obtained. When acetone was heated in a similar manner at  $400^\circ$  and 107 atmos. pressure, the pressure steadily diminished, but equilibrium was reached after sixteen hours. The gaseous products obtained were small quantities of olefines and carbon dioxide, 80% of hydrogen, and 16% of paraffins, whilst the liquid products were probably olefines and some isopropyl alcohol.

Similar experiments and at various temperatures and pressures were performed, using reduced nickel as catalyst (*Compt. rend*, 1903-4-5), and time-pressure curves are drawn for acetone, methyl ethyl ketone, benzaldehyde, and camphor. Under high pressures and with excess of hydrogen, ketones are converted quantitatively into secondary alcohols. Aromatic aldehydes are reduced first to aromatic and finally to polymethylene hydrocarbons. Fatty alcohols and also ethyl ether do not decompose below 300°. The reducing action is slow and reached a maximum, aldehydes and saturated hydrocarbons being produced. If hydrogen is not previously introduced, carbon monoxide is also formed. No olefines are produced in either case, since reduced nickel causes the change  $C_2H_4 \rightarrow C_2H_6$  to take place even at low temperatures. Experiments on benzene derivatives show that the benzene nucleus is not hydrogenated even at very high pressure (220 atmos.) and temperatures in presence of copper, aluminium, or iron. In the presence of reduced nickel the reduction of the nucleus proceeds slowly,  $dp/dt$  never reaching a very high value, and side chains containing oxygen in whatever form are completely reduced, thus  $COPh \cdot CHPh \cdot OH \rightarrow CH_2Ph \cdot CH_2Ph$ . Benzene is converted quantitatively into cyclohexane, whilst phenol probably yields hexanone at low temperatures and hydroxycyclohexane at high ones. Quinol is slowly converted into 1:4-dihydroxycyclohexane, but if the temperature exceeds 300°, the ring is destroyed and methane is the main product. Hexamethylene, when heated in an iron tube under ordinary, or under 150 atmos., pressure, gave benzene, hydrogen, and gaseous paraffins and olefines, whilst hydroxycyclohexane and menthol are converted into cyclic ketones.

Z. K.

**Catalytic Reactions at High Temperatures and Pressures.**  
**XII. Dehydration under the Influence of Alumina.** WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 92-97. Compare preceding abstract).—When isoamyl ether or alcohol is passed through a copper tube containing powdered alumina at 400-450°, the isomeric amylenes and water are produced; the same reaction takes place under high pressures, but in seven hours the pressure reaches a maximum and the reaction becomes reversible. The introduction of considerable quantities of water has no effect on the course of the reaction. When the vapour of acetaldehyde is passed through a copper tube containing alumina at 420-480°, a liquid is obtained consisting chiefly of acetaldehyde and paracetaldehyde, but no gases; isobutaldehyde behaves similarly. When ethylene glycol is heated under ordinary or high pressure, its dehydration proceeds very quickly and is complete in an hour. No gases are formed, the product of the reaction being water, acetaldehyde, and paracetaldehyde, and also small quantities of crotonaldehyde, according to the equation  $OH \cdot CH_2 \cdot CH_2 \cdot OH - H_2O = \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > O \rightarrow CH_3 \cdot CHO \rightarrow (C_2H_4O)_2$ , whilst crotonaldehyde is probably formed from aldol which is yielded by acetaldehyde. When heated at 300-320°, pinacone undergoes the following reaction:  $OH \cdot CMe_2 \cdot CMe_2 \cdot OH = CMe_3 \cdot COMe + H_2O$ . Cyclic alcohols, such as



menthol, borneol, and hydroxycyclohexane, under similar conditions lose water and yield unsaturated cyclic hydrocarbons. Z. K.

### Addition of Hypochlorous Acid to Ethylene Compounds.

LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 523—557).—A critical *résumé* is given of the work done since 1862 by the author on the nature of the chlorohydrins formed by the addition of hypochlorous acid to propylene, isobutylene, and amylene, and the bearing of the results of other investigators on this. The view previously mentioned (Abstr., 1902, i, 417; 1903, i, 2, 725), that with propylene a mixture of  $\alpha$ -chloroisopropyl and  $\beta$ -chloropropyl alcohols is formed, is extended to isobutylene and amylene, and it is suggested that in each of these cases the product formed on the addition of hypochlorous acid consists of a mixture of the two possible isomeric chloro-alcohols. The principal papers referred to are Henry, Abstr., 1874, i, 679, 978; 1875, i, 443; 1876, ii, 284, 620; Markownikoff, Abstr., 1876, i, 338; Michael, 1900, i, 321, [with Leighton] 1906, i, 551, 781, and Krassusky, Abstr., 1901, i, 246. T. A. H.

### [Addition of Hydrogen Chloride to *iso*Butylene Oxide].

LOUIS HENRY (*Ber.*, 1906, 39, 3677—3679).—Polemical, a reply to Michael, Abstr., 1906, i, 781. A. McK.

### Cycles of Reactions which Determine Isomerisation.

MAURICE DELACRE (*Bull. Soc. chim.*, 1906, [iii], 35, 1088—1092. Compare Abstr., 1906, i, 477, 518, 551, 784).—The isomerisation of substances brought about by the action of external agents such as alkalis is of two kinds, irreversible (true molecular transposition) and reversible. If pinacolin may be represented by a single formula, the following cycles of reactions in which two inverse isomerisations occur may be regarded as established: (1)  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OH} \rightarrow \text{CMe}_3\cdot\text{CMe} \rightarrow \text{CMe}_3\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{CMe}_2\cdot\text{CMe}_2 \rightarrow \text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OH}$ . (2)  $\text{CMe}_3\cdot\text{CH}\cdot\text{CH}_2 \rightarrow \text{CMe}_2\cdot\text{CMe}_2 \rightarrow \text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br} \rightarrow \text{CMe}_3\cdot\text{CMe} \rightarrow \text{CMe}_3\cdot\text{CCl}\cdot\text{CH}_2 \rightarrow \text{CMe}_3\cdot\text{CH}\cdot\text{CH}_2$ . In addition, therefore, to the well-authenticated cases of unsymmetrical isomerisation, there must now be recognised cases in which the reverse action takes place almost quantitatively, although it is possible that these are the result of the peculiar structure of pinacolin. T. A. H.

### Friedel's Pinacolyl Acetate. MAURICE DELACRE (*Bull. Soc. chim.*,

1906, [iii], 35, 1093—1094).—The iodide obtained by saturating tetramethylethylene ( $\beta\gamma$ -dimethyl- $\Delta^8$ -butylene) with hydrogen iodide, when warmed with silver acetate and then distilled, regenerates the original hydrocarbon. Similarly, the iodide obtained by treating pinacolyl alcohol with hydriodic acid at  $110^\circ$ , when treated with silver acetate, does not furnish pinacolyl acetate. The author is therefore unable to confirm Friedel's statements on these points (*Dict. chim.*, Wurtz, II, 1025; compare Henry, Abstr., 1906, i, 329, and Delacre, *ibid.*, i, 551). If the production of the acetate from the iodide is eventually realised, it must be assumed that in the above experiments the author has, by working under conditions differing from those

observed by Friedel, induced initially the change of the iodide  $\text{CMe}_3 \cdot \text{CHMeI}$  into  $\text{CHMe}_2 \cdot \text{CMe}_2\text{I}$ .  
T. A. H.

**Ethyl Propenyl Ether.** ALEXEI E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1906, [ii], 74, 423—424. Compare Abstr., 1906, i, 397).—Ethyl propenyl ether is obtained in a 70 to 80% yield by the slow distillation of  $\beta$ -ethoxymethylacrylic acid; the distillation residue consists of a small amount of a viscid *resin* which boils at a high temperature and is probably a polymerisation product of the ether. Ethyl propenyl ether forms a volatile, mobile, transparent liquid, b. p.  $69^\circ$ ,  $D_4^{20}$  0.7951, or  $D_4^{20}$  0.7754, is hygroscopic although only slightly soluble in water, is miscible with alcohol or ether, and rapidly decolorises potassium permanganate.

As  $\beta$ -ethoxyacrylic acid when boiled decomposes slowly, forming carbon dioxide and ethyl vinyl ether, the decomposition of  $\beta$ -alkoxyacids of the acrylic series seems to be a general method for the preparation of mixed ethers of unsaturated alcohols.  
G. Y.

**Structure of Phosphorous Acid and its Derivatives.** ALEXANDER E. ARBASOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 161—228. Compare Abstr., 1905, i, 316).—A summary of previous work on the structure of phosphorous acid and its esters is given. It is not possible to separate the two esters,  $\text{P}(\text{OC}_4\text{H}_9)_3$  and  $\text{P}(\text{OC}_4\text{H}_9)_2 \cdot \text{OH}$ , derived from *isobutyl* alcohol, owing to the proximity of their boiling points. In ascending the homologous series, the difference between the boiling points of the normal and acid esters steadily diminishes. The esters of phosphorous acid boil at a lower temperature than the corresponding arsenious esters. The preparation and purification of the compounds are described in detail. The formation of the esters  $\text{P}(\text{OR})_2 \cdot \text{OH}$  simultaneously with the normal esters in the action of alkali ethoxides on phosphorus trichloride is probably due to the presence of alkali hydroxide in the ethoxide employed, phosphorous acid being thus produced. The formation of the esters  $\text{PO}(\text{OR})_3$  has not been explained.  
Z. K.

**Two Cases of Catalysis which are in agreement with Euler's Theory.** ROBERT KREMANN (*Chem. Centr.*, 1906, ii, 1246; from *Verh. Ges. Deut. Naturf. Aerzte*, 77, ii, 83—86).—Euler's explanation of catalytic action as due to an increase in the concentration of the reacting ions is confirmed by the following observations. The velocity of hydrolysis of esters by sodium ethoxide in absolute alcohols is very small, whereas the addition of 1% of water to propyl alcohol increases the velocity tenfold. When the acetates of polyhydric alcohols are hydrolysed by means of alcoholic sodium hydroxide, an 80—90% yield of ethyl acetate is formed almost at once; the sodium hydroxide here acts as a catalytic agent. The esters of monatomic alcohols of high molecular weight when heated with sodium hydroxide in alcoholic solution are decomposed with the formation of the ester of the alcohol which is acting as the solvent; this change, which takes place very slowly in the absence of alkali, is accelerated by its addition owing to the increase in the concentration of the reacting ions thereby produced.

Ethyl acetate and glycerol in the same way give glyceryl acetate on the addition of alcoholic sodium hydroxide. P. H.

**Resolution of  $\alpha$ -Bromoisohexoic and of  $\alpha$ -Bromohydrocinnamic Acids.** EMIL FISCHER and HANS CARL (*Ber.*, 1906, 39, 3996—4003).— $\alpha$ -Bromoisohexoic acid is resolved into its components by means of the brucine salts. *l*- $\alpha$ -Bromoisohexoic acid, b. p.  $94^{\circ}/0.2-0.4$  mm. (corr.),  $[\alpha]_D^{20} - 49.43^{\circ}$ , with aqueous ammonia yields *d*-leucine having  $[\alpha]_D^{20} - 14.20^{\circ}$ . *d*- $\alpha$ -Bromoisohexoic acid,  $[\alpha]_D^{20} + 48.99^{\circ}$ , with aqueous ammonia yields *l*-leucine having  $[\alpha]_D^{20} + 13.92^{\circ}$ . A more convenient but less efficient method of preparing these active acids from leucine has been described (*Abstr.*, 1906, i, 808).

$\alpha$ -Bromohydrocinnamic acid is resolved by means of its brucine or quinine salts, and by Ramberg's method (*Abstr.*, 1906, i, 923). The solid acid necessary for the latter method is obtained by distilling benzylbromomalononic acid under  $0.2-0.5$  mm. pressure; the  $\alpha$ -bromohydrocinnamic acid solidifies in needles, m. p.  $48-49^{\circ}$ , b. p.  $138-141^{\circ}/0.2$  mm.,  $D^{20} 1.48$ .

*l*- $\alpha$ -Bromohydrocinnamic acid,  $[\alpha]_D^{20} - 8.3^{\circ}$ , is converted by aqueous ammonia into *d*-phenylalanine having  $[\alpha]_D^{20} + 31.78^{\circ}$ . *d*- $\alpha$ -Bromohydrocinnamic acid has  $[\alpha]_D^{20} + 7.9^{\circ}$ . C. S.

**The "Alcoholysis" of Fatty Substances.** ALBIN HALLER (*Compt. rend.*, 1906, 143, 657—661).—The author applies the term "*alcoholysis*" to the breaking down of a fat into glycerol and an alkyl ester of the fatty acid by heating it with the corresponding absolute alcohol containing a small quantity of mineral acid. This forms a convenient method for separating the fatty acids of (i) oils or fats which contain besides olein only glyceryl esters of saturated fatty acids such as butter, cocoa butter, suet, &c.; (ii) drying oils, such as linseed or poppy oil; (iii) oils containing glyceryl salts of hydroxy-acids, such as ricin. For this purpose the fat, previously dried, is heated in a reflux apparatus with its own weight of absolute methyl alcohol containing  $1-2\%$  of hydrogen chloride until the mixture becomes homogeneous, it is then poured into water or a brine solution, the methyl esters of the acids are removed by decantation or extracted with ether, washed with sodium carbonate solution, dried, and separated by fractional distillation in the case of acids of the series  $C_nH_{2n}O_2$  up to  $n = 12$ , whilst the separation of methyl oleate, which is a liquid at the ordinary temperature, from methyl myristate, palmitate, or stearate, is effected by crystallisation at low temperature and subsequent draining of the crystals on porous plates at  $0^{\circ}$ .

It is possible that the process of *alcoholysis* may consist in a preliminary hydrolysis of the fat by the water produced by the action of the catalytic mineral acid on the alcohol, and a subsequent etherification of the fatty acid thus produced by the alcohol. M. A. W.

**Observations Relating to Ethereal Equilibrium, and to the Mutual Displacement of Glycerol and the other Alcohols.** MARCELLIN BERTHELOT (*Compt. rend.*, 1906, 143, 717—718. Compare Haller, preceding abstract).—The author refers to his early work on

the mutual displacement of glycerol and the other alcohols in the ethereal salts of the fatty acids (*Ann. Chim. Phys.*, 1854, [iii], 41), and to the accelerating action of hydrochloric or other acids on the reaction; and objects to the use of the terms "hydrolysis" or "alcoholysis," on the ground that they are synonymous with the older expressions, "decompositions effected by water or alcohol." M. A. W.

**Alcoholysis of Cocoa Butter.** ALBIN HALLER and YOUSSEFIAN (*Compt. rend.*, 1906, 143, 803—806).—A specimen of cocoa butter having the following physical constants: solidifying point  $21-20.5^{\circ}$ ; m. p.  $23-25^{\circ}$ ; saponification number, 242.1; Reichert-Meissel number, 6.5; Hehner number, 90.5, and iodine number, 8.47, was treated with methyl alcohol containing 2% hydrochloric or phenyl-sulphonic acid at  $35^{\circ}$ , and by the "methanolysis" thus effected the following methyl esters were formed: methyl hexoate, b. p.  $52-53^{\circ}/15$  mm.; methyl octoate, m. p.  $-40-41^{\circ}$ , b. p.  $83^{\circ}/15$  mm.; methyl decoate, m. p.  $-18^{\circ}$ , b. p.  $114^{\circ}/15$  mm.; methyl laurate, m. p.  $5^{\circ}$ , b. p.  $141^{\circ}/15$  mm.; methyl myristate, m. p.  $18^{\circ}$ , b. p.  $167-168^{\circ}/15$  mm.; methyl palmitate, m. p.  $28^{\circ}$ , b. p.  $196^{\circ}/15$  mm.; methyl stearate, m. p.  $38^{\circ}$ , b. p.  $214-215^{\circ}/15$  mm., and methyl oleate, b. p.  $212-213^{\circ}/15$  mm.; there was no trace of methyl butyrate, and similar results were obtained with two other specimens of cocoa butter from different sources. Cocoa butters therefore consist of the glyceryl esters of the  $C_6$ ,  $C_8$ ,  $C_{10}$ ,  $C_{12}$ ,  $C_{14}$ ,  $C_{16}$ , and  $C_{18}$  saturated fatty acids and oleic acid, the esters of lauric and myristic acids preponderating (compare Lewkowitsch; Reijst, *Abstr.*, 1906, ii, 403; Ulzer, *Chem. Revue*, 1899, 203). M. A. W.

**The Theory of Saponification.** JULIUS LEWKOWITSCH (*Ber.*, 1906, 39, 4095—4097).—A reply to Marcusson (*Abstr.*, 1906, i, 924). G. Y.

**The Rôle of Metallic Hydrides in Reduction, and Data as to the Composition of Some Fats and Oils.** SERGIUS FOKIN (*Zeit. Elektrochem.*, 1906, 12, 749—762).—The electrolytic reduction of oleic acid to stearic acid was investigated. In the course of these experiments it was noticed that the yield of stearic acid is much improved by the presence of nickel. The most active nickel is that deposited as a fine black powder on the cathode or that obtained by reducing the oxide by hydrogen at  $300-360^{\circ}$ . It was found that iron or carbon brings about no reduction; experiments on the action of other metals were, therefore, made with an iron gauze or carbon cathode in a porous cell containing the solution of oleic acid in alcohol or acetone, the other metal being added in fine powder. It was found that platinum is more active than nickel and that palladium is more active still. Cobalt and copper also bring about the reduction. Silver, lead, mercury, manganese, chromium, zinc, bismuth, tungsten, vanadium, and aluminium are inactive. Iron occasionally gave a positive result.

Reduction of an alcoholic solution of oleic acid was also observed by treating the solution with palladium or platinum black and zinc and

sulphuric acid or with reduced nickel or cobalt and magnesium and hydrochloric acid. Similar experiments with copper gave negative results.

An alcoholic solution of oleic acid is also reduced by boiling it with palladium hydride in a current of hydrogen. Nickel, reduced by hydrogen at  $320^{\circ}$ , gave no reduction under these conditions, but when the temperature was raised by using amyl alcohol, slow reduction took place. By using glycerol as solvent the temperature could be raised to  $250^{\circ}$ , and a rapid reduction was observed.

The author considers that in all cases the reduction depends on the formation of a hydride of the metal.

The methods of reduction described are applied to some natural oils and fats, such as linseed oil, Chinese wood oil, castor oil, and fish oil. From the nature of the saturated fatty acids obtained, conclusions may be drawn as to the unsaturated acids in the original oils.

Crotonic, angelic, fumaric, and cinnamic acids, allyl alcohol, and carbon tetrachloride were also reduced both electrolytically and by the zinc or magnesium-palladium couple. The last-named substance yields chloroform together with lower chlorination products of methane.

T. E.

**Constitution of Oleic Acid, &c.** CARL D. HARRIES (*Ber.*, 1906, 39, 3728—3732).—Polemical. A reply to Molinari and Soncini (*Abstr.*, 1906, i, 792). A. McK.

**Hydrolytic Products of Oleic Acid Ozonide.** CARL D. HARRIES and HANS O. TÜRK (*Ber.*, 1906, 39, 3732—3737. Compare Harries and Thieme, *Abstr.*, 1906, i, 226; Molinari and Soncini, *ibid.*, i, 792).—The hydrolysis of the ozonides of oleic acid by water has been studied quantitatively; 15 grams of the viscid ozonide yield 2.0 grams of nonaldehyde, 4.2 grams of pelargonic acid, 4.4 grams of a mixture of azelaic acid and its semi-aldehyde, and 3.7 grams of a distillation residue which, on esterification by Fischer's method, yields the ethyl ester of azelaic acid and the ester-acetal of the semi-aldehyde of this acid, leaving only 1.5 grams of the ozonide unaccounted for. The product of the hydrolysis of 24 grams of the mobile ozonide of oleic acid contains 2.4 grams of nonaldehyde, 5.7 grams of pelargonic acid, 6.5 grams of distillation residue, 5 grams of azelaic acid, and 3.5 grams of the semi-aldehyde of azelaic acid.

G. Y.

**Constitution of the  $\beta$ -Fencholenic Acid Series.** FRIEDRICH W. SEMMLER and KONRAD BARTELL (*Ber.*, 1906, 39, 3960—3964).—Silver  $\beta$ -fencholenate and methyl iodide yield the *methyl* ester,  $C_9H_{15} \cdot CO_2Me$ , b. p.  $97-99^{\circ}/10$  mm.,  $D^{22}_D$  0.9608, and  $n^{20}_D$  1.46459. By reduction with sodium and alcohol, the *alcohol*,  $C_{10}H_{18}O$ , is obtained, b. p.  $106-108^{\circ}/10$  mm.,  $D^{22}_D$  0.9272, and  $n^{20}_D$  1.48033.

When  $\beta$ -fencholenolactone is shaken with dilute sodium hydroxide for twenty-four hours, *hydroxydihydrofencholenic acid*,  $C_{10}H_{18}O_3$ , is obtained, m. p.  $110^{\circ}$  (compare Mahla, *Abstr.*, 1902, i, 106).

$\beta$ -Fencholenic acid is oxidised by ozone to a ketonic acid,  $C_7H_{10}O_3$ , b. p.  $166-170^{\circ}/12$  mm.,  $D^{16}_D$  1.1533,  $n_D$  1.472,  $\alpha$   $13.15^{\circ}$ , which forms a

*semicarbazone*,  $C_8H_{13}O_3N_3$ , m. p. 198—199°, and an *oxime*, m. p. 145°. By oxidation with neutral or faintly alkaline potassium permanganate, the ketonic acid is converted into a tricarboxylic acid, which by distillation in a vacuum loses carbon dioxide and forms  $\alpha$ -methylglutaric acid.

A table is given showing how the preceding compounds are derivable from fenchone by the use of Semmler's fenchone formula, that of  $\beta$ -fencholenic acid being  $CO_2H \cdot CMe \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \end{array} \text{C} : CMe_2$ . C. S.

**Cineolic Acid. V. Cineolic Anhydride and Bromine.** HANS RUPE and WALTHER LOTZ (*Ber.*, 1906, 39, 4076—4083. Compare *Abstr.*, 1899, i, 340; 1900, i, 371; 1901, i, 119, 578; 1905, i, 409).—In absence of a solvent, the action of bromine on cineolic anhydride takes place with explosive violence, but in chloroform solution leads to the formation of carbon monoxide, two isomeric, crystalline *bromo*-compounds,  $C_9H_{11}O_3Br_3$ , which are separated by fractional crystallisation from methyl alcohol, and a yellow to brown oily product.

The *bromo*-compound, m. p. 156—157°, which is the less soluble in methyl alcohol, separates from alcohol in strongly doubly-refracting, white needles, as a granular, crystalline powder, or in small, glistening, rhombic plates [ $a : b : c = 0.7341 : 1 : 0.7686$ ].

The *bromo*-compound, m. p. 129°, crystallises from methyl alcohol in large, rhombic plates [ $a : b : c = 0.68256 : 1 : 0.65989$ ].

These *bromo*-compounds, one of which, if not both, must have the constitution  $CBr \begin{array}{c} \text{C}(\text{CH}_2\text{Br})_2 \cdot \text{O} \\ \text{CO} \cdot \text{O} \\ \text{CH}_2 - \text{CH}_2 \end{array} CMe$ , remain unchanged when boiled

with potassium or silver acetate solution or with alcoholic hydrogen chloride, and are insoluble in cold alkali hydroxide or carbonate solutions, but when boiled with these or with aqueous baryta are converted into an *acid*,  $C_9H_{12}O_4$  or  $C_9H_{14}O_4$ , m. p. 172—174°, which is stable towards potassium permanganate.

Reduction of the *bromo*-compounds with zinc dust and alcohol leads

to the formation of a  $\delta$ -lactone,  $CH \begin{array}{c} CMe_2 - O \\ CO \cdot O \\ CH_2 \cdot CH_2 \end{array} CMe$ , which crystal-

lises in transparent, white plates, m. p. 50—51°, b. p. 117—118.5°/14 mm. or 126—128°/20 mm., has a bitter taste, reddens litmus in aqueous solution, is not extracted from its ethereal solution by aqueous potassium carbonate, and only very slowly so by aqueous sodium carbonate. It is stable towards potassium permanganate, dissolves in concentrated sulphuric acid, forming a colourless solution, and decomposes at 170° under the ordinary pressure, forming carbon dioxide and methylheptenone.

The oily product from the action of bromine on cineolic anhydride readily resinifies, decomposes when distilled in a vacuum, and when reduced yields to some extent the same products as do the crystalline bromides, but with stannous chloride and alcoholic hydrogen chloride forms an *ester* from which cineolic acid is obtained on hydrolysis; when boiled with aqueous sodium hydroxide, the oily *bromo* compound yields a small amount of an *acid*, m. p. about 172°, which is stable

towards potassium permanganate, does not contain bromine, and may be identical with the acid obtained from the crystalline bromo-compounds. G. Y.

**Cineolic Acid. VI. Action of Sulphuric Acid on Cineolic Acid.** HANS RUPE and WALTHER LOTZ (*Ber.*, 1906, 39, 4083—4086. Compare preceding abstract; Bistrzycki and Reintke, *Abstr.*, 1905, i, 285; Bistrzycki and Siemiradzki, *Abstr.*, 1906, i, 135).—The lactone,  $C_9H_{14}O_3$ , m. p. 50—51° (see preceding abstract), is formed together with carbon monoxide when cineolic acid, or in a 90% yield when cineolic anhydride, is treated with concentrated sulphuric acid at the laboratory temperature.

2:4-Dimethylbenzoic acid is formed by heating the lactone, or cineolic acid or its anhydride with concentrated sulphuric acid on the water-bath.

2:4-Dimethylbenzoyl-*p*-toluidide, prepared by heating the acid with *p*-toluidine at 200—220°, crystallises in glistening, silky needles, m. p. 152°.

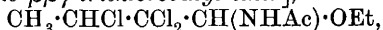
The action of zinc chloride on the lactone at 110° leads to the formation of dihydro-*m*-xylene, b. p. 132—134.5°,  $n_D^{20}$  1.46867 (Wallach and Gildemeister, *Abstr.*, 1888, 1205), and of a small amount of 2:4-dimethylbenzoic acid. G. Y.

**Reversible Conversion of Paraformaldehyde into Formaldehyde, and Sterilisation with Formaldehyde at High Temperatures.** LEON PERDRIX (*Ann. Inst. Pasteur*, 1906, 20, 881—900).—The curve representing the vapour tension of the transformation of paraformaldehyde into formaldehyde rises very rapidly with the temperature. This fact must be taken into account when using formaldehyde as a sterilising agent, an operation which should be carried out preferably at a moderately high temperature. The use of anhydrous formaldehyde is preferable to that of formol as a sterilising agent on account of the greater vapour pressure of the latter. Experiments made with anhydrous formaldehyde at 100° on various bacteria which are not easily destroyed by ordinary methods of sterilisation showed this to be in every case a very effective agent. E. F. A.

**Chlorination of Paracetaldehyde; Butylchloral.** PAUL FREUNDLER (*Compt. rend.*, 1906, 143, 682—684) —Pinner has shown that the chlorination of paracetaldehyde results in the formation of butylchloral (*Abstr.*, 1876, 552. Compare Lieben, *Abstr.*, 1883, 963), and the author finds that tetrabromobutaldehyde is the product of the bromination of paracetaldehyde (*Abstr.*, 1905, i, 569). In each case the first product of the reaction is the corresponding monohalogen derivative of acetaldehyde, which in the case of the chloro-compound condenses at the ordinary temperature with the unchanged acetaldehyde to form  $\alpha$ -chlorocrotonaldehyde; this on further chlorination yields butylchloral; whilst under similar conditions of temperature 2 mols. of bromoacetaldehyde condense to form  $\alpha$ - $\gamma$ -dibromocrotonaldehyde, which on further bromination yields tetrabromobutaldehyde.

Butylchloral hydrate, like chloral or bromal hydrate, behaves

as a dibasic acid; the *acetal*,  $\text{CH}_3 \cdot \text{CHCl} \cdot \text{CCl}_2 \cdot \text{CH}(\text{OEt})_2$ , boils at  $122-124^\circ/20-21$  mm.; the *ethyl ether* of the acetamide derivative [*ethyl  $\alpha$ -acetylamino- $\beta\beta$ -trichlorobutyl ether*],



m. p.  $86^\circ$ , b. p.  $163-164^\circ/15-16$  mm., crystallises from benzene and light petroleum in prisms. Contrary to Schiff's experience (Abstr., 1892, 1067), the author obtained only one acetamide and one benzamide derivative of butylchloral, m. p.  $206-208^\circ$  and  $176-178^\circ$  respectively, and not  $170^\circ$  and  $148^\circ$  as stated by Schiff. M. A. W.

**Methylethylacetaldehyde [ $\alpha$ -Methylbutaldehyde] and some of its Condensation Products.** VIKTOR NEUSTÄDTER (*Monatsh.*, 1906, 27, 879-934. Compare Lieben, Abstr., 1901, i, 449).—Of the aldehydes containing only one  $\alpha$ -hydrogen atom, *isobutaldehyde* alone has been fully investigated. This paper gives the results of the study of a second member of the same group.

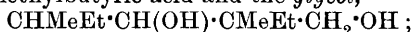
$\alpha$ -Methylbutaldehyde (methylethylacetaldehyde) was present probably in the valeraldehyde prepared from commercial amyl alcohol and utilised by Kohn (Abstr., 1896, i, 10; 1897, i, 396), Lederer (Abstr., 1901, i, 669), Rosinger (*ibid.*), and Morgenstern (Abstr., 1903, i, 787).

$\alpha$ -Methylbutaldehyde is prepared from methyl ethyl ketone by reduction to *sec.*-butyl alcohol, successive conversion of this into *sec.*-butyl bromide, and by means of Grignard's reaction with formic acid, *sec.*-butylcarbinol (Rainer, Abstr., 1905, i, 16), and finally by oxidation of the carbinol by means of potassium dichromate and dilute sulphuric acid.

The preparation of the aldehyde by Claisen's method (Abstr., 1905, i, 286) from methyl ethyl ketone by way of ethyl  $\beta$ -methyl- $\beta$ -ethylglycidate also is described. On distillation in a current of steam the glycidic acid is only partially decomposed to the aldehyde, the main portion forming the *dihydroxy-acid*,  $\text{OH} \cdot \text{CMeEt} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$ ; this is obtained as a greenish-yellow, viscid mass, which on distillation under atmospheric pressure decomposes at about  $185^\circ$ , forming carbon dioxide, water, and  $\alpha$ -methylbutaldehyde, the total yield of which amounts to 85% of the sodium methylethylglycidate.

When treated with hydrogen chloride in a freezing mixture,  $\alpha$ -methylbutaldehyde forms the *polymeride*,  $(\text{C}_5\text{H}_{10}\text{O})_3$ , which is obtained as a mobile oil having a characteristic odour, b. p.  $133^\circ/20$  mm., and yields the monoaldehyde when boiled with a small amount of concentrated sulphuric acid. The absence of *isovaleraldehyde* is shown by a determination of the solubility of the silver salt obtained on boiling the aldehyde with silver oxide and water (compare Sedlitzky, Abstr., 1888, 250).

The action of alcoholic potassium hydroxide on  $\alpha$ -methylbutaldehyde cooled by ice, and finally at the ordinary temperature, leads to the formation of  $\alpha$ -methylbutyric acid and the *glycol*,

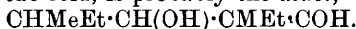


this is obtained as a viscid, colourless liquid, b. p.  $133^\circ/10$  mm., and has a sp. gr. less than that of water. It solidifies when cooled in a mixture of ether and carbon dioxide, has a cooling taste, and is readily



soluble in absolute alcohol, ether, light petroleum, or benzene, but only sparingly so in water or aqueous alcohol.

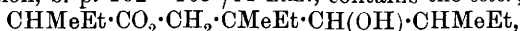
A colourless, viscid liquid, b. p.  $90^{\circ}/20$  mm., obtained by the action of solid potassium carbonate on  $\alpha$ -methylbutaldehyde in a sealed tube at  $155^{\circ}$ , or of a very small amount of alcoholic potassium hydroxide on the aldehyde in the cold, is probably the *aldol*,



The action of metallic sodium on  $\alpha$ -methylbutaldehyde at  $18-24^{\circ}$  leads to the formation of the glycol  $\text{C}_{10}\text{H}_{22}\text{O}_2$  and of two esters, b. p.  $70-72^{\circ}/11$  mm., and  $162-165^{\circ}/11$  mm. respectively.

isoAmyl  $\alpha$ -methylbutyrate,  $\text{CHMeEt}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CHMeEt}$ , is a mobile, yellow liquid having a pleasant ethereal odour, b. p.  $70-72^{\circ}/11$  mm., or  $183-184^{\circ}/741$  mm., and is hydrolysed by boiling alcoholic potassium hydroxide.

The fraction, b. p.  $162-165^{\circ}/11$  mm., contains the *ester*,



which is formed also by the action of sodium ethoxide in absolute alcoholic solution, and probably in small amounts by that of potassium carbonate or potassium hydroxide on the aldehyde under various conditions. It is a colourless, mobile liquid having a slight ester odour, b. p.  $272-274^{\circ}/741$  mm., and on hydrolysis with aqueous-alcoholic potassium hydroxide, yields the glycol  $\text{C}_{10}\text{H}_{22}\text{O}_2$  and  $\alpha$ -methylbutyric acid.

$\alpha$ -Methylbutaldoxime,  $\text{C}_5\text{H}_{11}\text{ON}$ , is obtained as a transparent, mobile oil, b. p.  $149-151^{\circ}/749$  mm.; when heated with acetic anhydride in a sealed tube at  $140^{\circ}$ , it yields  $\alpha$ -methylbutyronitrile as a colourless liquid, b. p.  $125^{\circ}/760$  mm.

The *aldazine*,  $\text{N}_2(\text{CH}\cdot\text{CHMeEt})_2$ , formed by the action of hydrazine sulphate and sodium carbonate on the aldehyde, is a mobile, ethereal, yellow liquid, b. p.  $200-202^{\circ}$  under the ordinary pressure; when treated with concentrated alcoholic hydrogen chloride in ethereal solution, it yields the aldehyde and hydrazine hydrochloride (compare Franke, Abstr., 1900, i, 212). G. Y.

**Reduction of Formylisobutaldol and its Oxime.** RUDOLF BÖHM (*Monatsh.*, 1906, 27, 947-962. Compare Wessely, Abstr., 1900, i, 428).—When distilled under atmospheric pressure, the oxime of formylisobutaldol decomposes, yielding water, an oil which on redistillation gives two fractions, b. p.  $65^{\circ}/34$  mm. and  $120^{\circ}/34$  mm. respectively, together with a small amount of a *substance* which crystallises in rhombic prisms, m. p.  $117^{\circ}$ , is more soluble in water than in ether, and evolves ammonia when heated with aqueous sodium hydroxide.

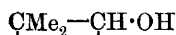
The fraction, b. p.  $65^{\circ}/34$  mm., consists of the *anhydride* of the

oxime,  $\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{CMe}_2\cdot\text{CH}\cdot\text{OH} \end{array}$ , which is obtained as a colourless oil, b. p.

$57^{\circ}/9$  mm. or  $137^{\circ}/760$  mm.; it has a pleasant ethereal odour, yields formylisobutaldol when heated with  $10\%$  hydrochloric acid, and reacts with sodium with evolution of hydrogen or with acetic acid with development of heat.

The fraction, b. p.  $120^{\circ}/34$  mm., contains *aa*-dimethylhydracrylonitrile, which forms a colourless oil, becoming brown on exposure to air, b. p.  $97^{\circ}/11$  mm., or  $103^{\circ}/15$  mm.; when boiled with 15% hydrochloric acid, it yields hydroxypivalic acid, the calcium salt,  $C_{10}H_{18}O_6Ca$ , of which is described. The acetate of *aa*-dimethylhydracrylonitrile,  $C_7H_{11}O_2N$ , formed by the action of acetic anhydride and sodium acetate on the oxime of formylisobutaldol, is obtained as a colourless oil having a pleasant ethereal odour, b. p.  $91.5^{\circ}/11$  mm. or  $97^{\circ}/15$  mm.; on hydrolysis it yields hydroxypivalic acid. Oxidation of the acetate with potassium permanganate in aqueous solution leads to the formation of *a*-cyanoisobutyric acid,  $CN \cdot CMe_2 \cdot CO_2H$ , which is formed also together with isobutyric acid by the oxidation of *a*-dimethylhydracrylonitrile; it crystallises in large, white leaflets, m. p.  $56-57^{\circ}$ .

Formylisobutaldol is reduced by sodium amalgam, forming the corresponding pentaglycol, or by zinc and hydrochloric acid, yielding two products, which must be formed by loss of water from hydrobenzoin-like derivatives of the aldol, and are separated by fractional recrystallisation from alcohol: (a)  $O \begin{matrix} \diagup CH \cdot CMe_2 \cdot CH_2 \cdot OH \\ \diagdown CH \cdot CMe_2 \cdot CH_2 \cdot OH \end{matrix}$  or



$CH_2 \cdot O \cdot CH \cdot CMe_2 \cdot CH_2 \cdot OH$  crystallises from alcohol in glistening, silky needles, m. p.  $137.5^{\circ}$ , and forms a diacetyl derivative crystallising in long, flat, white needles, m. p.  $87^{\circ}$ ; (b)  $C_{10}H_{20}O_3$ , crystallises in large prisms or long, slender spears, m. p.  $63.5^{\circ}$ . If the reduction with zinc and hydrochloric acid is carried out at higher temperatures, a third product crystallising in glistening plates, m. p.  $184^{\circ}$ , is formed.

Electrolytic reduction of the aldol in 30–31% sulphuric acid solution with a lead cathode and a carbon anode and a current density of 2 amperes per square decimetre leads to the formation of oily products only, but with a current density of 5 amperes per square decimetre to the formation also of the two crystalline products, m. p.  $63.5^{\circ}$  and  $137.5^{\circ}$  respectively. G. Y.

**The Pinacolin from the Pinacone of Methyl Ethyl Ketone.** BERTA BRAUN and HANS KITTEL (*Monatsh.*, 1906, 27, 803–821).—Glücksmann (Abstr., 1892, 38) and Schindler (Abstr., 1893, i, 71) found that the action of 90% sulphuric acid on  $\beta$ -trimethylethylidenelactic acid leads to the formation of methyl isopropyl ketone and not to that of the expected aldehyde. The object of the present work is to compare the behaviour of an homologous lactic acid.

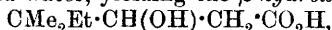
Reduction of methyl ethyl ketone by means of sodium in ethereal solution under an aqueous solution of potassium carbonate leads to the formation of *sec*-butyl alcohol (65%), pinacone (10–12%), and an analogue of phorone (12%), b. p.  $256^{\circ}$  (compare Schramm, Abstr., 1883, 1079), 10% of the ketone remaining unchanged.

The substance,  $CMeEt \cdot C_2H_5 \cdot CMe \cdot C_2H_5 \cdot COMe$ , b. p.  $256^{\circ}$ , is a slightly yellow oil, forms an additive compound with 2 mols. of bromine, and yields an oxime,  $C_{13}H_{20} \cdot N \cdot OH$ , b. p.  $260^{\circ}$ .

On oxidation with potassium permanganate in aqueous sodium hydroxide solution, the pinacolin, b. p.  $148-154^{\circ}$ , obtained by boiling

pinacone with 10% sulphuric acid (compare Zelinsky and Krapivin, *Abstr.*, 1893, i, 390; Herschmann, *ibid.*, 547), yields an acid,  $C_8H_{14}O_3$ , together with small amounts of acetic and *aa*-dimethylbutyric acids.

*$\beta$ -Keto- $\gamma\gamma$ -dimethylhexoic acid*,  $CMe_2Et \cdot CO \cdot CH_2 \cdot CO_2H$ , forms a *silver* salt,  $C_8H_{13}O_3Ag$ , crystallising in long needles, and is reduced with sodium amalgam and water, yielding the  *$\beta$ -hydroxy-acid*,



which crystallises in small plates, m. p.  $82^\circ$ , and is not volatile in a current of steam; the crystalline *silver*,  $C_8H_{15}O_3Ag$ , and *potassium* salts were analysed. When heated with concentrated phosphoric acid and lead dioxide, the  *$\beta$ -hydroxy-acid* evolves a gas, and on distillation in a current of steam yields an acid distillate.

The action of boiling 90% sulphuric acid on  *$\beta$ -hydroxy- $\gamma\gamma$ -dimethylhexoic acid* leads to the formation of methyl *aa*-dimethylpropyl ketone, b. p.  $131$ — $132^\circ$ . No trace of an aldehyde could be found in the sulphuric acid solution. G. Y.

**Fermentation of Sugar without Enzymes.** EDUARD BUCHNER, JAKOB MEISENHEIMER, and H. SCHADE (*Ber.*, 1906, 39, 4217—4231).—Contrary to Schade's statement that sugars in alkaline solution are decomposed by air or hydrogen peroxide, yielding equal molecular quantities of formic acid and acetaldehyde (or acetic acid) (*Abstr.*, 1906, i, 931), the authors find that the acid products of decomposition, in the case of *lævulose*, are formic, glycollic, and *i*-erythritic acids; acetic, lactic, and oxalic acids are not formed. Hydrogen is evolved, probably in accordance with the equation  $2CH_2O + H_2O_2 = 2H \cdot CO_2H + H_2$ , the formaldehyde being an initial product of the decomposition of the sugar. C. S.

**Connexion between the Chemical Nature of the Amines and their Power to form Complex Compounds.** LEO A. TCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 9—12. Compare *Abstr.*, 1905, i, 865).—In order to ascertain how far the observations previously made regarding the behaviour of the amines towards copper succinimide could be applied to other analogous cases, the action of various amines towards copper chloride, silver nitrate, potassium platinosochloride, and platinic chloride has been investigated. The results completely confirm those previously found. The primary amines easily form complexes, the secondary do so much less readily, whilst the tertiary do not yield complex compounds, but the inorganic salt is often reduced. Contrary to the generally accepted view as to these reactions, it is considered that the reactivity of the amines depends, to a very large extent, on the number of free hydrogen atoms attached directly to the nitrogen atom. The reason Jörgensen adopted the opposite view was that he employed pyridine, which, being a heterocyclic amine, forms an exception to the general rule; the latter also only holds for those cases in which the amine as such forms the compound, or, according to Abegg, the neutral part of a complex ion, but the tertiary amines, just like the primary or secondary, easily enter into binary combinations when they form complex ammonia radicles. Z. K.

**Salts of Quaternary Ammonium Bases with Organic Acids.**  
**Tetramethylammonium Formate.** L. VANZETTI (*Chem. Centr.*, 1906, ii, 1347; from *Boll. Chim. Farm.*, 45, 593—598).—*Tetramethylammonium formate* (*Forgenin*),  $\text{H}\cdot\text{CO}_2\cdot\text{NMe}_4$ , obtained by the action of tetramethylammonium iodide on silver formate, is a white crystalline, odourless, hygroscopic substance, which gives the reactions of formates, and evolves carbon monoxide on warming with sulphuric acid. It is stable in dry air or in solution, but decomposes at above  $200^\circ$ . Unlike other quaternary bases its physiological action does not resemble that of curare. P. H.

**Novaine.** FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1906, 49, 47—49).—When a concentrated solution of novaine hydrochloride is distilled with crystallised barium hydroxide, trimethylamine is formed, and if the operation is repeated some twelve times with the addition of fresh amounts of water, practically the whole of the nitrogen is evolved in this form. This reaction indicates that novaine is closely related to the choline bases. It is probably a higher homologue of muscarine, and the formula  $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})_2$  is suggested. The oblitine molecule probably contains two novaine residues.

J. J. S.

**Stereochemistry of 2:5-Diketopiperazines.** EMIL FISCHER and KARL RASKE (*Ber.*, 1906, 39, 3981—3995).—Mainly an account of work already published (compare Abstr., 1906, i, 457).

*d-Bromopropionyl-l-alanine*,  $\text{C}_6\text{H}_{10}\text{O}_3\text{NBr}$ , obtained from *l*-alanine in a similar manner to its optical antipode, separates from hot water in octahedra, m. p.  $170^\circ$ , decomposing,  $[\alpha]_D^{20} + 67\cdot91^\circ$ , and by treatment with aqueous ammonia yields *d-alanyl-l-alanine*, which closely resembles its optical isomeride, differing in m. p.  $275\text{—}276^\circ$  (corr.) and  $[\alpha]_D^{20} + 68\cdot94^\circ$ , and yields *trans*-alanine anhydride. By hydrolysis with hydrochloric acid at  $100^\circ$ , the dipeptide yields racemic alanine hydrochloride.

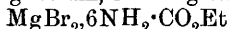
*d-α-Bromopropionic acid* is obtained readily from *l*-alanine in a similar manner to the *l*-acid (compare Abstr., 1905, i, 692), and has  $\alpha_D^{20} + 44\cdot2^\circ$ . C. S.

**Action of Nitrous Acid on Lysine.** LEO SZYDLOWSKI (*Monatsh.*, 1906, 27, 821—830. Compare Fischer and Tiemann, Abstr., 1894, i, 167; Fischer and Weigert, Abstr., 1902, i, 352; Neuberg and Wolff, Abstr., 1903, i, 74).—The action of barium or silver nitrite on lysine sulphate or hydrochloride in aqueous solution cooled by ice leads to the formation of  $\alpha\epsilon$ -dihydroxyhexoic acid, an aminohydroxyhexoic acid, and a small amount of an alkaline, yellow, amorphous substance,  $\text{C}_6\text{H}_{13}\text{O}_3\text{N}$ , m. p.  $176\text{—}178^\circ$ .

*αε-Dihydroxyhexoic acid* is isolated in the form of its calcium salt,  $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_4)_2$ .

The aminohydroxyhexoic acid crystallises in needles, m. p.  $200\text{—}201^\circ$ , and may be identical with Fischer and Tiemann's and Neuberg and Wolff's acids. G. Y.

**Action of Magnesium Bromide and Iodide on some Derivatives of Carbamide.** VII. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 4).—Urethane reacts readily with both the iodide and bromide of magnesium, forming the *compounds*



and  $\text{MgI}_2 \cdot 6\text{NH}_2 \cdot \text{CO}_2\text{Et}$ ; the eutectic point of the system lies at  $35^\circ$ . The solubility curve of the *compound*  $\text{MgBr}_2 \cdot 6\text{NH}_2 \cdot \text{CO}_2\text{Et}$ , in presence of traces of the *compound*  $\text{MgBr}_2 \cdot 4\text{NH}_2 \cdot \text{CO}_2\text{Et}$ , is broken at  $91^\circ$  when the system  $\text{MgBr}_2 \cdot 6 \cdot 55\text{NH}_2 \cdot \text{CO}_2\text{Et}$ , is formed, but when the lower compound is completely absent, the melting point of the *compound*  $\text{MgBr}_2 \cdot 6\text{NH}_2 \cdot \text{CO}_2\text{Et}$ ,  $91 \cdot 5^\circ$ , can be reached. The solubility curve of the *compound*  $\text{MgBr}_2 \cdot 4\text{NH}_2 \cdot \text{CO}_2\text{Et}$  in urethane ends at its melting point,  $123^\circ$ , which is again lowered by any further addition of magnesium bromide. The system magnesium iodide-urethane gives similar results, but the eutectic point,  $32^\circ$ , is lower, as is also the melting point,  $87^\circ$ , of the *compound*  $\text{MgI}_2 \cdot 6\text{NH}_2 \cdot \text{CO}_2\text{Et}$ . Carbamide forms *compounds* with magnesium bromide equally well. The eutectic point is  $108^\circ$ . At  $130 \cdot 5^\circ$  there is a break in the solubility curve, at the composition  $\text{MgBr}_2 \cdot 9 \cdot 21\text{CO}(\text{NH}_2)_2$ . The next curve continues to  $170^\circ$ , when decomposition occurs. Probably the first curve corresponds with the *compound*  $\text{MgBr}_2 \cdot 6\text{CO} \cdot (\text{NH}_2)_2$ , and the second with the *compound*  $\text{MgBr}_2 \cdot 4\text{CO}(\text{NH}_2)_2$ .

Z. K.

**Compounds of Magnesium Bromide with Derivatives of the Acids.** VI. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 3).—As the amount of magnesium bromide is increased in the system magnesium bromide-acetamide, the m. p. of acetamide ( $82^\circ$ ) is lowered until the eutectic point  $50 \cdot 5^\circ$  is reached, the composition of the system then being  $\text{MgBr}_2 \cdot 13 \cdot 17\text{COMe} \cdot \text{NH}_2$ . The solubility curve of the *compound*  $\text{MgBr}_2 \cdot 6\text{COMe} \cdot \text{NH}_2$  in acetamide ends at  $169^\circ$ , its m. p. On further addition of magnesium bromide, the m. p. is at first lowered to  $136^\circ$ , corresponding with the *compound*  $\text{MgBr}_2 \cdot 3 \cdot 75\text{COMe} \cdot \text{NH}_2$ , it then again rises to  $160^\circ$ , the m. p. of the *compound*  $\text{MgBr}_2 \cdot 2\text{COMe} \cdot \text{NH}_2$ , but it is not quite certain whether a compound containing 2 mols. of acetamide is really formed. Acetanilide with magnesium bromide yields the *compound*  $\text{MgBr}_2 \cdot 6\text{COMe} \cdot \text{NHPh}$ . The eutectic point lies  $4 \cdot 5^\circ$  lower than its m. p.,  $112^\circ$ . The solubility curve of this compound in acetanilide ends at  $209^\circ$ , its m. p., and any further addition of magnesium bromide gives results similar to those with acetamide.

Z. K.

**Action of Hydrogen Cyanide on Aldehyde-Ammonia.** GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1906, **39**, 3942—3959. Compare Delépine, *Abstr.*, 1904, i, 148).—When aldehyde-ammonia is acted on by a 3% solution of hydrocyanic acid either in light or in the dark, the following substances are obtained: (1) two isomeric compounds,  $\text{C}_6\text{H}_{12}\text{O}_5\text{N}_2$ , of which the one more sparingly soluble in water than the other has m. p.  $232^\circ$ , whilst the isomeride has m. p.  $210^\circ$ ; (2) a compound,  $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$ , m. p.  $186^\circ$ , soluble in ether; (3) alanine; (4) an amorphous, indefinite compound.

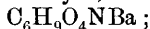
The compound  $C_6H_{12}O_3N_2$ , m. p.  $232^\circ$ , is the monoamide of the  $\alpha$ -iminodipropionic acid (m. p.  $254$ — $255^\circ$ , termed by the authors A- $\alpha$ -iminodipropionic acid), whilst the isomeride  $C_6H_{12}O_3N_2$ , m. p.  $210^\circ$ , is the monoamide of the  $\alpha$ -iminodipropionic acid (m. p.  $234$ — $235^\circ$ ; B- $\alpha$ -iminodipropionic acid). It is pointed out that the two isomeric  $\alpha$ -iminodipropionic acids referred to bear the same relationship to one another as that which exists between racemic and mesotartaric acids.

The compound  $C_6H_{10}O_2N_2$  is the imide of B- $\alpha$ -iminodipropionic acid.

A- $\alpha$ -Iminodipropionic monoamide (m. p.  $232^\circ$ ) crystallises from water in hexagonal plates. Its aqueous solution gives an acid reaction and exhibits the biuret reaction. B- $\alpha$ -Iminodipropionic monoamide (m. p.  $210^\circ$ ) separates in colourless prisms.

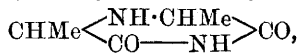
When the A-amide is boiled with baryta, it forms the *barium* salt,  $(C_6H_{10}O_4N)_2Ba$ , which crystallises in needles and yields the corresponding A- $\alpha$ -iminodipropionic acid. The latter forms a *hydrogen potassium* salt,  $C_6H_{10}O_4NK$ , which separates from aqueous alcohol in colourless prisms; the *silver double* salt,  $C_6H_{10}O_4NAg, AgNO_3$ , and the *silver* salt,  $C_6H_9O_4NAg_2$ , are described. The *diethyl* ester,  $C_6H_9O_4NEt_2$ , is a viscid oil, b. p.  $123$ — $124^\circ/15$  mm., which forms the *nitroso*-derivative,  $C_6H_8O_4Et_2N \cdot NO$ , a yellow oil, b. p.  $177^\circ/18$  mm., giving a strong Liebermann reaction.

B- $\alpha$ -Iminodipropionic monoamide separates from water in prisms containing  $1\frac{1}{2}H_2O$ , and is more sparingly soluble in water than its isomeride. When boiled with baryta, it forms the *barium* salt,



the *hydrogen barium* salt,  $(C_6H_{10}O_4N)_2Ba$ , is also described. B- $\alpha$ -Iminodipropionic acid crystallises in prisms, m. p.  $234$ — $235^\circ$ . The *compound*  $(C_6H_{10}O_4NAg)_2, AgNO_3$  crystallises in leaflets; the *silver* salt is described; the *diethyl* ester,  $C_6H_9O_4NEt_2$ , is an oil, b. p.  $121$ — $122^\circ/15$  mm., m. p.  $-5^\circ$ ; which forms a *nitroso*-derivative,  $C_6H_8O_4Et_2N \cdot NO$ , an oil, b. p.  $163$ — $164^\circ/17$  mm., and giving a strong Liebermann reaction.

B- $\alpha$ -Iminodipropionic acid forms the imide



which was isolated as one of the products of the action of hydrogen cyanide on aldehyde-ammonia; it separates from benzene in needles or prisms, m. p.  $186^\circ$ .

When the action of hydrogen cyanide on aldehyde-ammonia is conducted in the dark instead of in the light, the same products are formed, but in different proportions.

Experiments carried out by heating molecular amounts of aldehyde-ammonia and hydrocyanic acid ( $12\%$ ) at the temperature of a boiling water-bath, showed that Erlenmeyer and Passavant's  $\alpha$ -iminopropionitrile (Abstr., 1880, 313) yields on hydrolysis alanine and A- $\alpha$ -iminodipropionic acid.

A. McK.

**Method of Preparing the Oxynitriles,  $OR \cdot CH_2 \cdot CN$ .**  
D. GAUTHIER (*Compt. rend.*, 1906, 143, 831—832).—Chloromethyl alkyl

ethers of the type  $\text{RO}\cdot\text{CH}_2\text{Cl}$ , prepared by the action of hydrogen chloride on a mixture of the corresponding alcohol  $\text{ROH}$  and formaldehyde (Henry), are readily converted into the corresponding cyanoalkyloxymethanes,  $\text{RO}\cdot\text{CH}_2\cdot\text{CN}$ , by the action of mercuric, or, preferably, cuprous cyanide; the reaction takes place in the cold, the yield is 60–70% of the theoretical, and the following compounds were thus prepared. *Methoxyacetoneitrile*,  $\text{OMe}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 118–119°; *propoxyacetoneitrile*,  $\text{C}_3\text{H}_7\text{O}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 147–148°; *isobutyloxyacetoneitrile*,  $\text{C}_4\text{H}_9\text{O}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 158–160°; and *amyloxyacetoneitrile*,  $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 183–184°. M. A. W.

**Nitriles of Alkylglycollic Acids [Cyanoalkyloxymethanes].** MARCEL SOMMELET (*Compt. rend.*, 1906, 143, 827–828).—Cyanoalkyloxymethanes [alkyloxyacetoneitriles] (compare Abstr., 1904, i, 222), originally prepared by dehydrating the corresponding alkyloxyacetamides by means of phosphoric oxide (Henry, Abstr., 1873, 879), are more conveniently obtained by the action of silver or mercuric cyanide on the corresponding chloromethyl alkyl ether, and the following compounds were thus prepared. *Methoxyacetoneitrile*,  $\text{OMe}\cdot\text{CH}_2\cdot\text{CN}$ , prepared by the action of mercuric cyanide in the cold on chloromethyl methyl ether, is a colourless liquid, b. p. 120°, with an odour recalling that of ethyl formate. *Ethoxyacetoneitrile*,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 135.4°/760 mm., is prepared by the action of silver cyanide on chloromethyl ethyl ether; the yield is 70%. The following derivatives were also prepared: *Ethoxyacetic acid*, b. p. 156–157°; the *amide*, m. p. 82°, and the *thioamide*, m. p. 81°. *Propoxyacetoneitrile*,  $\text{OPr}^a\cdot\text{CH}_2\cdot\text{CN}$ , is a colourless liquid with a sweet odour, b. p. 151–152°/758 mm., the *thioamide*, m. p. 63°. *isobutoxyacetoneitrile*,  $\text{C}_4\text{H}_9\text{O}\cdot\text{CH}_2\cdot\text{CN}$ , is a colourless liquid, b. p. 80–82°/44 mm.; the *thioamide*, m. p. 60–61°. *isoAmyloxyacetoneitrile*,  $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CH}_2\cdot\text{CN}$ , is a colourless, slightly oily liquid with a strong odour, b. p. 99°/44 mm. M. A. W.

**$\psi$ -Diazoacetamide.** THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1906, 39, 3776–3783. Compare Abstr., 1906, i, 939; Curtius and Lang, Abstr., 1889, 369; Curtius and Thompson, Abstr., 1906, i, 940; Pinner, Abstr., 1898, i, 94; Hantzsch and Silberrad, Abstr., 1900, i, 261; Hantzsch and Lehmann, Abstr., 1901, i, 678; Silberrad, Trans., 1900, 77, 1185).—The constitutions of bisdiazoacetamide and  $\psi$ -diazoacetamide are discussed in the light of Bulow's paper (Abstr., 1906, i, 905). Bisdiazoacetamide is probably 1:2-dihydrotetrazine-3:6-dicarboxylamide, and  $\psi$ -diazoacetamide 3:6-dihydrotetrazine-3:6-dicarboxylamide, but a definite decision on these points or on the question of the existence of 1:4-dihydrotetrazine apart from 1-amino-1:3:4-triazole cannot yet be reached.

G. Y.

**Syntheses with Azoimides. V. Diazoaminomethane (Dimethyltriazen).** OTTO DIMROTH (*Ber.*, 1906, 39, 3905–3912. Compare Abstr., 1905, i, 311).—The author describes the preparation of

diazoaminomethane, a compound of special interest as being the simplest representative of the diazoamino-series. The isolation of the compound was attended with difficulties owing to its instability and to the fact that it is miscible with water in all proportions.

Diazoaminomethane is obtained by the action of magnesium methyl iodide on methylazoimide (compare Dimroth and Wislicenus, Abstr., 1905, i, 422) and decomposition of the resulting compound with water. Its formation is represented by the equations: (1)  $\text{MeMgI} + \text{Me}\cdot\text{N}_3 = \text{NMe}\cdot\text{N}\cdot\text{NMe}\cdot\text{MgI}$  and (2)  $\text{NMe}\cdot\text{N}\cdot\text{NMe}\cdot\text{MgI} + \text{H}_2\text{O} = \text{NMe}\cdot\text{N}\cdot\text{NHMe} + \text{MgI}(\text{OH})$ .

During its formation, diazoaminomethane is decomposed with evolution of nitrogen to an extent which may be lessened if the Grignard reagent be filtered from the impurities present in the commercial magnesium used, the latter impurities having a catalytic effect on the decomposition. The aqueous solution of diazoaminomethane was extracted with a large amount of ether, the copper compound formed and the latter dried and heated with an equivalent quantity of diazoaminobenzene in a glycerol bath, which was gradually raised to  $100^\circ$  whilst the pressure was maintained at about 200 mm. The action is represented by the equation  $\text{N}_3\text{Me}_2\text{Cu} + \text{N}_3\text{HPh}_2 = \text{N}_3\text{Me}_2\text{H} + \text{N}_3\text{CuPh}_2$ .

*Diazoaminomethane (dimethyltriazene)*,  $\text{N}_3\text{Me}_2\text{H}$ , obtained by this method, is a colourless liquid which solidifies when immersed in a mixture of carbon dioxide and ether; m. p.  $-12^\circ$ , b. p.  $92^\circ$ . When heated quickly, it explodes. It has unpleasant physiological effects. As distinct from aromatic and fatty-aromatic diazoamino-compounds, it is a base; it does not, however, form salts, since acids, even the weakest, decompose it with evolution of nitrogen. It reacts with hydrochloric acid according to the equation  $\text{N}_3\text{Me}_2\text{H} + 2\text{HCl} = \text{MeCl} + \text{N}_2 + \text{NH}_2\text{Me}\cdot\text{HCl}$ , whilst with sulphuric acid it forms methyl hydrogen sulphate in an analogous manner. It decomposes in contact with finely-divided platinum. *Copper dimethyltriazene*,  $\text{N}_3\text{Me}_2\text{Cu}$ , separates from ether in glistening, yellow prisms, m. p.  $185-186^\circ$ ; it is decomposed by dilute sulphuric acid. *Silver dimethyltriazene*,  $\text{N}_3\text{Me}_2\text{Ag}$ , forms colourless, silky needles.

Dimethyltriazene combines in ethereal solution with phenylcarbimide to form the *carbamide*  $\text{N}_3\text{Me}_2\cdot\text{CO}\cdot\text{NHPh}$ , which separates from light petroleum in needles or plates, m. p.  $62^\circ$ . A. McK.

**The Action of Magnesium on Ethyl Bromoisobutyrate.** JULIUS SALKIND (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 97-103).—Magnesium alone acts very slowly on an ethereal solution of ethyl  $\alpha$ -bromoisobutyrate, but the addition of a little iodine greatly facilitates the reaction whilst the presence of acetyl chloride retards it. The most probable final product of the reaction is *ethyl tetramethylacetoacetate*, containing a little bromine, b. p.  $199-201^\circ$ ; its *semicarbazide* derivative, m. p.  $136-137^\circ$ . The reaction probably proceeds in the following stages:  $2\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Et} \rightarrow 2\text{MgBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et} \rightarrow \text{MgBr}\cdot\text{CMe}_2\cdot\text{C}(\text{OEt})(\text{OMgBr})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et} \rightarrow \text{CHMe}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ . Z. K.



**The Action of Magnesium on the Esters of Bromo-acids and on a Mixture of these Esters and Aldehydes.** J. ZELTNER and SERGIUS REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 103—109. Compare preceding abstract).—*Ethyl tetramethylacetoacetate* has been obtained by a slightly different method from that used by Salkind. The following is proposed as a possible alternative for the second and third stages of the reaction :

$2\text{MgBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et} = \text{MgBr}\cdot\text{OEt} + \text{MgBr}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , which, with water, yields ethyl tetramethylacetoacetate (compare *ibid.*, 1905, **37**, 881). Semicarbazide gives with it a *crystalline* compound, m. p. 228—230°. Magnesium acts on a mixture of ethyl bromoisobutyrate and benzaldehyde, forming a neutral, crystalline *substance*, possibly  $\text{CMe}_2\begin{matrix} \text{CO}\cdot\text{CMe}_2 \\ \text{CO}\text{---}\text{O} \end{matrix}\text{CHPh}$ , m. p. 134—135°. By substituting *p*-tolualdehyde for benzaldehyde, an analogous *substance* is produced, m. p. 138—139°. Z. K.

### Reactions which Generate Organo-magnesium Compounds.

ALBERT REYCHLER (*Bull. Soc. chim.*, 1906, [iii], **35**, 1079—1088. Compare Abstr., 1906, ii, 836).—Mercury ethyl and mercury phenyl do not excite a reaction between magnesium and bromobenzene in presence of ether, and scarcely affect the action of ethyl bromide on the metal. Zinc ethyl, on the contrary, induces an immediate action between magnesium and bromobenzene, especially in the proportion of 1 mol. of the exciting reagent to from 75—100 mols. of bromobenzene. This reaction is retarded and finally paralysed by the further addition of chloroform.

Baeyer's "active magnesium" (Abstr., 1905, i, 766) can be prepared by the careful addition of excess of metallic magnesium to a solution of iodine in ether. The solid phase (the residual magnesium) of this mixture is inactive. The liquid phase is colourless, becomes yellow on exposure to air, conducts electricity feebly, on the removal of even small quantities of the solvent by the passage of an inert gas deposits the compound  $\text{Mg}(\text{OEt}_2\text{I})_2$  (compare Zelinsky, Abstr., 1903, i, 802), and powerfully accelerates the attack of magnesium by bromobenzene.

Its action as an accelerating agent in this case is peculiar; it is very active in small quantities (1 mol. in 3000 of ether and bromobenzene), less active in medium quantity, and again more active when present in larger amount. Chloroform retards its accelerating action, and has least influence when the accelerating agent is present in the optimum quantity, and ultimately paralyses it when the number of molecules of chloroform present is 0·0015 to 0·0017 of the total number of molecules.

The accelerating action of zinc ethyl is probably indirect in the above reactions, and due to one or other of the following changes : (1)  $\text{ZnEt}_2 + 2\text{PhBr} = 2\text{EtPh} + \text{ZnBr}_2$ ; (2)  $\text{ZnEt}_2 + \text{PhBr} = \text{EtPh} + \text{EtZnBr}$ . The accelerating action of Baeyer's active magnesium, or the ethereal solution of this prepared as described above, and of the exciting agents already mentioned (*loc. cit.*), is probably due to the presence of increasing quantities of substances of the type  $\text{RMgX}$ , where X is a halogen. T. A. H.

**Nomenclature of Derivatives of Camphane and Fenchane.** IWAN KONDAKOFF (*J. pr. Chem.*, 1906, [ii], 74, 420—422).—Considering that the close relationship of camphane and fenchane and their derivatives should be expressed by the nomenclature, the author proposes to name them as derivatives of *dicycloheptane*. The following examples are given as showing the extent to which isomerism is possible when a methyl group is introduced into the hexatomic ring of dimethyldicycloheptanes having the group :CMe<sub>2</sub> in the pentatomic and hexatomic rings respectively.

The *ortho*-derivative, camphane (1:7:7-trimethyldicycloheptane),  

$$\begin{array}{c} \text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_2 \\ | \quad | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array}$$
, and the *meta*-derivative, dihydrofenchene (2:7:7-tri-

methyldicycloheptane), 
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CHMe} \\ | \quad | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array}$$
, are related to norcamphane

(7:7-dimethyldicycloheptane), 
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array}$$
.

To norisocamphane (2:2-dimethyldicycloheptane), 
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2 \\ | \quad | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array}$$
,

are related two *ortho*-derivatives: 1:2:2-trimethyl- and 2:2:3-trimethyl- (*isocamphane*), two *meta*-derivatives: 2:2:4-trimethyl- (*fenchane*) and 2:2:6-trimethyl-, and one *para*-derivative: 2:2:5-trimethyldicycloheptane (*isofenchane*). G. Y.

**tert.-Amylbenzene Derivatives.** MILE. ELLEN GLEDITSCH (*Bull. Soc. chim.*, 1906, [iii], 35, 1094—1097. Compare Abstr., 1906, i, 942).—*tert.*-Amylbenzene, prepared by condensing *isoamyl* chloride with benzene in presence of aluminium chloride (compare Boedker, Abstr., 1901, i, 684; Konowaloff and Egoroff, Abstr., 1899, i, 801), has b. p. 189—190°, D<sub>4</sub><sup>21.5</sup> 0.8657, and n<sub>D</sub><sup>23</sup> 1.49154. *p*-Chloro-*tert.*-*amylbenzene*, obtained by condensing *isoamyl* chloride with chlorobenzene in presence of aluminium chloride, is a colourless liquid with an aromatic odour, b. p. 229°, D<sub>4</sub><sup>22</sup> 1.0070, n<sub>D</sub><sup>21</sup> 1.59394. On nitration, it furnishes 4-chloro-2:3-dinitro-*tert.*-*amylbenzene*, which separates from boiling alcohol in small, yellow crystals, m. p. 78°.

*p*-Bromo-*tert.*-*amylbenzene*, similarly prepared, is a colourless liquid with an aromatic odour, b. p. 246°, D<sub>4</sub><sup>22</sup> 1.2223, and n<sub>D</sub><sup>21</sup> 1.53242. On nitration, it furnishes 4-bromo-2:3-dinitro-*tert.*-*amylbenzene*, which crystallises in small, yellow needles, m. p. 71°.

When chlorobenzene is treated with ethyl bromide or propyl chloride in presence of aluminium chloride, a mixture of products is obtained, which, on oxidation with chromic acid, yields both *o*- and *p*-chlorobenzoic acids, whence it appears that the comparatively light alkyl radicles, ethyl and propyl, are able, under these conditions, to enter the benzene ring both in the *ortho*- and *para*-positions.

T. A. H.

**A New Mode of Formation of Phenylacetylene.** GOTTFRIED MÜHLHAUSEN (*Ber.*, 1906, **39**, 4146—4147).—Phenylacetylene is formed in 10% yield when dibenzylideneacetone tetrabromide is heated with alcoholic potassium hydroxide. A. McK.

**Existence of Additive Compounds of Aromatic Nitro-derivatives with Haloid Mercury Salts.** LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 459—466. Compare Abstr., 1905, i, 869).—The author has examined the melting-point curves of mixtures of (1) mercuric chloride with nitrobenzene, *o*-, *m*-, or *p*-nitrotoluene, *p*-nitroanisole, or  $\alpha$ -nitronaphthalene, and of (2) mercuric bromide with *p*-nitrotoluene, in order to ascertain whether double compounds are formed between these pairs of salts.

The results show that the property of forming double salts with mercuric chloride is an almost general property of aromatic nitro-derivatives, which hence behave similarly to the somewhat analogously constituted iodoxy-derivatives. Unlike the compounds formed by the latter, those yielded by the nitro-derivatives are only slightly stable and in no case exhibit a definite melting point. The property of forming double salts with mercuric bromide is not general with the aromatic nitro-derivatives, and is only manifested by those substances with which mercuric chloride gives a relatively stable double salt. The nitro-compounds resemble the iodoxy-derivatives in not forming double salts with mercuric iodide. T. H. P.

**Solubility of Sodium Naphthalene- $\beta$ -sulphonate in Water and in Hydrochloric Acid.** EMIL FISCHER (*Ber.*, 1906, **39**, 4144—4145).—The numbers 6.04, 6.47, 5.35, 4.13, and 2.42 respectively represent the number of parts of sodium naphthalene- $\beta$ -sulphonate, which are described by 100 parts of water, *N*-hydrochloric acid, 2*N*-hydrochloric acid, 3*N*-hydrochloric acid, and 5*N*-hydrochloric acid respectively at 23.9°. A. McK.

**Constitutional Formula of some Dimethylantracenes.** JAMES LAVAUX (*Compt. rend.*, 1906, **143**, 687—690).—Additional evidence that B-dimethylantracene (Abstr., 1905, i, 125) is the 2:7-dimethylantracene (Abstr., 1905, i, 698) is afforded by the facts (1) that  $\beta$ -methylantracene is formed when the corresponding methylantracenecarboxylic acid (obtained by reducing the methylanthraquinonecarboxylic acid with zinc and ammonia) is distilled with soda lime; (2) that a mixture of *isophthalic* and *terephthalic* acids is produced when the corresponding anthraquinonedicarboxylic acid is fused with potassium hydroxide, which shows that the anthraquinonedicarboxylic acid must have been the 2:7- or the 2:6-compound. As, however, 2:6-dimethylantracene has been isolated by Dewar and Jones (*Trans.*, 1904, **85**, 217) and is distinct from B-dimethylantracene, the latter must be the 2:7-isomeride.

When the methylantracenecarboxylic acid obtained from the A-dimethylantracene is distilled with soda lime the product is  $\beta$ -methylantracene, showing that one of the methyl groups in the original hydrocarbon is in the  $\beta$ -position; further, when the

corresponding anthraquinonedicarboxylic acid is fused with potassium hydroxide at 260° for thirteen days of twenty-four hours each, a mixture of phthalic, isophthalic, and terephthalic acids is obtained, and only the 1:6- or the 1:7-isomeride would yield the three isomeric phthalic acids; the A-dimethylantracene is therefore the 1:6- or the 1:7-isomeride.

M. A. W.

**Phenanthrene Series. XIX. 2:9:10-Trichlorophenanthrene and 2-Chlorophenanthraquinone.** JULIUS SCHMIDT and RICHARD SCHALL (*Ber.*, 1906, **39**, 3891—3895).—2:9:10-*Trichlorophenanthrene*,  $C_{14}H_7Cl_3$ , is formed when phenanthrene is chlorinated in the presence of a small amount of iodine, or even better by passing chlorine into 9-bromophenanthrene heated on the water-bath and kept in sunlight. When the chlorination is incomplete, 9:10-dichlorophenanthrene is formed. The trichloro-derivative crystallises from alcohol in colourless needles, m. p. 123—124°. When oxidised with an aqueous acetic acid solution of chromic acid, it yields 2-*chlorophenanthraquinone*,  $C_{14}H_9O_2Cl$ , which crystallises from glacial acetic acid in yellowish-red needles, m. p. 235—237°. When mixed with phenanthraquinone, this melts at 190° and cannot be purified by crystallisation. The *oxime*,  $C_{14}H_9O_2NCl$ , forms greenish-yellow needles, m. p. 140—141°. The constitution of the chlorophenanthraquinone has been established by conversion into *p-chlorodiphenic acid*,  $C_{14}H_9O_4Cl$ , which has been obtained also from *p*-aminodiphenic acid by Sandmeyer's reaction. It crystallises in colourless needles, m. p. 237°.

J. J. S.

**Triphenylmethyl and Tervalent Carbon. Constitution of Benzopinacolin.** JULIUS SCHMIDLIN (*Ber.*, 1906, **39**, 4183—4198. Compare Abstr., 1906, i, 392).—Further attempts to elucidate the constitution of triphenylmethyl. Magnesium triphenylmethyl chloride exists in two modifications. The  $\alpha$ -form, prepared as described previously (*loc. cit.*), is not particularly stable, and by heating, alone or in benzene solution, for three hours at 80—90°, changes into the  $\beta$ -isomeride which exhibits the normal reactions of a Grignard reagent. The  $\alpha$ -form, prepared in absolutely dry ether, yields about 50% each of triphenylmethyl and triphenylmethane by the action of dilute hydrochloric acid in an atmosphere of hydrogen, but the presence of a trace of moisture in the solvent causes the formation of triphenylcarbinol by the action of the mineral acid. Carbon dioxide, acting on the  $\alpha$ -form at the moment of its production, gives triphenylacetic acid in 83% yield, but when the gas is passed into a solution, already prepared, the main product is triphenylmethyl.

A vigorous reaction ensues when benzaldehyde and  $\alpha$ -magnesium triphenylmethyl chloride are mixed in anhydrous ethyl ether-benzene solution, the liquid becomes dark red, and  $\gamma$ -*benzopinacolin*,  $C_{26}H_{20}O$ , is obtained, m. p. 165—166°, which seems to be identical with Bourcet's *p*-benzoyltriphenylmethane, m. p. 164° (Abstr., 1897, i, 566). In the presence of moisture, a red coloration is not produced in the preceding reaction and benzoin is formed.

Both the  $\alpha$ - and the  $\beta$ -modifications in ethereal solution yield triphenylmethane with cold glacial acetic acid.

The normal  $\beta$ -form,  $\text{MgCl} \cdot \text{CPh}_3$ , reacts with benzaldehyde to form  $\beta$ -benzopinacolin, which therefore has the constitution  $\text{CPh}_3 \cdot \text{COPh}$  (compare Thörner and Zincke, *Abstr.*, 1878, 425; Wertheimer, *Abstr.*, 1906, i, 271).

In answer to Gomberg and Cone's contention (*Abstr.*, 1906, i, 414), the author shows that the ethereal solution of  $\alpha$ -magnesium triphenylmethyl chloride cannot contain free triphenylmethyl, because (1) after conversion of the  $\alpha$ - into the  $\beta$ -modification the solution does not contain triphenylmethyl, and (2) triphenylmethyl, by similar treatment, remains unchanged,

Since the  $\alpha$ -form cannot contain the group  $\text{CPh}_3$ , the triphenylmethyl obtained from it cannot have the constitution  $\text{CPh}_3$ . C. S.

**"Triphenylmethyl" and its Haloid Derivatives.** ALEXEI E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1906, [ii], 74, 340—344. Compare *Abstr.*, 1905, i, 125, 270).—A criticism of Hantzsch's paper (*Abstr.*, 1906, i, 617) and a claim for priority. Whilst the analogy drawn between the derivatives of triphenylmethane and trinitromethane is new, Hantzsch's experiments are insufficient to show that hexanitroethane cannot exist.

The relation of the colour of triphenylmethyl and its haloid derivatives to the structure of triphenylmethyl is discussed shortly.

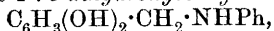
G. Y.

**Hexaphenylethane.** JULIUS SCHMIDLIN (*Ber.*, 1906, 39, 4198—4204).—Various unsuccessful attempts to synthesise hexaphenylethane are described. The most promising result is obtained by the interaction of  $\beta$ -magnesium triphenylmethyl chloride and triphenylchloromethane, whereby a white, crystalline substance is formed, which gives analytical results approximating to the formula  $\text{C}_2\text{Ph}_6$ ; this, however, has not yet been obtained free from magnesium. It sinters at 240—260°, and has m. p. 275—276°. C. S.

**A New Method of Nitrating.** OTTO N. WITT and ALFRED UTERMANN (*Ber.*, 1906, 39, 3901—3905. Compare Orton, *Trans.*, 1902, 81, 806).—When a cold glacial acetic acid solution of acetanilide is nitrated with a cold glacial acetic acid solution of fuming nitric acid containing a small amount of carbamide, an 87% yield of mononitro-products is obtained. Three-fourths consists of the ortho- and one-fourth of the para-compound, whereas when an excess of nitric acid alone is used the chief product is the para-compound. The ortho- and para-derivatives can be separated readily by means of an aqueous alcoholic solution of potassium hydroxide in which the ortho-compound is soluble at 0°. J. J. S.

**[Adipanilide].** EYVIND BÖDTKER (*Ber.*, 1906, 39, 4003).—Adipanilide (*Abstr.*, 1906, i, 827) has been prepared by Balbiano (*Abstr.*, 1902, i, 741). C. S.

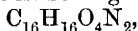
**Decomposition of N : N'-Diarylmethylenediamines.** CARL A. BISCHOFF and EMANUEL FRÖHLICH (*Ber.*, 1906, **39**, 3964—3981. Compare Abstr., 1903, i, 26).—*o*-Hydroxybenzylaniline and the para-isomeride occur among the products obtained by heating methylenedianiline and phenol at 200°. With resorcinol in acetone-benzene solution the base yields 1 : 3-*dihydroxybenzylaniline*,



m. p. 159, whilst oxanilide and *o*-hydroxybenzylaniline are obtained when methylenedianiline is heated with phenyl oxalate in xylene solution. Oxalo-*o*-toluidide is obtained from phenyl oxalate and *o*-toluidine or methylenedi-*o*-toluidine in boiling benzene.

Methylenedi-*p*-toluidine, when heated with phenol in xylene solution, yields *o*-hydroxybenzyl-*p*-toluidine (m. p. 121°); with resorcinol, a *m-dihydroxybenzyl-p-toluidine*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , is obtained, m. p. 165°, and with phenyl oxalate, oxalo-*p*-toluidide (m. p. 266°) is formed.

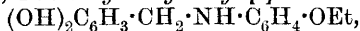
Methylenedi-*o*-anisidine, b. p. 160°/25 mm., yields with phenol in boiling benzene, Paal's *o*-hydroxybenzyl-*o*-anisidine (Abstr., 1903, i, 340), with phenol at 180—200°, the para-isomeride,  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}$ , m. p. 125°, and with phenyl oxalate in boiling xylene, oxalo-*o*-anisidide,



m. p. 246°, which is obtained also from phenyl oxalate and *o*-anisidine. *p*-Anisidine phenoxide,  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}$ , m. p. 60°, forms colourless prisms.

Methylenedi-*p*-anisidine yields *o*-hydroxybenzyl-*p*-anisidine with phenol at 180° or in boiling xylene, oxalo-*p*-anisidide,  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$ , m. p. 260—261°, with phenyl oxalate, and 1 : 3-*dihydroxybenzyl-p-anisidine*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 149°, with resorcinol in benzene solution.

Methylenedi-*p*-phenetidine, b. p. 174°/12 mm., yields the following compounds by reactions similar to the preceding : *p*-phenetidine phenoxide, m. p. 52°; *p*-hydroxybenzyl-*p*-phenetidine,  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}$ , m. p. 106°; oxalo-*p*-phenetidide, 1 : 3-*dihydroxybenzyl-p-phenetidine*,



m. p. 156°.

Phenyl oxalate was also heated with the following bases : methylaniline at 200° gave a mixture of dimethyloxanilide,  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$ , m. p. 86°, and phenyl methyloxanilate; phenylhydrazine in boiling benzene gave oxalyldiphenylhydrazine; benzylaniline at 110—130°/50 mm., gave *phenyl benzyloxanilate*,  $\text{C}_{21}\text{H}_{17}\text{O}_3\text{N}$ , m. p. 93—94°; diphenylamine, when heated in a vacuum and subsequently at 180° under ordinary pressure, gave *phenyl phenyloxanilate*,  $\text{C}_{20}\text{H}_{15}\text{O}_3\text{N}$ , m. p. 127—128°; carbazole had no action.

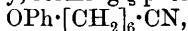
C. S.

**Cyclic Imines. II. Attempts to Synthesise Heptamethyleneimine.** JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1906, **39**, 4110—4119. Compare Braun and Steindorff, Abstr., 1905, i, 826).—Heptamethyleneimine might be formed by elimination of ammonia from heptamethylenediamine or of the hydrogen haloid from  $\eta$ -chloro- or  $\eta$ -bromo-heptylamine. The diamine is easily prepared in large quantities by reduction of pimelonitrile (Abstr., 1905, i, 636), but the

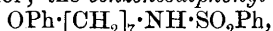
action of phosphorus pentachloride on dibenzoylheptamethylenediamine leads to the formation chiefly of  $\alpha\eta$ -dichloroheptane and only of small quantities of  $\eta$ -chloroheptylamine (Abstr., 1905, i, 634).  $\eta$ -Chloro- and  $\eta$ -bromo-heptylamine are obtained, however, in good yields from  $\zeta$ -phenoxyhexylamine through the following series of compounds.

The action of phosphorus pentachloride on benzoyl- $\zeta$ -phenoxyhexylamine (Braun and Steindorff, *loc. cit.*) leads to the formation of benzonitrile and *phenyl  $\zeta$ -chlorohexyl ether*,  $\text{OPh} \cdot [\text{CH}_2]_6 \cdot \text{Cl}$ , which forms a colourless, aromatic oil, b. p. 164—165°/11 mm., and when boiled with sodium iodide in alcoholic solution yields *phenyl  $\zeta$ -iodohexyl ether*,  $\text{OPh} \cdot [\text{CH}_2]_6 \cdot \text{I}$ . This is obtained in white crystals, m. p. 25°, b. p. 183—184°/11 mm., and forms  $\alpha\zeta$ -diphenoxyhexane when heated with an excess of sodium phenoxide.

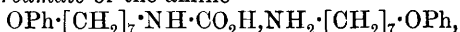
When boiled with potassium cyanide in aqueous-alcoholic solution, phenyl  $\zeta$ -chlorohexyl ether reacts only slowly, but the  $\zeta$ -iodo-ether more quickly and completely, forming  $\zeta$ -phenoxyheptonitrile,



which crystallises from light petroleum in snow-white leaflets, m. p. 32°, and on reduction with sodium and alcohol yields  *$\eta$ -phenoxyheptylamine*,  $\text{OPh} \cdot [\text{CH}_2]_7 \cdot \text{NH}_2$ , m. p. 32—34°, b. p. 185°/11 mm. This is precipitated on addition of an alkali hydroxide to its acid solution, and absorbs moisture and carbon dioxide from the atmosphere; the *hydrochloride*,  $\text{OPh} \cdot [\text{CH}_2]_7 \cdot \text{NH}_2 \cdot \text{HCl}$ , m. p. 125—127°, crystallises from water or a mixture of alcohol and ether; the *platinichloride*,  $(\text{C}_{13}\text{H}_{21}\text{ON})_2\text{H}_2\text{PtCl}_6$ , commences to blacken at 200° and is melted at 210°. The *benzoyl* derivative,  $\text{OPh} \cdot [\text{CH}_2]_7 \cdot \text{NHBz}$ , m. p. 89—90°, crystallises from alcohol; the *benzenesulphonyl* derivative,



m. p. 47°, crystallises from aqueous alcohol. The action of carbon dioxide on  $\eta$ -phenoxyheptylamine in aqueous solution in presence of a small amount of sodium hydroxide leads to the formation of the substituted *carbamate* of the amine



which separates as a delicate, white powder, m. p. 90—98°, and decomposes and evolves gas at 120°.  $\eta$ -Chloroheptylamine (Abstr., 1905, i, 634) is formed by heating  $\eta$ -phenoxyheptylamine hydrochloride with concentrated hydrochloric acid at 90° under pressure for six hours. The *picrate*,  $\text{NH}_2 \cdot [\text{CH}_2]_7 \cdot \text{Cl} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , forms a yellow, crystalline powder, m. p. 102—104°.

*$\eta$ -Bromoheptylamine*,  $\text{NH}_2 \cdot [\text{CH}_2]_7 \cdot \text{Br}$ , obtained by heating the phenoxy-compound with hydrobromic acid at 80°, is isolated as the *hydrobromide*, which forms a hygroscopic, reddish-brown mass; the *picrate*,  $\text{Br} \cdot [\text{CH}_2]_7 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , m. p. 100—102°. The *benzoyl* derivative,  $\text{Br} \cdot [\text{CH}_2]_7 \cdot \text{NHBz}$ , m. p. 69°, crystallises from a mixture of ether and light petroleum. The yield of  $\eta$ -bromoheptylamine, calculated from the benzoyl- $\zeta$ -phenoxyhexylamine, amounts to about 50% of the theoretical.

When heated with an aqueous alkali hydroxide,  $\eta$ -bromoheptylamine hydrobromide yields traces of a basic *substance*, which is volatile in a current of steam, has an odour resembling that of piperidine, and forms a *platinichloride* and a *product* having the empirical formula of hepta-

methyleneimine,  $C_7H_{15}N$ . This forms a wax-like mass, is not volatile with steam, is readily soluble in alcohol, chloroform, or acids, and absorbs carbon dioxide from the atmosphere. The *platinichloride*,  $(C_7H_{15}N)_2H_2PtCl_6$ , is amorphous, commences to blacken at  $205^\circ$ , m. p.  $238^\circ$ , decomposing. The quaternary *iodide*,  $C_7H_{14}NMe_3I$ , obtained on methylation, crystallises from a mixture of ether and methyl alcohol; a stable liquid hydrosol of silver iodide is formed on addition of silver nitrate to the aqueous solution of the quaternary iodide.

$\eta$ -Chloroheptylamine reacts with alkali hydroxides in the same manner as, but more slowly than, the  $\eta$ -bromo-base. A pure, crystalline derivative of the secondary base suitable for a molecular weight determination could not be obtained.

When heated alone, heptamethylenediamine hydrochloride decomposes into a black, carbonaceous mass, but on distillation with soda-lime, yields traces of ammonia and a colourless, basic, liquid distillate consisting chiefly of heptamethylenediamine.

These results are in agreement with the formation of only the acyclic diamine on reduction of pimelonitrile, whereas both acyclic diamines and cyclic imines are formed on reduction of the analogous ethylene and trimethylene dicyanides. G. Y.

**Behaviour towards Boiling Hydriodic Acid of Alkyl Groups attached to Nitrogen.** GUIDO GOLDSCHMIEDT (*Monatsh.*, 1906, 27, 849—877. Compare Goldschmiedt and Hönigschmid, *Abstr.*, 1903, ii, 578; 1904, i, 86; *ibid.*, ii, 94; Busch, *Abstr.*, 1902, i, 501; Decker, *Abstr.*, 1903, ii, 763).—The author has investigated the behaviour towards boiling hydriodic acid of forty-four substances containing the group  $:NMe$  or  $:NEt$ . The tabulated results show that the great majority of these lose the alkyl group as the alkyl iodide; the velocity of the reaction, however, varies considerably, depending on the structure of the nucleus and the nature and position of substituting groups, being often so small that the heating must be prolonged far past the time necessary for a methoxyl determination before a weighable quantity of silver iodide is obtained. In general, the ethyl are more stable than the methyl compounds.

Of the substances investigated, only three, diphenylmethylamine and *o*- and *p*-dimethylaminobenzaldehydes, yield methyl iodide in such manner as to simulate the presence of methoxyl groups. In most cases, the silver solution remains clear for at least an hour, and then suddenly deposits the double salt of silver iodide and nitrate (*Abstr.*, 1904, ii, 94); in this, methyl and ethyl compounds behave similarly. On the other hand, methylanthranilic acid, dimethylantranilic acid, anthraquinone derivatives, methylcarbazole, and pyrimidone yield methyl iodide with sufficient rapidity to cause a *plus* error in the estimation of methoxyl in the analysis of a methoxy-derivative.

The influence of the benzene nucleus on the mobility of the alkyl group is shown by the behaviour of diphenylmethylamine, tetramethyldiaminodiphenylmethane, and tetramethyldiaminotriphenylmethane. The influence of the naphthalene nucleus is much greater in  $\alpha$ - than in  $\beta$ -derivatives. The velocity of the formation of methyl iodide by methylaniline is increased by the introduction of negative substituting



groups in the para-position, in the order  $\text{Br}$ ,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot$ ,  $\text{NO}$ ,  $\cdot\text{CO}\cdot$ ,  $\cdot\text{CO}_2\text{H}$ , and  $\cdot\text{COH}$ . Negative substituting groups have greater influence in the para- than in the ortho-, and least in the meta-position.

In an aryl dimethylamine the average stability of the methyl groups is greater than the stability of the methyl of the corresponding aryl-methylamine, unless a negative substituting group is present when the relative stabilities are the converse.

It is noted that in equal periods of time, diphenylmethylamine yields four times as much methyl iodide as does the closely-related methyl-carbazole. Whilst antipyrine causes no turbidity of the silver nitrate solution in six hours, its dimethylamino-derivative loses 25% of the methyl of the side chain in two hours, and on prolonged boiling not only the whole of the methyl of the dimethylamino- but also part of the methyl of the methylimino-group of the nucleus. G. Y.

**Halogen Derivatives of 4-Aminodiphenyl and of 4-Aminodiphenyl-4'-oxamic Acid.** P. GELMO (*Ber.*, 1906, 39, 4175—4183).—4-Chloro-4'-aminodiphenyl,  $\text{C}_{12}\text{H}_{10}\text{NCl}$ , obtained from Täuber's diazo-solution (*Abstr.*, 1894, i, 597) by the Sandmeyer reaction, forms colourless leaflets, m. p.  $134^\circ$  (corr.). The *hydrochloride* and the *sulphate* are mentioned; the *acetyl* derivative has m. p.  $245^\circ$  (corr.). 4-Bromo-4'-aminodiphenyl forms yellow leaflets, m. p.  $145^\circ$  (corr.); the *acetyl* derivative has m. p.  $247^\circ$  (corr.). 4-Iodo-4'-aminodiphenyl forms yellow leaflets, m. p.  $166^\circ$  (corr.); the *acetyl* derivative has m. p.  $250^\circ$  (corr.).

Diazotised benzidineoxamic acid forms an orange-yellow, crystalline mass which decomposes at  $110^\circ$ . From it the following substances are prepared in the usual way. 4-Hydroxydiphenyl-4'-oxamic acid,  $\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}$ , decomposes above  $270^\circ$ , and by hydrolysis yields 4-amino-4'-hydroxydiphenyl. 4-Chlorodiphenyl-4'-oxamic acid forms yellowish-white needles and decomposes at  $213^\circ$ ; the *ammonium* salt decomposes at  $247^\circ$ . The corresponding *bromo*-compound and its *ammonium* salt decompose at  $240^\circ$  and  $260^\circ$  respectively, the *iodo*-compound and its *ammonium* salt at  $280^\circ$  and  $290^\circ$  respectively. By hydrolysis these oxamic acids yield the compounds mentioned previously. C. S.

**Methylpicramic Acid.** WALTHER BORSCHKE and ARNOLD HEYDE (*Ber.*, 1906, 39, 4092—4093. Compare *Abstr.*, 1906, i, 15).—As *o*-nitrophenols having a hydrogen atom in the ortho-position to the nitro-group yield purpurates when treated with potassium cyanide, methylpicramic acid must be 2:6-dinitro-4-amino-*m*-cresol, and not 2:4-dinitro-6-amino- or 4:6-dinitro-2-amino-*m*-cresol, since, when heated with potassium cyanide in aqueous solution on the water-bath, it forms potassium methylpicramate and not a methylpicramopurpurate, hydrogen cyanide being liberated. G. Y.

**Action of Phosphorus Pentabromide and Pentachloride on Phenyl Alkyl Ethers.** WILHELM AUTENRIETH and PAUL MÜHLINGHAUS (*Ber.*, 1906, 39, 4098—4106. Compare Autenrieth, *Abstr.*, 1895, i, 511; Bachmann, *Abstr.*, 1883, 726).—Phosphorus

pentabromide or pentachloride reacts with phenyl alkyl ethers at the laboratory temperature or when gently heated on the water-bath, according to the equation  $C_6H_5 \cdot OR + PX_5 = C_6H_4X \cdot OR + PX_3 + HX$ . The reaction has been extended to a number of ethers of substituted phenols, some of which require prolonged heating on the water-bath, and to alkyl naphthoxides, which enter readily into the reaction.

Phenetole and phosphorus pentabromide form *p*-bromophenetole, b. p. 225—226° (233°, Lippmann, *Jahresber.*, 1870, 548), which, when heated with fuming hydrochloric acid at 180° under pressure, is hydrolysed, forming *p*-bromophenol, b. p. 235—236°.

A molecular mixture of anisole and phosphorus pentabromide yields *p*-bromoanisole,  $C_7H_7OBr$ , b. p. 213—216°, in a 90% yield. When heated with fuming hydrochloric acid this forms *p*-bromophenol, which is identified by conversion into its benzoyl derivative. The action of 2 mols. of phosphorus pentabromide on 1 mol. of anisole leads to the formation of 2 : 4-dibromoanisole in an almost theoretical yield.

2 : 4-Dibromophenetole,  $C_6H_3Br_2 \cdot OEt$ , formed by heating *p*-bromophenetole with phosphorus pentabromide on the water-bath, crystallises from alcohol in large, rhombic plates, m. p. 50°, and has a disagreeable odour of fennel.

A molecular mixture of phenetole and phosphorus pentachloride yields *p*-chlorophenetole, m. p. 212—214° (210—212°, Beilstein and Kurbatoff, *Annalen*, 1875, 176, 30), which reacts only slowly with a second mol. of phosphorus pentachloride, forming probably 2 : 4-dichlorophenetole.

*p*-Tolyl ethyl ether and phosphorus pentabromide form *bromo-p-tolyl ethyl ether*,  $C_6H_3BrMe \cdot OEt$  [ $Me : Br : OEt = 1 : 3 (t) : 4$ ], which is obtained as a colourless liquid, b. p. 239—240°.

The action of phosphorus pentachloride on *p*-tolyl ethyl ether at 40° leads to the formation of (a) 3-chloro-*p*-tolyl ethyl ether,  $C_6H_3ClMe \cdot OEt$ , which forms a colourless, mobile liquid having a pleasant odour, b. p. 133—138°/26 mm. or 233—238°/760 mm., and when heated with fuming hydrochloric acid yields 3-chloro-*p*-cresol, and (b) 3 : 5-dichloro-*p*-tolyl ethyl ether,  $C_6H_2Cl_2Me \cdot OEt$  [ $Me : Cl_2 : OEt = 1 : 3 : 5 : 4$ ], b. p. 147—154°/26 mm., which on hydrolysis yields 3 : 5-dichloro-*p*-cresol.

1-Bromo- $\beta$ -naphthyl methyl ether,  $C_{10}H_6Br \cdot OMe$ , formed by the action of phosphorus pentabromide on  $\beta$ -naphthyl methyl ether, crystallises in glistening, white leaflets, m. p. 84—85°. 4-Bromo-1-naphthyl ethyl ether,  $C_{10}H_6Br \cdot OEt$ , formed in the same manner from  $\alpha$ -naphthyl ethyl ether, crystallises in white prisms, m. p. 48°.

The action of phosphorus pentachloride on  $\alpha$ -naphthyl ethyl ether leads to the formation of two products, b. p. 302—306°, decomposing slightly, and 360° respectively. G. Y.

**Formation of Chains. LXVI. Reactions of Phenyl and Toly Esters of  $\alpha$ -Bromo-fatty Acids with Sodium Phenoxide and Tolyloxide.** CARL A. BISCHOFF (*Ber.*, 1906, 39, 3830—3839. Compare Abstr., 1905, i, 157).—The products of the reaction  $R \cdot O \cdot Na + CR''R'''Br \cdot CO_2R = R \cdot O \cdot CR''R''' \cdot CO_2R + NaBr$ , in which  $R =$  phenyl,

the three tolyls, carvacryl, thymyl, guaiacyl, the naphthyls, and the three nitrophenyls are described in this and the three following abstracts. The aryl esters of the bromo-fatty acids are prepared by the action of the acid bromides on the phenols or their sodium salts. The formation of the aryl ester of the  $\alpha$ -aryloxy-fatty acid takes place with 78–90°/o yields on boiling the  $\alpha$ -bromo-ester with the sodium aryl oxide in xylene solution for twenty hours.

[With W. WACHSMUTH.]—*Phenyl  $\alpha$ -bromopropionate*,  
 $\text{CHMeBr}\cdot\text{CO}_2\text{Ph}$ ,

is a colourless oil, b. p. 126°/12 mm., 153°/34 mm., or 248–249°/765 mm.,  $D_{15}^{15}$  1.412. *Phenyl  $\alpha$ -bromobutyrate*,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ , b. p. 157°/31 mm. or 263–264°/765 mm.,  $D_{15}^{15}$  1.373. *Phenyl  $\alpha$ -bromoisobutyrate* is obtained as a fuming, yellow oil, b. p. 157°/42 mm., decomposes at 248°/765 mm.,  $D_{15}^{15}$  1.366. *Phenyl  $\alpha$ -bromoisovalerate*,  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{Br}$ , forms a colourless oil, b. p. 183°/33 mm.,  $D_{15}^{15}$  1.315; when boiled in air, it becomes yellow and evolves hydrogen bromide.

*Phenyl  $\alpha$ -phenoxypropionate*,  $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{Ph}$ , crystallises from methyl alcohol in needles, m. p. 52°, b. p. 190°/18 mm.,  $D_{15}^{15}$  1.147; it distils and decomposes slightly above 300°/760 mm., yielding a colourless oil. *Phenyl  $\alpha$ -phenoxybutyrate*,  $\text{C}_{16}\text{H}_{16}\text{O}_3$ , crystallises from methyl alcohol in prisms, m. p. 48–49°, b. p. 202–203°/25 mm.,  $D_{15}^{15}$  1.136. *Phenyl  $\alpha$ -phenoxyisobutyrate* crystallises in white needles, m. p. 24–26°, b. p. 194–195°/16 mm. *Phenyl  $\alpha$ -phenoxyisovalerate*,  $\text{C}_{17}\text{H}_{18}\text{O}_3$ , crystallises from light petroleum in stout, colourless, rhombic plates, m. p. 44°, b. p. 196–197°/26 mm.

A table is given showing the weights and boiling points of the fractions obtained on distilling the crude phenyl  $\alpha$ -phenoxy-esters.

[With J. BIHMANN.]—*o-Tolyl  $\alpha$ -bromopropionate*,  
 $\text{CHMeBr}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_7\text{H}_7$ ,

b. p. 139°/12 mm. *o-Tolyl  $\alpha$ -bromobutyrate*,  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{Br}$ , b. p. 139.5°/12 mm. *o-Tolyl  $\alpha$ -bromoisobutyrate*, b. p. 127.5°/12 mm.,  $D_{15}^{15}$  1.332. *o-Tolyl  $\alpha$ -bromoisovalerate*,  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{Br}$ , b. p. 143°/12 mm.,  $D_{15}^{15}$  1.296. When distilled under atmospheric pressure, the *o*-tolyl  $\alpha$ -bromo-esters decompose, evolving hydrogen bromide.

*o-Tolyl  $\alpha$ -o-tolylxypropionate*,  $\text{C}_{17}\text{H}_{18}\text{O}_3$ , forms a light yellow oil, b. p. 188°/13 mm.,  $D_{15}^{15}$  1.103. *o-Tolyl  $\alpha$ -o-tolylxybutyrate*,  $\text{C}_{18}\text{H}_{20}\text{O}_3$ , is obtained as a slightly yellow oil, b. p. 189°/12 mm.,  $D_{15}^{15}$  1.091. *o-Tolyl  $\alpha$ -o-tolylxyisobutyrate* forms a light yellow oil, b. p. 185°/11 mm.,  $D_{15}^{15}$  1.092. *o-Tolyl  $\alpha$ -o-tolylxyisovalerate*,  $\text{C}_{19}\text{H}_{22}\text{O}_3$ , forms a light yellow oil, b. p. 191°/15 mm.,  $D_{15}^{15}$  1.073.

[With K. SMOLNIKOFF.]—*m-Tolyl  $\alpha$ -bromopropionate*, b. p. 137.5°/12 mm. *m-Tolyl  $\alpha$ -bromobutyrate* forms a slightly yellow oil, b. p. 144°/12 mm. *m-Tolyl  $\alpha$ -bromoisobutyrate*, a light yellow oil, b. p. 134°/12 mm. *m-Tolyl  $\alpha$ -bromoisovalerate*, a light yellow oil, b. p. 150°/12 mm.

*m-Tolyl  $\alpha$ -m-tolylxypropionate* forms a slightly yellow oil, b. p. 199°/15 mm. *m-Tolyl  $\alpha$ -m-tolylxybutyrate*, b. p. 202°/15 mm. *m-Tolyl  $\alpha$ -m-tolylxyisobutyrate*, b. p. 201°/15 mm. *m-Tolyl  $\alpha$ -m-tolylxyisovalerate*, b. p. 202°/15 mm.

[With A. GUSSEW.]—*p-Tolyl  $\alpha$ -bromopropionate*, b. p. 137°/12 mm. *p-Tolyl  $\alpha$ -bromobutyrate*, b. p. 148.5°/12 mm. *p-Tolyl  $\alpha$ -bromoisobutyrate*

crystallises from light petroleum in pyramids, m. p.  $39^{\circ}$ , b. p.  $135.2^{\circ}/12$  mm. *p-Tolyl  $\alpha$ -bromoisovalerate*, b. p.  $154.5^{\circ}/12$  mm.

*p-Tolyl  $\alpha$ -p-tolyloxypropionate* crystallises in small, nodular aggregates of colourless needles, m. p.  $90^{\circ}$ , b. p.  $200^{\circ}/15$  mm. *p-Tolyl  $\alpha$ -p-tolyloxybutyrate*, b. p.  $203^{\circ}/15$  mm. *p-Tolyl  $\alpha$ -p-tolyloxyisobutyrate*, b. p.  $197^{\circ}/15$  mm. *p-Tolyl  $\alpha$ -p-tolyloxyisovalerate* forms a colourless, viscid oil, b. p.  $215^{\circ}/15$  mm. G. Y.

**Formation of Chains. LXVII. Reactions of Carvacryl and Thymyl Esters of  $\alpha$ -Bromo-fatty Acids with Sodium Carvacryl and Thymyl Oxides.** CARL A. BISCHOFF (*Ber.*, 1906, 39, 3840—3846. Compare preceding abstract).—[with A. BLUMENTHAL].—*Carvacryl  $\alpha$ -bromopropionate*,  $C_{13}H_{17}O_2Br$ , b. p.  $157^{\circ}/12$  mm. *Carvacryl  $\alpha$ -bromobutyrate*,  $C_{14}H_{19}O_2Br$ , b. p.  $163^{\circ}/12$  mm. *Carvacryl  $\alpha$ -bromoisobutyrate*, b. p.  $155.5^{\circ}/12$  mm. *Carvacryl  $\alpha$ -bromoisovalerate*,  $C_{15}H_{21}O_2Br$ , b. p.  $172.5^{\circ}/12$  mm. These four esters are formed only by the action of the acid bromides on sodium carvacryl oxide.

*Carvacryl  $\alpha$ -carvacryloxypropionate*,  $C_{23}H_{30}O_3$ , crystallises in colourless prisms, m. p.  $39^{\circ}$ , b. p.  $220^{\circ}/15$  mm. *Carvacryl  $\alpha$ -carvacryloxybutyrate*,  $C_{24}H_{32}O_3$ , forms a colourless oil, b. p.  $226^{\circ}/15$  mm. *Carvacryl  $\alpha$ -carvacryloxyisobutyrate* is obtained as a colourless oil, b. p.  $219^{\circ}/15$  mm. *Carvacryl  $\alpha$ -carvacryloxyisovalerate*,  $C_{25}H_{34}O_3$ , a colourless oil, b. p.  $227^{\circ}/15$  mm.

A table is given showing the boiling points and weights of the fractions obtained on distilling the four crude carvacryl  $\alpha$ -carvacryloxyesters.

[With K. KOWERSKI].—*Thymyl  $\alpha$ -bromopropionate*,  $C_{13}H_{17}O_2Br$ , forms a colourless oil, b. p.  $155^{\circ}/12$  mm. *Thymyl  $\alpha$ -bromobutyrate*,  $C_{14}H_{19}O_2Br$ , is obtained as a colourless oil, b. p.  $162^{\circ}/12$  mm. *Thymyl  $\alpha$ -bromoisobutyrate*, a colourless oil, b. p.  $151^{\circ}/12$  mm. *Thymyl  $\alpha$ -bromoisovalerate*,  $C_{15}H_{21}O_2Br$ , a colourless oil, b. p.  $166^{\circ}/12$  mm. These four esters are formed by the action of the acid bromides on thymol.

*Thymyl  $\alpha$ -thymoxypropionate*,  $C_{23}H_{30}O_3$ , forms a yellow, viscid liquid, b. p.  $217^{\circ}/15$  mm. *Thymyl  $\alpha$ -thymoxybutyrate*,  $C_{24}H_{32}O_3$ , forms a light-yellow, viscid oil, b. p.  $222.5^{\circ}/15$  mm. *Thymyl  $\alpha$ -thymoxyisobutyrate* is obtained as a light yellow, viscid oil, b. p.  $218^{\circ}/15$  mm. *Thymyl  $\alpha$ -thymoxyisovalerate*,  $C_{25}H_{34}O_3$ , a light yellow, viscid oil, b. p.  $221.5^{\circ}/15$  mm. G. Y.

**Formation of Chains. LXVIII. Reactions of Naphthyl and Guaiacyl Esters of  $\alpha$ -Bromo-fatty Acids with Sodium Naphthoxides and Guaiacyl Oxide.** CARL A. BISCHOFF (*Ber.*, 1906, 39, 3846—3854. Compare preceding abstracts).—[With M. GUSSEW].—Of the  $\alpha$ -naphthyl esters of the  $\alpha$ -bromo-fatty acids only the  $\alpha$ -bromoisovalerate can be prepared in a state of purity by the action of the acid bromide on  $\alpha$ -naphthol; the lower homologues are prepared from sodium  $\alpha$ -naphthoxide.

*$\alpha$ -Naphthyl  $\alpha$ -bromopropionate*,  $C_{13}H_{11}O_2Br$ , forms a light yellow, viscid oil, b. p.  $190^{\circ}/15$  mm. (corr.).  *$\alpha$ -Naphthyl  $\alpha$ -bromobutyrate*,  $C_{14}H_{13}O_2Br$ , a light yellow, viscid oil, b. p.  $198^{\circ}/15$  mm. (corr.).  *$\alpha$ -Naphthyl  $\alpha$ -bromoisobutyrate*, a light yellow, viscid oil, b. p.

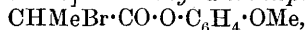
186.5°/15 mm. (corr.), decomposing. *α*-Naphthyl *α*-bromoisovalerate,  $C_{15}H_{15}O_2Br$ , crystallises in colourless leaflets, m. p. 68°.

*α*-Naphthyl *α*-*α*-naphthoxypropionate,  $C_{23}H_{18}O_3$ , crystallises from glacial acetic acid, m. p. 94—96°. *α*-Naphthyl *α*-*α*-naphthoxybutyrate,  $C_{24}H_{20}O_3$ , crystallises in leaflets, m. p. 96°. *α*-Naphthyl *α*-bromoisobutyrate and *α*-bromoisovalerate react with sodium *α*-naphthoxide, forming 91 and 85 % of sodium bromide respectively, but the organic products could not be purified.

[With A. WILLUMS.]—*β*-Naphthyl *α*-bromopropionate crystallises in nodular aggregates, m. p. 74°, b. p. 194°/15 mm. *β*-Naphthyl *α*-bromobutyrate,  $C_{14}H_{13}O_2Br$ , crystallises from light petroleum in colourless leaflets, m. p. 54°, b. p. 202°/15 mm. *β*-Naphthyl *α*-bromoisobutyrate crystallises from light petroleum in colourless leaflets, m. p. 97—98°, b. p. 185°/15 mm. *β*-Naphthyl *α*-bromoisovalerate forms heavy, crystalline masses, m. p. 51°, b. p. 205°/15 mm.

*β*-Naphthyl *α*-*β*-naphthoxypropionate crystallises in slender needles, m. p. 95—96°. *β*-Naphthyl *α*-*β*-naphthoxybutyrate crystallises from glacial acetic in leaflets, m. p. 80—82°. *β*-Naphthyl *α*-*β*-naphthoxyisobutyrate crystallises in stout needles, m. p. 100°. *β*-Naphthyl *α*-*β*-naphthoxyisovalerate crystallises in stout, prismatic needles, m. p. 106°.

[With J. WIELOWIEYSKI.]—*Guaiacyl α*-bromopropionate,



forms a light yellow oil, b. p. 153°/12 mm. *Guaiacyl α*-bromobutyrate,  $C_{11}H_{13}O_3Br$ , is obtained as a colourless oil, b. p. 159°/15 mm. *Guaiacyl α*-bromoisobutyrate,  $C_{11}H_{13}O_3Br$ , a colourless, viscid oil, b. p. 149.5°/12 mm. *Guaiacyl α*-bromoisovalerate,  $C_{12}H_{15}O_3Br$ , crystallises from light petroleum in monoclinic prisms, m. p. 69°, b. p. 165—165.3°/12 mm.

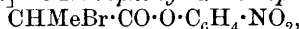
*Guaiacyl α*-*guaiacyloxy*propionate,  $C_{17}H_{18}O_5$ , crystallises from dilute alcohol, m. p. 64°, b. p. 226°/15 mm. (corr.). *Guaiacyl α*-*guaiacyloxy*butyrate,  $C_{18}H_{20}O_5$ , forms a colourless, very viscid oil, b. p. 231°/15 mm. (corr.). *Guaiacyl α*-*guaiacyloxy*isobutyrate forms a colourless, viscid oil, b. p. 221°/15 mm. (corr.). *Guaiacyl α*-*guaiacyloxy*isovalerate,  $C_{19}H_{22}O_5$ , b. p. 259—262°/25 mm. or 230°/15 mm. (corr.). Free *guaiacol* is formed in the preparation of this ester. G. Y.

**Formation of Chains. LXIX. Nitrophenyl Esters of *α*-Bromo-fatty Acids.** CARL A. BISCHOFF (*Ber.*, 1906, 39, 3854—3861. Compare preceding abstracts; Bischoff and Walden, *Abstr.*, 1894, i, 403; Bischoff, *Abstr.*, 1900, i, 442; 1901, i, 525).—Whilst phenyl *α*-bromopropionate and *α*-bromoisobutyrate when boiled with sodium phenoxide in xylene solution for ten hours form 76% and 83% of the calculated amounts of sodium bromide respectively, only 1.2% of sodium bromide is formed when these esters are boiled with sodium *o*-nitrophenoxide in xylene solution for sixty-seven hours. When boiled with sodium phenoxide in xylene solution, *o*-nitrophenyl *α*-bromopropionate does not form sodium bromide in thirty hours; *p*-nitrophenyl *α*-bromopropionate forms 14% of the calculated sodium bromide in four hours, and *p*-nitrophenyl *α*-bromoisobutyrate 12% in fifteen hours; in these cases the nitrophenyl is substituted by the phenyl group. *o*-Nitrophenyl *α*-bromopropionate and sodium phenoxide when

shaken in benzene solution react, forming phenyl  $\alpha$ -bromopropionate, which is formed also from *p*-nitrophenyl  $\alpha$ -bromopropionate and sodium phenoxide.

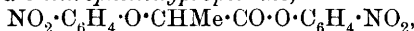
Sodium *o*-nitrophenoxide does not react with thymyl  $\alpha$ -bromopropionate or *o*-nitrophenyl  $\alpha$ -bromopropionate; sodium *p*-nitrophenoxide does not react with the four *p*-nitrophenyl  $\alpha$ -bromo-fatty esters. Sodium *m*-nitrophenoxide, on the other hand, reacts with *m*-nitrophenyl  $\alpha$ -bromopropionate in thirty hours to the extent of 74%.

[With SCHMÄHLING.]—*o*-Nitrophenyl  $\alpha$ -bromopropionate,



crystallises from light petroleum in white needles, m. p. 48°, b. p. 188°/12 mm. (corr.); when heated in contact with air, it becomes brown, and decomposes at 220°. *o*-Nitrophenyl  $\alpha$ -bromobutyrate,  $\text{C}_{10}\text{H}_{10}\text{O}_4\text{NBr}$ , forms a light yellow oil, b. p. 187°/10 mm. (corr.). *o*-Nitrophenyl  $\alpha$ -bromoisobutyrate, b. p. 183—184°/12 mm. *o*-Nitrophenyl  $\alpha$ -bromoisovalerate, b. p. 190°/12 mm. These four esters are prepared by the action of the acid bromides on sodium *o*-nitrophenoxide in boiling benzene solution.

*o*-Nitrophenyl  $\alpha$ -*o*-nitrophenoxypropionate,



is prepared from *o*-*o*-nitrophenoxypropionic acid by the action of phosphorus pentachloride, and treatment of the resulting *acid chloride* with sodium *o*-nitrophenoxide in boiling benzene solution; it crystallises in sheaves of yellow needles or microscopic prisms, m. p. 137°.

*m*-Nitrophenyl  $\alpha$ -bromopropionate, prepared by the action of the acid bromide on sodium *m*-nitrophenoxide, b. p. 245°/120 mm., fumes on exposure to air, and absorbs moisture, forming *m*-nitrophenol and  $\alpha$ -bromopropionic acid.

*m*-Nitrophenyl  $\alpha$ -*m*-nitrophenoxypropionate, formed by the action of *m*-nitrophenyl  $\alpha$ -bromopropionate or of  $\alpha$ -bromopropionyl bromide on sodium *m*-nitrophenoxide in boiling xylene solution, crystallises from methyl alcohol, m. p. 109—110°; evaporation of the methyl alcoholic filtrate leads to the formation of *m*-nitrophenol and methyl  $\alpha$ -*m*-nitrophenoxypropionate,  $\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}$ , b. p. 173—175°/20 mm.

*m*-Nitrophenyl  $\alpha$ -bromobutyrate forms an unstable, fuming, yellowish-brown oil, b. p. 247°/100 mm. *m*-Nitrophenyl  $\alpha$ -bromoisobutyrate crystallises from light petroleum in long, yellow needles, m. p. 90—91°. *m*-Nitrophenyl  $\alpha$ -bromoisovalerate forms an unstable, light yellow oil, b. p. 248°/98 mm.

[With AMBARDANOFF.]—*p*-Nitrophenyl  $\alpha$ -bromopropionate crystallises from a mixture of alcohol and light petroleum in needles and plates, or from concentrated solutions in plates and prisms, m. p. 42—46°. *p*-Nitrophenyl  $\alpha$ -bromobutyrate crystallises from alcohol in prisms, m. p. 48—49°. *p*-Nitrophenyl  $\alpha$ -bromoisobutyrate crystallises from light petroleum in plates and prisms, m. p. 79—80°. *p*-Nitrophenyl  $\alpha$ -bromoisovalerate crystallises in plates, m. p. 42—43°.

*p*-Nitrophenyl  $\alpha$ -*p*-nitrophenoxypropionate is prepared from *o*-*p*-nitrophenoxypropionic acid by conversion of this into its *chloride*, which is then boiled with sodium *p*-nitrophenoxide in benzene solution. It crystallises from alcohol in microscopic rhombohedra, m. p. 137°, and is soluble in the ordinary organic solvents.

G. Y.

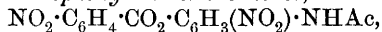
**Nitration of 4-Benzoylaminophenyl Acetate and of 4-Acetylaminophenyl Benzoate.** FRÉDÉRIC REVERDIN [with L. CUISINIER] (*Ber.*, 1906, 39, 3793—3797. Compare Reverdin and Dresel, *Abstr.*, 1905, i, 54, 430; Reverdin and Delétra, *Abstr.*, 1906, i, 165; Reverdin and Bucky, *ibid.*, 748).—It is found that of the diacetyl-dibenzoyl and acetyl-benzoyl derivatives of *p*-aminophenol, 4-acetylaminophenyl benzoate alone does not yield a dinitro-derivative containing both nitro-groups in the phenol nucleus. Even when more concentrated nitric acid or a mixture of nitric and sulphuric acids is used only a mononitro-derivative is formed.

4-Benzoylaminophenyl acetate,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{OAc}$ , prepared by heating 4-benzoylaminophenol with acetic anhydride at  $120^\circ$ , finally with addition of a small amount of concentrated sulphuric acid, crystallises in white leaflets, m. p.  $171^\circ$ .

4-Acetylaminophenyl benzoate,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$ , prepared by shaking 4-acetylaminophenol with benzoyl chloride in aqueous sodium carbonate solution, crystallises in white needles, m. p.  $171^\circ$ . A mixture of this with the preceding substance melts at  $155^\circ$ .

Treatment of benzoylaminophenyl acetate with nitric and sulphuric acids at  $-8^\circ$ , and finally at  $40^\circ$ , leads to the hydrolysis of the acetyl group, and consequently to the formation of 2:6-dinitro-4-benzoylaminophenol, which is formed also by direct nitration of 4-benzoylaminophenol. 3:5-Dinitro-4-benzoylaminophenyl acetate,  $\text{C}_{16}\text{H}_{11}\text{O}_7\text{N}_3$ , is formed from 4-benzoylaminophenyl acetate by nitration with a mixture of sulphuric and nitric acids in acetic anhydride under  $0^\circ$ , and finally at  $30^\circ$ , or in an impure state by nitration with nitric acid, D 1.5 at  $-10^\circ$  to  $-5^\circ$ ; it crystallises from alcohol in slender, white needles, m. p.  $215^\circ$ .

3-Nitro-4-acetylaminophenyl *m*-nitrobenzoate,



is formed together with 2:6-dinitro-4-acetylaminophenol by the action of nitric and sulphuric acids on 4-acetylaminophenyl benzoate, the final temperature not exceeding  $17^\circ$ . It is formed also by nitration of 4-acetylaminophenyl benzoate with nitric acid alone, or with a mixture of nitric and sulphuric acids in presence of acetic anhydride. It crystallises in slender, yellow needles, m. p.  $184^\circ$ , and on hydrolysis with boiling sulphuric acid yields *m*-nitrobenzoic acid and 3-nitro-4-aminophenol. G. Y.

**Action of Carbon Tetrachloride and Aluminium Chloride on *p*-Cresol and its Derivatives.** THEODOR ZINCKE and R. SUHL (*Ber.*, 1906, 39, 4148—4153).—3:5-Dichloro-2:6-dibromo-*p*-cresol, obtained by brominating 3:5-dichloro-*p*-cresol in carbon tetrachloride in the presence of iron, forms white needles, m. p.  $196^\circ$ , and is converted by nitric acid into a *quinonitrole* and a  $\psi$ -*quinol*; the latter forms yellow needles, has m. p.  $197^\circ$ , and is converted by alcoholic hydrogen chloride into a tetrachloroquinone.

3:5-Dichloro-2:6-dibromo-*p*-tolyl carbonate,  $(\text{C}_6\text{MeCl}_2\text{Br}_2)_2\text{CO}_3$ , obtained from the dichlorodibromo-*p*-cresol and aluminium chloride in carbon tetrachloride, is a white, crystalline powder, m. p.  $>275^\circ$ , yields dichlorodibromo-*p*-cresol with fused potassium hydroxide, carb-

anilides with primary aromatic amines, and carbamic acid derivatives with secondary amines; the substance,  $\text{NPhMe} \cdot \text{CO}_2 \cdot \text{C}_6\text{MeCl}_2\text{Br}_2$ , obtained from methylaniline, forms white needles, m. p.  $162^\circ$ ; the ethyl compound,  $\text{NPhEt} \cdot \text{CO}_2 \cdot \text{C}_6\text{MeCl}_2\text{Br}_2$ , has m. p.  $172^\circ$ .

*Tetrabromo-p-tolyl carbonate*,  $(\text{C}_6\text{MeBr}_4)_2\text{CO}_3$ , m. p.  $>330^\circ$ , is obtained from *p*-cresol, aluminium, and bromine in carbon tetrachloride, and resembles the preceding carbonate.

1-Methyl-1-trichloromethyl-4-ketodihydrobenzene,



obtained from aluminium chloride and *p*-cresol in carbon tetrachloride, forms large prisms, m. p.  $105^\circ$ , and is volatile with steam. The ketone is converted by warm concentrated sulphuric acid into hydrogen chloride, carbonyl chloride, and cresolsulphonic acid, by nitric acid into di-nitro-*p*-cresol, by alcohol and hydrochloric acid into *p*-cresol, by hydroxylamine into the *oxime*,  $\text{C}_8\text{H}_8\text{ONCl}_3$ , m. p.  $134^\circ$  (which yields an *acetyl* derivative, m. p.  $85-86^\circ$ ), and by phenylhydrazine into the *phenylhydrazone*,  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{Cl}_3$ , which forms yellow needles and darkens at  $95^\circ$  and has m. p.  $130^\circ$ , decomposing. C S.

**Phenylation of Phenols.** FRITZ ULLMANN and PAUL SPONAGEL (*Annalen*, 1906, 350, 83—107. Compare Abstr., 1905, i, 644).—In the reaction between an alkali phenoxide and a phenyl halide in the presence of copper as a catalyst, chlorobenzene reacts most slowly and iodobenzene most rapidly, the yield in the latter case being about the same as with bromobenzene. With potassium phenoxide the yields of ether are 25, 78.2, and  $91.5\%$  respectively; by the use of sodium phenoxide the yield with bromobenzene is only  $33\%$ .

The following ethers have been prepared from bromobenzene: *phenyl o-tolyl ether*, b. p.  $267^\circ/738.5$  mm., m. p.  $21.5-22^\circ$ , yield  $77\%$ ; *phenyl m-tolyl ether*, b. p.  $274.5^\circ/738$  mm., yield  $81.1\%$ ; *phenyl p-tolyl ether*, b. p.  $277-278^\circ/745.5$  mm., yield  $69.1\%$ ; *phenyl thymyl ether*, b. p.  $176^\circ/25$  mm.,  $297^\circ/766$  mm.,  $D_{15}^{20} 1.0113$ ; *phenyl  $\alpha$ -naphthyl ether*, m. p.  $54^\circ$ , yield  $40\%$ . The same ether is obtained from  $\alpha$ -bromonaphthalene and phenol in  $71.7\%$  yield. Phenyl  $\beta$ -naphthyl ether, b. p.  $335.5^\circ/753$  mm., m. p.  $45^\circ$  (compare Hönigschmid, Abstr., 1903, i, 165).

From  $\alpha$ -bromonaphthalene have been obtained  $\alpha\alpha'$ -dinaphthyl ether and  $\alpha\beta'$ -dinaphthyl ether, the latter having b. p.  $264^\circ/15$  mm., m. p.  $81^\circ$ , and forming a *picrate*,  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , which crystallises in orange-yellow needles and has m. p.  $121-122^\circ$ .

Of the dibromobenzenes, the para-isomeride is the most reactive. *Catechyl diphenyl ether*, m. p.  $93^\circ$ , is obtained in  $80.6\%$  yield from phenol and *o*-dibromobenzene; *resorcyldiphenyl ether*, m. p.  $61.5^\circ$ ; *quinoldiphenyl ether*, m. p.  $77^\circ$ , b. p.  $371-372^\circ/720$  mm. (compare Häussermann and Müller, Abstr., 1901, i, 382).

An excess of the cresols must be used to obtain good yields of the three following compounds from *p*-dibromobenzene: *quinol o-ditolyl ether*, m. p.  $51^\circ$ , b. p.  $243^\circ/18$  mm.; *quinol m-ditolyl ether*, m. p.  $57^\circ$ , b. p.  $253^\circ/23$  mm., whilst the corresponding isomeride from *p*-cresol has m. p.  $102-103^\circ$ .



Hoffmeister's dibromophenyl ether (*Annalen*, 1872, 159, 200) condenses with phenol to form *diphenoxydiphenyl ether*,  $O(C_6H_4 \cdot OPh)_2$ , which probably has the para-constitution; it has m. p.  $111^\circ$  and the yield is 89 %.

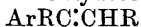
*m*-Aminodiphenyl ether, obtained from *m*-bromoaniline and phenol, or by the reduction of the *m*-nitrodiphenyl ether described previously (*loc. cit.*), separates from light petroleum in large prisms, m. p.  $37^\circ$ , b. p.  $190-191^\circ/14$  mm., and forms a *hydrochloride*, m. p.  $139^\circ$ , a *sulphate*, m. p.  $187-189^\circ$ , and an *acetyl* derivative, m. p.  $83^\circ$ .

*p*-Aminodiphenyl ether must be prepared in an atmosphere of hydrogen to prevent the formation of coloured by-products.

*o*-Phenoxybenzoic acid, obtained from bromobenzene and salicylic acid, cannot be separated from the unchanged acid; it is therefore converted into xanthone, which is obtained in 21% yield.

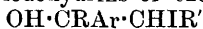
Small quantities of diphenyl ether and phenol are obtained by the prolonged heating of bromobenzene, potassium, alcohol, and copper under pressure at  $150^\circ$ . C. S.

**Migration of the Phenyl Group ; "Residual Valency" Structure of Intermediate Compounds.** MARC TIFFENEAU (*Compt. rend.*, 1906, 143, 684—687. Compare *Abstr.*, 1902, i, 666 ; 1904, i, 63, 133 ; *Abstr.*, 1906, i, 662, 965).—A theoretical paper in which the author discusses four possible formulæ for the unstable intermediate compounds which are formed by the elimination of hydrogen iodide from the iodohydrins of ethylenic hydrocarbons of the types



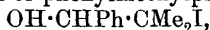
and  $ArCH:CR'R'$ , which by an intramolecular rearrangement involving the migration of a phenyl radicle are converted into the isomeric aldehyde or ketone. The ethylene oxide formula is untenable because in certain cases these oxides have been prepared and they are stable compounds, and are converted into the isomeric ketone or aldehyde without the migration of the phenyl group, thus  $O \begin{smallmatrix} \nearrow CH_2 \\ \searrow CMePh \end{smallmatrix} \rightarrow$

$CHMePh \cdot CHO$  and  $O \begin{smallmatrix} \nearrow CHMe \\ \searrow CHPh \end{smallmatrix} \rightarrow CH_2Ph \cdot CO \cdot CH_3$  (*Abstr.*, 1905, i, 523, 591). The unstable compounds cannot be regarded as homologues of vinyl alcohol because iodohydrins of the type



could not form such a compound by elimination of HI. The most probable structure therefore of the unstable intermediate compound is one in which a carbon atom or an oxygen and a carbon atom exhibit "residual valencies," and of the two possible formulæ based on this

assumption,  $\begin{smallmatrix} ArRC \cdot OH \\ | \\ HC = \end{smallmatrix}$  and  $\begin{smallmatrix} ArRC \cdot O - \\ | \\ RHC - \end{smallmatrix}$ , the former is untenable in the case of the iodohydrin of phenylmethylpropylene,

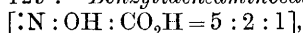


and other compounds, whilst the latter affords a satisfactory explanation of the formation of an ethylene oxide or a ketone according as the residual valency of the oxygen atom is orientated towards the neigh-

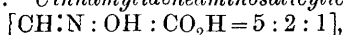
bouring unsaturated carbon atom, or towards the carbon atom with which it is associated. M. A. W.

**Influence of the Carbon Double-linking on the Colour of Azomethine Compounds.** RICHARD MÖHLAU and RICHARD ADAM (*Zeit. Farb. Ind.*, 1906, 5, 377—383 and 402—412).—The authors give an extensive summary of previous work on the connexion between colour and constitution, adopting as their standpoint the conception of chromophorous groupings. They have investigated experimentally the influence of the  $-C:N-$  group on the production of colour, by preparing the following compounds by combining certain aldehydes with different amines or aminophenols.

1-Benzylideneamino- $\beta$ -naphthol,  $CHPh \cdot N \cdot C_{10}H_6 \cdot OH$ , prepared by condensing benzaldehyde with 1-amino- $\beta$ -naphthol, crystallises from a mixture of chloroform and light petroleum in sheaves of bright yellow needles, m. p.  $129^\circ$ . Benzylideneaminosalicylic acid,

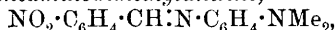


prepared from the corresponding aminosalicic acid, forms bright yellow needles, and is insoluble in all solvents; m. p.  $256^\circ$ . 4-Cinnamylideneamino- $\alpha$ -naphthol,  $CHPh \cdot CH \cdot CH \cdot N \cdot C_{10}H_6 \cdot OH$ , prepared from cinnamaldehyde and 4-amino- $\alpha$ -naphthol in light petroleum, crystallises from acetone in lustrous yellow needles, m. p.  $187^\circ$ . 1-Cinnamylideneamino- $\beta$ -naphthol crystallises from light petroleum in dark yellow, felted needles, m. p.  $128^\circ$ . Cinnamylideneaminosalicylic acid,



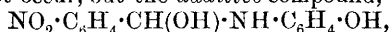
crystallises from a mixture of alcohol and chloroform in dark red prisms, m. p.  $164^\circ$ .

p-2-Nitrobenzylideneaminodimethylaniline,



separates from light petroleum in dark red crystals, m. p.  $90^\circ$ .

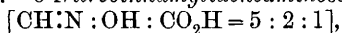
When *o*-nitrobenzaldehyde dissolved in toluene and *p*-aminophenol hydrochloride and aqueous sodium acetate are brought together, condensation does not occur, but the *additive* compound,



is formed; it crystallises from toluene in yellow needles, m. p.  $156^\circ$ . *o*-Aminophenol, under similar conditions, also gives a corresponding *additive compound*, which crystallises from carbon tetrachloride in yellow needles, m. p.  $104^\circ$ .

By slightly modifying the conditions, however, 4-*o*-nitrobenzylideneamino- $\alpha$ -naphthol,  $NO_2 \cdot C_6H_4 \cdot CH : N \cdot C_{10}H_6 \cdot OH$ , can be obtained; it crystallises from chloroform or light petroleum in yellow needles, m. p.  $148^\circ$ . 1-*o*-Nitrobenzylideneamino- $\beta$ -naphthol crystallises from carbon tetrachloride or toluene in yellow needles, m. p.  $123^\circ$ . p-2-Nitrocinnamylideneaminodimethylaniline separates from alcohol in dark red needles, m. p.  $90^\circ$ . p-2-Nitrocinnamylideneaminophenol separates from toluene in yellow crystals, m. p.  $168^\circ$ ; the corresponding *o*-aminophenol derivative crystallises from alcohol in well-formed, golden prisms, m. p.  $125^\circ$ . 4-*o*-Nitrocinnamylideneamino- $\alpha$ -naphthol crystallises from a mixture of acetone and light petroleum in brownish-yellow plates, m. p.  $173^\circ$ ; the corresponding *derivative* of 1-amino- $\beta$ -naphthol crystal-

lises from chloroform containing light petroleum in yellowish-brown needles, m. p. 100°. *o*-Nitrocinnamylideneaminosalicylic acid,



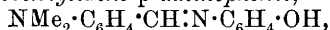
forms yellow crystals, m. p. 194°.

*p*-3-Nitrobenzylideneaminodimethylaniline crystallises from carbon tetrachloride or ether in orange-yellow plates, m. p. 156°. *m*-Nitrobenzaldehyde combines with *p*-aminophenol to form the *additive* compound,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , which crystallises from toluene in large, dark yellow plates, m. p. 158°; the analogous compound from *o*-aminophenol crystallises from carbon tetrachloride in slightly yellow needles, m. p. 131°. 4-*m*-Nitrobenzylideneamino-*a*-naphthol crystallises from a mixture of xylene and toluene in brownish-yellow plates, m. p. 184°; the corresponding 1-amino- $\beta$ -naphthol *derivative* crystallises in yellow needles, m. p. 105°.

*p*-3-Nitrocinnamylideneaminodimethylaniline crystallises from ethyl acetate and light petroleum in bright red leaflets, m. p. 192°. *p*-3-Nitrocinnamylideneaminophenol crystallises from alcohol in rhombic, yellow plates, m. p. 196°; the corresponding *o*-aminophenol *derivative* crystallises from carbon tetrachloride in slender, yellow needles, m. p. 137°. 4-*m*-Nitrocinnamylideneamino-*a*-naphthol crystallises from alcohol containing xylene in yellow, rhombic plates, m. p. 204°; the analogous *derivative* from 1-amino- $\beta$ -naphthol crystallises from carbon tetrachloride in dark yellow needles, m. p. 164°. *m*-Nitrocinnamylideneaminosalicylic acid  $[\text{CH:N : OH : CO}_2\text{H} = 5 : 2 : 1]$  crystallises in bright red, lanceolate needles, m. p. 198°.

*p*-Nitrobenzaldehyde combines with *p*-aminophenol to form the *additive* compound,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , which crystallises from ether or toluene in intensely yellow prisms, m. p. 166°; the analogous *derivative* from *o*-aminophenol crystallises from carbon tetrachloride in yellow needles, m. p. 158°. *p*-4-Nitrocinnamylideneaminodimethylaniline crystallises from toluene in red, hexagonal plates, m. p. 227°. *p*-4-Nitrocinnamylideneaminophenol crystallises from alcohol in yellow needles, m. p. 191°; the analogous *o*-aminophenol *derivative* is similar, m. p. 158°. 4-*p*-Nitrocinnamylideneamino-*a*-naphthol crystallises from ethyl acetate or chloroform in red needles, m. p. 210°; the corresponding *derivative* of 1 : 2-aminophenol crystallises from alcohol containing acetone in bright red plates, m. p. 164°. *p*-Nitrocinnamylideneaminosalicylic acid  $[\text{CH:N : OH : CO}_2\text{H} = 5 : 2 : 1]$  crystallises from alcohol in stellate aggregates of reddish-yellow needles, m. p. 155°.

*p*-4-Dimethylaminobenzylidene-*p*-aminophenol,



prepared from *p*-dimethylaminobenzaldehyde and *p*-aminophenol, crystallises from alcohol containing dilute acetic acid in yellow prisms, m. p. 265°; the corresponding *derivative* of *o*-aminophenol crystallises from alcohol or light petroleum in yellow needles, m. p. 119°. 4-*p*-Dimethylaminobenzylideneamino-*a*-naphthol crystallises from xylene in yellow needles, m. p. 199°; the corresponding *derivative* from 1-amino- $\beta$ -naphthol crystallises from toluene in yellow leaflets, m. p. 109°. *p*-Dimethylaminobenzylideneaminosalicylic acid  $[\text{CH:N : OH : CO}_2\text{H} = 5 : 2 : 1]$  forms bright red crystals, m. p. 265°, and is sparingly soluble in all

solvents. *p*-4-Dimethylaminocinnamylidenaminodimethylaniline crystallises from light petroleum and ethyl acetate in brownish-yellow needles, m. p. 196°. *p*-4-Dimethylaminocinnamylidenaminophenol forms brownish-yellow crystals, m. p. 260°; the corresponding derivative from *o*-aminophenol crystallises from carbon tetrachloride in brown plates, m. p. 143°. *p*-Dimethylaminocinnamylidenaminocinnamic acid forms dark red needles, m. p. 206°.

The colour and structure of the compounds described are compared by means of a table, and the following conclusions drawn. The group C:C exercises a marked influence on the colour of the azomethine compounds. A nitro-group introduced into the nucleus of the aldehyde portion darkens the colour; the influence exerted is greatest when the group is in the para-position, somewhat less when in the ortho-, and least in the meta-position; analogous observations have been made in the case of the fulgides (Stobbe, Abstr., 1906, i, 91, 183, 278). The auxochromic dimethylamino-group, NMe<sub>2</sub>, exercises less influence in darkening the colour than the chromophore NO<sub>2</sub> in the same position in the aldehydic component. The auxochromes OH and NMe<sub>2</sub> also darken the colour when present as substituents in the aminic component, the influence of the NMe<sub>2</sub> being the greater. The influence of hydroxyl is greatest when it is present in the ortho-position.

W. A. D.

**5-Nitroguaiacol.** FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1906, 39, 4232).—The compound described by the authors as 4-nitroguaiacol (Abstr., 1903, i, 624) is really the 5-nitro-isomeride (compare Paul, Abstr., 1906, i, 843).

C. S.

**Sulphonation of Guaiacol.** ADOLF RISING (*Ber.*, 1906, 39, 3685—3693).—A mixture of almost equal amounts of  $\alpha$ - and  $\beta$ -guaiacolsulphonic acids is primarily obtained by the sulphonation of guaiacol independently of the temperature conditions. The potassium salt of the  $\alpha$ -acid is identical with the "free *o*-guaiacolsulphonic acid" described by Barell (*Pharm. Zeit.*, 1899, No. 13) and with the potassium salt of *p*-guaiacolsulphonic acid described by von Heyden (*Patentanmeldung*, C 18820, Kl. 12g.) and with the para-salt described by Paul (Abstr., 1906, i, 843). The basic calcium salt of the  $\beta$ -acid corresponds with von Heyden's basic calcium salt of "*o*-guaiacolsulphonic acid." When heated above 100°, both the  $\alpha$ - and  $\beta$ -acids are transformed into a third acid, the  $\gamma$ -acid. The potassium salt of the  $\gamma$ -acid is identical with the "free *p*-guaiacolsulphonic acid" of Barell and with the compound described by F. Hoffman-La Roche & Co. (D.R.-P., 105052). The pharmaceutical preparations "Thiocol" and "Kalium sulfoguaiacolicum" are mixtures of normal and basic potassium salts of  $\alpha$ - and  $\beta$ -guaiacolsulphonic acids. In the  $\alpha$ -acid the groups OH, OMe, SO<sub>3</sub>H are in the positions 1, 2, and 4 respectively, in the  $\beta$ -acid in the positions 1, 2, and 5, and in the  $\gamma$ -acid in the vicinal position.

The  $\gamma$ -acid forms colourless crystals, m. p. 92°

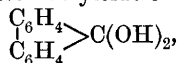
A. McK.

**3- or 6-Guaiacolsulphonic Acid.** LUDWIG PAUL (*Ber.*, 1906, **39**, 4093—4095).—Barell's *p*-guaiacolsulphonic acid (*Pharm. Zeit.*, 1899, No. 13) and Rising's *v*-guaiacolsulphonic acid (preceding abstract) are both catechol-4-sulphonic acid which is converted by potassium hydroxide and methyl iodide into potassium veratrolesulphonate (*Abstr.*, 1906, i, 843). Hence the isomeric change of 4- or 5- into *v*-guaiacolsulphonic acid assumed by Rising (*loc. cit.*) does not take place. G. Y.

**Propylguaiacol.** PARRAIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 1098—1099).—*Propylguaiacol*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{OH}$  (3:1:4), was isolated from the mixed phenols present in wood creosote by agitating the former with milk of strontia and fractionally distilling the phenols regenerated from the mixed insoluble strontium derivatives thus formed. It is purified finally through the benzoyl derivative, and then is a colourless liquid with an odour of cloves, b. p.  $246^\circ$ ,  $D_0^{20}$  1.060,  $D_4^{25}$  1.049, and on treatment with hydrogen bromide at  $100^\circ$  yields 3:4-dihydroxy-1-propylbenzene. The *benzoyl* derivative, m. p.  $72^\circ$ , crystallises from alcohol, and the *carbonate* crystallises in needles, m. p.  $66^\circ$ . T. A. H.

**9-Dihydroxyfluorene and Stereoisomeric 9-Acetoxyfluorenes.** JULIUS SCHMIDT and ROBERT MEZGER (*Ber.*, 1906, **39**, 3895—3901. Compare *Abstr.*, 1906, i, 27).—*Methyl 9-hydroxyfluorene-9-carboxylate*

(*methyl diphenyleneglycollate*),  $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{OH})\cdot\text{CO}_2\text{Me}$ , obtained by the catalytic method of esterification, crystallises from 60 per cent. ethyl alcohol in rhombic prisms, m. p.  $158$ — $160^\circ$ . The *ethyl* ester and its *acetyl* derivative melt at  $96^\circ$  and  $103$ — $104^\circ$  respectively; the *acetyl* derivative of the methyl ester crystallises in colourless plates, m. p.  $147$ — $148^\circ$ . When 9-acetoxyfluorene-9-carboxylic acid is boiled for five hours with acetic anhydride, carbon dioxide is eliminated and a mixture of two stereoisomeric 9-acetoxyfluorenes (*fluorenyl acetates*),  $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{CH}\cdot\text{OAc}$ , is formed. The  $\beta$ -compound is less readily soluble in all solvents, crystallises from glacial acetic acid in minute, colourless prisms, m. p.  $208$ — $209^\circ$ . When heated with ethyl alcohol at  $200^\circ$ , it is transformed into the isomeric  $\alpha$ -compound, which crystallises from alcohol in long, colourless prisms, m. p.  $169$ — $170^\circ$ . Both compounds dissolve in concentrated sulphuric acid, yielding blue solutions. When hydrolysed by boiling with concentrated hydrochloric acid in a reflux apparatus, the  $\alpha$ -acetyl derivative yields 9-dihydroxyfluorene,



in the form of colourless, glistening plates, m. p.  $94^\circ$ . Its constitution follows from the readiness with which it loses water, yielding fluorenone. J. J. S.

**Alkylation of the Nucleus of Phenols.** JOSEF HERZIG and FRANZ WENZEL (*Monatsh.*, 1906, **27**, 781—802. Compare *Abstr.*, 1904, i, 246; Herzig and Zeisel, *Abstr.*, 1888, 822; 1889, 247, 966).—In view of Kaufer's rule (*Abstr.*, 1901, i, 206) that on the alkyl-

ation of tautomeric substances the tendency to the formation of the true ether increases with the size of the alkyl group, the amount of the  $\psi$ -ester formed being correspondingly decreased, the meagre results obtained in the nucleus alkylation of phenols may be ascribed to the employment of ethyl iodide, and further progress was to be expected from the study of the methyl derivatives.

The action of diazomethane on phloroglucinol in ethereal solution leads to the formation of the trimethyl ether in a 37% yield, together with a mixture of the mono- and di-methyl ethers, that of methyl sulphate on phloroglucinol in alkaline solution to the formation of the trimethyl ether in a 37.9% yield, together with a mixture of the mono- and di-methyl ethers. The trimethyl ether is formed also in a 65% yield when phloroglucinol is heated with methyl iodide and sodium methoxide in methyl-alcoholic solution on the water-bath. In both experiments in alkaline solution, small amounts of an oil which is insoluble in alkali hydroxides and is the product of the nucleus alkylation are obtained.

[With E. HORNSTEIN.]—The action of methyl iodide on orcinol or orcinolcarboxylic acid in presence of a large excess of an alkali hydroxide leads to the formation of tetramethyl- $\psi$ -orcinol (4:6-diketo-2:3:5:5-pentamethyl- $\Delta^1$ -cyclohexene?),  $C_{11}H_{16}O_2$ , (Abstr., 1904, i, 246), which crystallises from alcohol in long, glistening needles, m. p. 63°, b. p. about 128°/17 mm., and forms a crystalline *bromide*.

If the product obtained by heating orcinolcarboxylic acid with methyl iodide in alkaline methyl-alcoholic solution is treated with an alkali hydroxide and the insoluble portion distilled, the fraction with the highest boiling point contains a *substance*,  $C_9H_7O(OMe)_3$ , m. p. 84°; on hydrolysis with boiling potassium hydroxide, this yields the *dimethyl ether* of methylorcinolcarboxylic acid,  $C_6HMe_2(OMe)_2 \cdot CO_2H$ , which crystallises in quadratic leaflets, m. p. with decomposition 183°. The portion of the original product soluble in alkali hydroxides contains  $\beta$ -orcinol; this does not react with diazomethane. The *diacetate* of  $\beta$ -orcinol,  $C_6H_2Me_2(OAc)_2$ , crystallises from alcohol in long, white needles, m. p. 69°.

Kurzweil's dimethylorcinol (*Monatsh.*, 1903, 24, 747) could not be isolated from the products of the action of methyl iodide on orcinolcarboxylic acid.

The methylation of orcinolcarboxylic acid by means of methyl iodide in ethyl-alcoholic solution leads to the formation of tetramethyl- $\psi$ -orcinol, the trimethyl ether-ester, m. p. 84°, and *methylorcinol* (3:5-dihydroxy-1:2-dimethylbenzene),  $C_6H_2Me_2(OH)_2$ , which is isomeric with  $\beta$ -orcinol. It crystallises from benzene in glistening, silky needles, m. p. 115—117°, b. p. 170—180°/12 mm., and is soluble in aqueous alkali hydroxides; with diazomethane in ethereal solution it forms a *monomethyl ether*,  $OH \cdot C_6H_2Me_2 \cdot OMe$ , which crystallises from benzene; m. p. 83°, b. p. 192—202°/20 mm. With bromine in glacial acetic acid solution, methylorcinol forms a *monobromo-derivative*,



which crystallises from 50% acetic acid, m. p. 142°.

The experiments in the nucleus methylation of orcinol are carried out under the same conditions as those with the carboxylic acid, but

only in ethyl-alcoholic solution. The portion of the product soluble in alkali hydroxides deposits directly a *substance*,  $(C_3H_4O)_n$ , which crystallises from alcohol; m. p. 187—192°, decomposing. On distillation the remainder of this portion of the product yields *dimethylorcinol*,  $C_9H_{12}O_2$ , which crystallises from benzene in long, white needles, m. p. 145—147°, together with the *methyl ether of β-orcinol* (*2-hydroxy-6-methoxy-1:4-xylene*),  $OH \cdot C_6H_2Me_2 \cdot OMe$ , m. p. 118—121°; this crystallises from benzene, and on hydrolysis yields β-orcinol.

The portion of the original product insoluble in alkali hydroxides yields tetramethyl-ψ-orcinol and the methyl ether of β-orcinol.

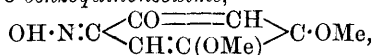
G. Y.

**Action of Nitric Acid and of Nitrous Acid on Asaronic Acid.** RUDOLF FABINY and TIBOR SZÉKI (*Ber.*, 1906, **39**, 3679—3685).—When asaronic acid is nitrated in glacial acetic acid solution with concentrated nitric acid, it forms *4-nitro-1:2:5-trimethoxybenzene*,  $C_6H_2(OMe)_3 \cdot NO_2$ , m. p. 130°, and forms a red solution with concentrated sulphuric acid.

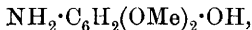
*4-Amino-1:2:5-trimethoxybenzene* (*asarylamine*),  $C_6H_2(OMe)_3 \cdot NH_2$ , obtained by the reduction of the preceding compound with tin and hydrochloric acid, separates from a mixture of benzene and light petroleum in felted, slightly pink needles, m. p. 95°, unstable in moist air. Its *benzoyl* derivative crystallises from alcohol in needles, m. p. 138°.

*4(1:2:5)-Trimethoxybenzylidene-4-amino-1:2:5-trimethoxybenzene* (*asaryl asarylidenamine*),  $C_6H_2(OMe)_3 \cdot CH:N \cdot C_6H_2(OMe)_3$ , obtained by the addition of a few drops of concentrated hydrochloric acid to a solution of a mixture of asarylaldehyde and asarylamine in ethyl alcohol, separates from alcohol in greenish-yellow needles, m. p. 142·5°.

*4:5-Dimethoxy-o-benzoquinoneoxime*,



which may be the tautomeric *4-nitroso-1:2-dimethoxy-5-phenol*, is obtained by boiling an aqueous solution of asaronic acid with an excess of sodium nitrite; it forms glistening, ruby-red crystals. When heated, it decomposes explosively. It does not give the Liebermann reaction for nitroso-phenols. Its *acetyl* derivative forms yellow crystals, m. p. 195—197°, decomposing. Its *benzoyl* derivative forms yellow needles, m. p. 190—193°, decomposing. When reduced by tin and hydrochloric acid, it forms *6-amino-3:4-dimethoxyphenol*,

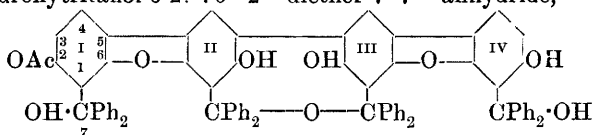


m. p. 152°, and yields on benzylation, *6-benzoylamino-3:4-dimethoxyphenyl benzoate*,  $NHBz \cdot C_6H_2(OMe)_2 \cdot OBz$ , which separates from glacial acetic acid in leaflets, m. p. 209°, decomposing.

A. McK.

**Condensation of Benzil with Resorcinol. II. Derivatives of *m*-Tetra-2:6-dihydroxytritanol.** HANS VON LIEBIG [and, in part, H. HÜRT] (*J. pr. Chem.*, 1906, [ii], **74**, 345—419. Compare *Abstr.*, 1905, i, 781).—The condensation of benzil with resorcinol by

fusion with potassium hydroxide or carbonate at 130—140° leads to the formation of ten substances. When boiled with glacial acetic acid, the mixture of products yields a red dye, 2<sup>I</sup>-acetoxy- $\bar{m}$ -tetra-2:6-dihydroxytritanol-6<sup>I</sup>2<sup>II</sup>:6<sup>III</sup>2<sup>IV</sup>-diether-7<sup>II</sup>7<sup>III</sup>-anhydride,



(The word "tritan" represents the triphenylmethane nucleus,  $\text{Ph}_3\text{C}\cdot$ , "ether" denotes the phenyl ether linking  $\text{Ph}\cdot\text{O}\cdot\text{Ph}$ , and  $\bar{o}$ ,  $\bar{m}$ ,  $\bar{p}$  before the Greek numerals, tetra, &c., indicate that a direct union takes place between the corresponding number of phenyl groups (in the above case, four) in the  $\bar{o}$ -,  $\bar{m}$ -, or  $\bar{p}$ -position. "Anhydride" indicates the etheric union between the aliphatic carbon atoms, and "anhydro" denotes that water has been eliminated between the groups numbered.)

The constitution and spacial relations of this and its derivatives are discussed. Those in which the second and third benzene nuclei are in close proximity as the 2<sup>I</sup>7<sup>II</sup>-anhydropenta-acetyl derivative of the

triether,  $\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{OAc}$ , are yellow, whilst the 7<sup>II</sup>6<sup>II</sup>:7<sup>III</sup>2<sup>III</sup>-dianhydrotetra-acetyl derivative of

the triether,  $\text{CO}-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{CO}$ , in which the first and fourth benzene nuclei are in proximity, is blue;

the red dye occupies an intermediate position in the series. With the exception of the blue dianhydrotetra-acetyl-triether, all the coloured substances of this group are quinones, or contain an ether or an anhydride linking between the second and third benzene nuclei, whilst in the colourless substances these are joined only by a C-C linking. All the coloured substances cannot be formulated as quinones, and it is suggested that the cause of colour in organic compounds may be the relative arrangement in space of a number of ethylene linkings.

Some of the derivatives of  $\bar{m}$ -tetra-2:6-dihydroxytritanol form *additive* compounds with hydrogen chloride which are not decomposed by water, and according to Collie and Tickle's theory (Trans., 1899, 75, 710) must be salts of oxonium bases. A number of objections to the oxonium theory are raised, and it is urged that the formation of the so-called oxonium salts is explained better by assuming an opening of the ring and the formation of a chlorohydrin or other derivative of a glycol,  $\text{CH}_2\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{O} + \text{HCl} \rightleftharpoons \text{CH}_2\langle\text{CH}_2\cdot\text{CH}_2\text{Cl}\rangle\text{OH}$  (compare Willstätter and Pummerer, Abstr., 1904, i, 1043; 1905, i, 457; Diels and Rosenmund, Abstr., 1906, i, 673).

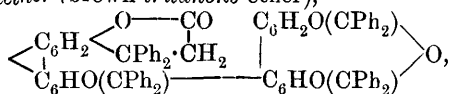


2<sup>1</sup>-Acetoxy- $\bar{m}$ -tetra-2 : 6-dihydroxytritanol-6<sup>12</sup><sup>II</sup> : 6<sup>III</sup>2<sup>IV</sup>-diether-7<sup>II</sup>7<sup>III</sup>-anhydride, C<sub>78</sub>H<sub>54</sub>O<sub>10</sub>, crystallises from alcohol, acetone, or glacial acetic acid in slender, yellow needles or rectangular leaflets from alcohol and aqueous ammonia on evaporation of the ammonia in brown, rectangular rods, m. p. 288°; it forms yellow solutions having a lively green fluorescence, gives with concentrated sulphuric acid a violet, with acetic anhydride and concentrated sulphuric acid a deep violet coloration, becoming red on addition of alcohol. When distilled alone or with zinc dust, it decomposes very readily in the form of its alkali salts, forming diphenylmethane; only benzaldehyde, benzoic acid, and resorcinol can be isolated from the product obtained on fusion with potassium hydroxide or on oxidation. The sodium,

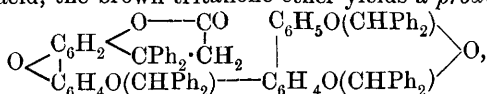
and potassium, C<sub>78</sub>H<sub>51</sub>O<sub>10</sub>Na<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>O, salts are described.

When boiled with zinc dust and glacial acetic acid, the acetoxy-anhydride is reduced to  $\bar{m}$ -tetra-2 : 6-dihydroxytritan-6<sup>12</sup><sup>II</sup> : 6<sup>III</sup>2<sup>IV</sup>-diether,  $\text{O} \begin{array}{c} \text{C}_6\text{H}_2(\text{CHPh}_2) \cdot \text{OH} \\ \text{C}_6\text{H}(\text{CHPh}_2)(\text{OH}) - \text{C}_6\text{H}_2(\text{CHPh}_2)(\text{OH}) \end{array} \text{O}$ , which crystallises from benzene in colourless prisms containing C<sub>6</sub>H<sub>6</sub>, loses C<sub>6</sub>H<sub>6</sub> at 150°, m. p. 215—216°, and forms colourless solutions with blue fluorescence.

2<sup>7</sup><sup>I</sup>-Anhydro-2<sup>1</sup>-acetoxy- $\bar{m}$ -tetra-2 : 6-dihydroxytritan-I-ol-II, III, IV-one-6<sup>12</sup><sup>II</sup>, 6<sup>III</sup>2<sup>IV</sup>-diether (brown tritanone ether),



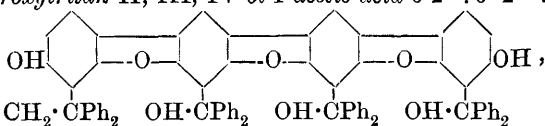
formed by heating the acetoxy-anhydride at 280—320°, crystallises from benzene in glistening, dark brown leaflets, m. p. 273°, dissolves in chloroform, forming a brown solution with green fluorescence, forms brownish-violet salts with mineral acids, and when boiled with acetic anhydride and sodium acetate is converted into the red tritanone ether and its acetyl derivatives. When reduced with zinc dust and glacial acetic acid, the brown tritanone ether yields a product,



which crystallises in spherical aggregates of silky needles, m. p. with decomposition 213—215°.

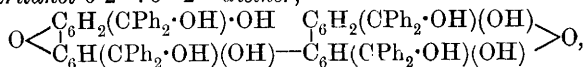
$\bar{m}$ -Tetra-2 : 6-dihydroxytritan-II, III, IV-ol-I-acetic acid-6<sup>12</sup><sup>II</sup> : 6<sup>III</sup>2<sup>III</sup> :

6<sup>III</sup>2<sup>IV</sup>-triether,



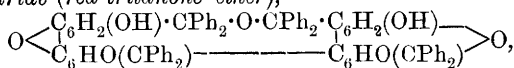
is obtained by boiling the residue from the estimation of acetyl groups in the anhydropenta-acetyl derivative of the triether successively with dilute ammonia, acetic acid, and benzene, and crystallising the insoluble remainder from much alcohol; it crystallises in yellow leaflets, m. p. above 300°. On evaporation of the benzene solution, there is obtained a varnish and a few colourless crystals, m. p. 167—168°.

When boiled with potassium hydroxide and alcohol, the acetoxy-diether-anhydride is converted into (a) *m̄-tetra-2:6-dihydroxytritanol-6<sup>12II</sup>:6<sup>12III</sup>:6<sup>12IV</sup>-triether*,  $C_{76}H_{52}O_9$ , which crystallises from alcohol or acetone in yellow leaflets, does not melt at  $300^\circ$ , and forms yellow solutions with brilliant green fluorescence, and (b) *m̄-tetra-2:6-dihydroxytritanol-6<sup>12II</sup>:6<sup>12IV</sup>-diether*,

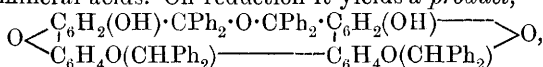


which forms a brown, crystalline mass, m. p.  $151^\circ$ .

*m̄-Tetra-2:6-dihydroxytritan-I, IV-one-II, III-ol-6<sup>12II</sup>:6<sup>12IV</sup>-diether-7<sup>12VII</sup>-anhydride (red tritanone ether)*,

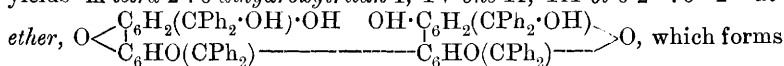


is formed from the acetoxy-diether-anhydride by the action of hydrogen chloride in boiling alcoholic solution, by boiling with glacial acetic acid and a small amount of concentrated sulphuric acid, by heating with concentrated hydrochloric acid at  $100-200^\circ$  under pressure, or by shaking with acetic anhydride and sulphuric acid, and from the diacetyl derivative of the diether by the action of heat. It crystallises from benzene in glistening, scarlet, hexagonal leaflets, from chloroform in slender, red needles, m. p.  $274^\circ$ , has a green fluorescence in chloroform solution, dissolves in alcoholic potassium hydroxide forming a red solution with green fluorescence, becoming colourless, and depositing a red substance on addition of water, and forms crystalline, violet salts with mineral acids. On reduction it yields a *product*,



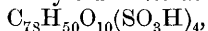
which crystallises in silky needles, m. p.  $210-211^\circ$ , forms solutions with blue fluorescence, and is converted again into the red ether.

When heated successively with ammonia and acetic acid and recrystallised from alcohol, the red residue obtained on estimation of the acetyl groups in the *α*-diacetyl derivative of the diether anhydride yields *m̄-tetra-2:6-dihydroxytritan-I, IV-one-II, III-ol-6<sup>12II</sup>:6<sup>12IV</sup>-diether*,



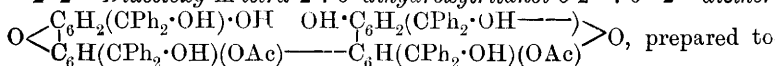
which forms a red powder, commences to sinter at  $160^\circ$ , m. p.  $200^\circ$ , swells up above  $200^\circ$ , dissolves in alcohol, forming a dark red solution decolorised on addition of aqueous potassium hydroxide, and gives a violet coloration with concentrated sulphuric or hydrochloric acid.

When heated with concentrated sulphuric acid on the water-bath, the acetoxy-diether-anhydride yields a *tetrasulphonic acid*,



which crystallises in dark red leaflets, m. p. above  $330^\circ$ , is soluble in cold water or alcohol, forming red solutions becoming dark red with slight green fluorescence on addition of potassium hydroxide, and gives a dark coloration with ferric chloride.

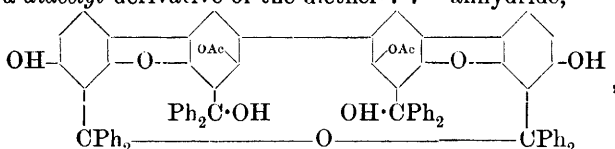
*2<sup>12III</sup>-Diacetoxy-m̄-tetra-2:6-dihydroxytritanol-6<sup>12II</sup>:6<sup>12IV</sup>-diether*,



prepared to

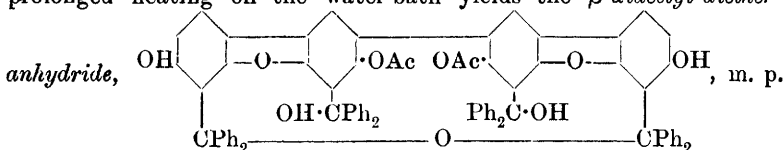
gether with the tetra-acetyl derivative by heating the acetoxy-diether-anhydride with acetic anhydride and concentrated sulphuric acid on the water-bath, and crystallising the product from a mixture of ether and light petroleum, crystallises from ether on evaporation in glistening leaflets. On evaporation of the ether-light petroleum filtrate and treatment of the residue with cold benzene, there are obtained the tetra-acetyl derivative and an *additive* compound of the diacetyl-diether and benzene,  $C_{80}H_{58}O_{12}, C_6H_6$ , which is formed also by the action of cold benzene on the diacetyl-diether or the  $\alpha$ -diacetyl-diether-anhydride; it crystallises in slender, white needles, sinters at  $130^\circ$ , swells up at  $140$ – $143^\circ$ , and resolidifies and melts again at  $205$ – $206^\circ$ ; when boiled with benzene it is converted into the benzene additive compound of  $\beta$ -diacetyl-diether-anhydride. The *additive* compound,  $C_{80}H_{58}O_{12}, C_4H_8O_2$ , formed by evaporating the solution of the diacetyl-diether or  $\alpha$ -diacetyl-diether-anhydride in ethyl acetate, crystallises in long, rectangular leaflets, and decomposes at  $140^\circ$ , losing ethyl acetate and water, and after resolidifying has m. p.  $205$ – $206^\circ$ .

The  $\alpha$ -diacetyl derivative of the diether-7<sup>17</sup><sub>IV</sub>-anhydride,



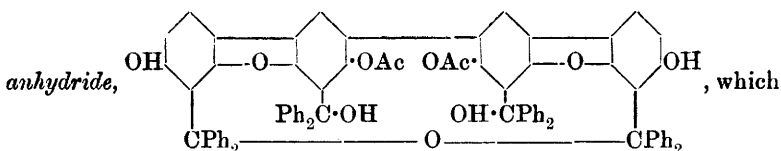
formed by boiling the diacetyl-diether with ether, crystallises in rhombic leaflets, m. p.  $150^\circ$ , and again at  $205$ – $206^\circ$ , and is converted by boiling acetone and benzene into the corresponding additive compounds of the  $\beta$ -derivative.

The *additive* compound of the  $\beta$ -diacetyl derivative and benzene,  $C_{80}H_{56}O_{11}, 3C_6H_6$ , crystallises in slender, white needles or long, rectangular plates, loses  $2C_6H_6$  slowly at the laboratory temperature but quickly on the water-bath, sinters at  $150^\circ$ , m. p.  $208$ – $209^\circ$ , and is converted by boiling acetone into the corresponding acetone compound, or by boiling alcohol partially into the additive compound of the  $\gamma$ -diacetyl derivative. The *additive* compound of acetone and the  $\beta$ -diacetyl-diether-anhydride,  $C_{80}H_{56}O_{11}, C_3H_6O$ , crystallises in glistening rhombohedra, loses  $C_3H_6O$  on the water-bath, m. p.  $208^\circ$ , and on prolonged heating on the water-bath yields the  $\beta$ -diacetyl-diether-



$208^\circ$ , which, after being heated above its melting point and cooled, resolidifies and then has m. p.  $120$ – $130^\circ$ .

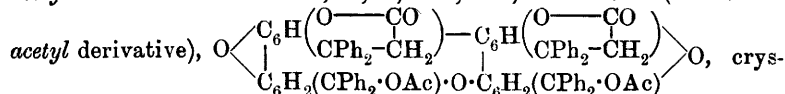
The *ethyl alcohol* derivative of the  $\gamma$ -diacetyl-diether-anhydride,  $C_{80}H_{54}O_{10}, C_2H_6O$ , formed by shaking the diacetyl-diether with alcohol and evaporating the solution, or by boiling any of the diacetyl derivatives with ethyl alcohol, crystallises in slender needles or pointed, rhombic leaflets, sinters at  $180^\circ$ , m. p.  $180$ – $182^\circ$ , and when heated at  $190$ – $200^\circ$  for some minutes yields the  $\gamma$ -diacetyl-diether-

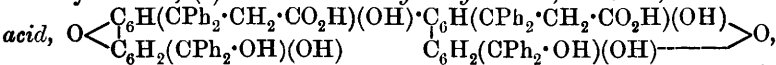


sinters at 120°, m. p. 120—130°. The *ethyl acetate* derivative,  $C_{80}H_{54}O_{16}C_4H_8O_2$ , formed by the action of boiling ethyl acetate on the  $\gamma$ -diacetyl compound or its alcohol or acetone derivative, separates in glistening, microscopic, double pyramids, and loses  $C_4H_8O_2$  at 190°, m. p. 190—191°. The *acetone* derivative,  $C_{80}H_{56}O_{11}C_3H_6O$ , crystallises in white, pointed, rhombic needles or leaflets, m. p. 180—190°. The *methyl alcohol* derivative,  $C_{80}H_{54}O_{10}CH_4O$ , formed by boiling the compounds of the  $\alpha$ - and  $\beta$ -diacetyl series with methyl alcohol, crystallises in hexagonal leaflets, m. p. 210°.

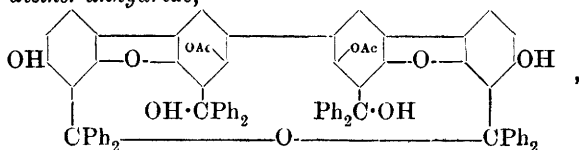
These diacetyl compounds decompose on prolonged heating, forming the red tritanone ether; they form solutions having a slight blue fluorescence, and dissolve in a small amount of glacial acetic acid to a violet, in much acetic acid to a green solution which gradually becomes red. Violet *oxonium* salts are formed on addition of concentrated hydrochloric or sulphuric acid to the solid compounds or to the solutions in glacial acetic acid or alcohol; the diacetyl compounds behave towards alkali hydroxides in the same manner as the red tritanone ether, and are hydrolysed by alcoholic potassium hydroxide. The constitutions of the diacetyl-compounds and of their additive compounds are discussed.

If one of the diacetyl compounds or the brown or red tritanone ether is boiled with sodium acetate and acetic anhydride and poured into water, a greyish-black precipitate is formed, which on extraction with ether yields a residue of the red tritanone ether. The ethereal solution contains three products: (a)  $7^{III}6^{II} : 7^{III}2^{III}$ -*dianhydro-tetra-acetyl-m-tetra-2 : 6-tritanol-II*, I; I, IV; IV, III-*triether* (blue tetra-



tallises on pouring the ether into alcohol as a bluish-black powder, m. p. about 200°, forms blue solutions, is precipitated from its alcoholic solution by hydrochloric acid as a blue, by sulphuric acid as a brown powder, gives a characteristic milky-blue coloration with alcoholic ammonia, and yields an olive-green solution when boiled with alcoholic potassium hydroxide; (b) *m-tetra-2 : 6-dihydroxytritan-I*, IV-*ol-II*, III-*acetic acid*, , O,

crystallises on evaporation of the ethereal-alcoholic filtrate from (a), is washed with ether, and recrystallised from a mixture of acetone and alcohol; it forms slender, white needles, m. p. 222—224°; (c) the  $\delta$ -*diacetyl-diether-anhydride*,



crystallises from the ethereal washings of the preceding substance on evaporation with alcohol in red needles, m. p. with decomposition  $180-190^{\circ}$ , and on prolonged boiling with alcohol forms  $7^{II}6^{II}$ ;  $7^{III}2^{III}$ -*dianhydro- $\bar{m}$ -tetra-2 : 6-dihydroxytritan-I,IV-ol-II,III-acetic acid- $7^{IV}7^{IV}$ -anhydride*,  $C_{80}H_{52}O_9, 2C_2H_6O$ , m. p.  $180-190^{\circ}$ . These three acetyl compounds lose acetic acid when strongly heated but do not form a tritanone ether.

The *tetra-acetyl* derivative of the diether,  $C_{84}H_{62}O_{14}$ , formed together with the diacetyl derivative, is obtained on evaporation of its benzene solution as a varnish or on addition of its benzene or ethereal solution to light petroleum as a yellow, amorphous precipitate, sinters at  $115^{\circ}$ , and on further heating melts slowly, becomes viscous, and melts again at  $190^{\circ}$ ; when heated above  $200^{\circ}$  it loses acetic anhydride and forms the brown tritanone ether.  $2^{IV}7^{IV}$ -*Anhydrotetra-acetyl- $\bar{m}$ -tetra-2 : 6-dihydroxytritanol-6 $^{II}2^{II}$  :  $6^{III}2^{IV}$ -diether*,  $C_{84}H_{60}O_{13}$ , crystallises when the ethereal solution of the preceding substance is poured into alcohol as a yellowish-white, sandy powder, when heated behaves in the same manner as the tetra-acetyl derivative, and forms brownish-violet oxonium salts of the brown tritanone ether when treated with concentrated hydrochloric or sulphuric acid.

When boiled with sodium acetate and acetic anhydride, the acetoxy-diether-anhydride yields three products: (a) the  $2^{IV}7^{IV}$ -*anhydropenta-acetyl* derivative of the triether,  $C_{86}H_{60}O_{13}$ , crystallises from a mixture of alcohol and chloroform in yellow or reddish-yellow, quadratic leaflets, m. p.  $247^{\circ}$ , loses acetic acid when strongly heated, forms yellow solutions with green fluorescence, is hydrolysed slowly by boiling aqueous potassium hydroxide forming the triether, and becomes brownish-violet on treatment with concentrated sulphuric acid; (b) the *penta-acetyl* derivative of the triether,  $C_{86}H_{62}O_{14}$ , is obtained on evaporation of the ethereal washings from the anhydro-compound and crystallisation from alcohol as a brown powder; (c) the  $2^{IV}7^{IV}$ -*anhydrohexa-acetyl* derivative of the diether,  $C_{88}H_{64}O_{15}, C_2H_6O$ , separates from the alcoholic filtrate from the preceding substance on concentration at the laboratory temperature, sinters and swells up slightly at  $115^{\circ}$ , decomposes with effervescence above  $160^{\circ}$ , loses acetic anhydride and forms the brown tritanone ether on prolonged heating at high temperatures, and gives a brownish-violet coloration with concentrated hydrochloric or sulphuric acid.

Simultaneous reduction and acetylation of the acetoxy-diether-anhydride by boiling with sodium acetate, zinc dust, and acetic anhydride leads to the formation of the  $2^{IV}7^{IV}$ ;  $2^{III}7^{II}$ ;  $2^{III}7^{III}$ -*trianhydro-octa-acetyl* derivative of the octahydrodiether,  $C_{92}H_{72}O_{15}$ , which is obtained in two modifications; one of these is insoluble in cold ether and separates from a mixture of alcohol and benzene in colourless, spicular crystals, m. p.  $174^{\circ}$ . The second modification is soluble in cold ether and on evaporation of its ethereal-alcoholic solution separates as a white, granular mass, m. p.  $104-105^{\circ}$ , or after heating on the water-bath,  $120-125^{\circ}$ ; when repeatedly dissolved in ether and evaporated with alcohol, it changes gradually into the first modification. In one experiment, a *product*,  $C_{92}H_{74}O_{15}$ , forming colourless crystals, m. p.  $242^{\circ}$ , was obtained. When distilled in a vacuum, the colourless

isomerides decompose, forming diphenylmethane, acetic and benzoic acids, and a *substance* which crystallises from alcohol, m. p. about  $135^{\circ}$ , has a characteristic, aromatic odour, and dissolves in aqueous potassium hydroxide, forming a solution with blue fluorescence.

When boiled with alcoholic potassium hydroxide, all the acetyl derivatives described, with the exception of the diacetyl derivatives, dissolve, forming a bluish-red solution which has a green fluorescence and becomes colourless on dilution with water.

The following oxonium salts and derivatives are described:—Of the diacetyl-diether-anhydride: the *hydrochloride*,  $C_{78}H_{54}O_{10}, 2HCl, H_2O$ , crystallises in slender, yellow needles, and loses hydrogen chloride at about  $200^{\circ}$ ; the *sulphate*,  $C_{78}H_{54}O_{10}, 2H_2SO_4, 2H_2O$ , forms microscopic, yellow leaflets, m. p. about  $260^{\circ}$ ; the *phosphate* forms a yellow powder; the *picrate* forms yellow, microscopic, rhombic leaflets, m. p.  $135-140^{\circ}$ ; the *acetyl chloride* derivative forms an unstable, yellow, crystalline powder, and decomposes on the water-bath; the *methyl sulphate* compound,  $C_{78}H_{54}O_{10}, SO_4Me_2$ , forms a glistening, brownish-yellow, crystalline powder, the alcoholic filtrate from which deposits the methyl sulphate compound of the red tritanone ether in glistening, violet needles.

Derivatives of the triether: the *hydrochloride*,  $C_{76}H_{52}O_9, 3HCl$ , forms transparent, brownish-yellow needles having a greenish-blue lustre; the *sulphate*,  $C_{76}H_{52}O_9, 1\frac{1}{2}H_2SO_4$ , crystallises in glistening, golden-yellow, quadratic leaflets; the *phosphate* forms brownish-yellow, granular crystals; the *acetyl chloride* derivative,  $C_{76}H_{52}O_9, C_2H_3OCl$ , forms a delicate, yellow, crystalline powder.

The anhydropenta-acetyl derivative of the triether forms a *hydrochloride*,  $C_{86}H_{60}O_{13}, 3HCl$ , crystallising in yellow needles or brown, rhombic leaflets, and a *sulphate*,  $C_{86}H_{60}O_{13}, 2\frac{1}{2}H_2SO_4$ , crystallising in brownish-yellow, rectangular rods.

The brown tritanone ether forms a *hydrochloride*,  $C_{78}H_{48}O_7, 2HCl$ , and a brownish-violet *sulphate*,  $C_{78}H_{48}O_7, H_2SO_4$ , or in another preparation,  $C_{78}H_{48}O_7, 2H_2SO_4$ .

The following are derivatives of the red tritanone ether: the *hydrochloride*,  $C_{76}H_{48}O_7, 2HCl$ , *sulphate*,  $C_{76}H_{48}O_7, H_2SO_4$ , *phosphate*,

$C_{76}H_{48}O_7, \frac{1}{2}H_3PO_4$ , and *methyl sulphate* derivative,  $C_{76}H_{48}O_7, SO_4Me_2$ , crystallises in violet to violet-blue needles; the *acetyl chloride* derivative,

$C_{76}H_{48}O_7, 2C_2H_3OCl$ , separates from alcohol as a bluish-black, granular powder.

The oxonium salts are decomposed by cold alcoholic potassium hydroxide or by boiling water; the acetyl chloride and methyl sulphate derivatives are attacked by cold water. G. Y.

**Fission by Means of Hydrogen Chloride.** FELIX HERRMANN (*Ber.*, 1906, 39, 3812—3816. Compare *Abstr.*, 1905, i, 733).—It has been shown previously that the oxidation which takes place during the formation of complex organic auric compounds such as aurodibenzylsulphine chloride and auric dibenzyl sulphide dichloride and leads to the formation of dibenzylsulphine oxide is a reversible reaction. Similarly, the action of hydrogen chloride on aurodibenzylsulphine

chloride and diphenylsulphine oxide in chloroform solution leads to the formation of the sparingly soluble *auric* compound,  $S(C_7H_7)_2AuCl_2$ , and diphenyl sulphide. Other readily oxidisable substances are not oxidised in this manner.

The action of hydrogen chloride on 3 mols. of dibenzylsulphine oxide in chloroform solution in the absence of the gold compound, leads to the formation of 2 mols. of benzaldehyde and 1 mol. each of dibenzyl disulphide, dibenzyl sulphide, and water. If the action of the hydrogen chloride is prolonged, absorption takes place, the temperature rises to  $40^\circ$ , and after some time the contents of the flask boil suddenly with escaping hydrogen chloride and become turbid in consequence of the formation of water. The products of the reaction are then benzaldehyde, dibenzyl disulphide, water, and small amounts of benzyl chloride. The intermediate labile *additive* product of dibenzylsulphine oxide and hydrogen chloride, isolated by cooling the reacting mixture with ice, crystallises in white needles and in the absence of moisture remains unchanged for long periods. G. Y.

**Transformation of Cinnamyl Alcohol into Phenylpropylene (Allylbenzene) and Phenylpropyl Alcohol by Metal ammoniums.** E. CHABLAY (*Compt. rend.*, 1906, 143, 829—831. Compare Abstr., 1905, i, 503).—Cinnamyl alcohol is reduced by sodium ammonium at  $-80^\circ$  to form a small quantity of phenylpropylene (allylbenzene), b. p.  $165-170^\circ$ , yielding a dibromo-derivative, m. p.  $67^\circ$  (Fittig gives  $66.5^\circ$ , Abstr., 1874, 894, and Senfter and Tafel give  $65-66^\circ$ , Abstr., 1894, i, 580), but the chief product of the reduction is  $\gamma$ -phenylpropyl alcohol (compare Fittig, Abstr., 1873, 899; and Rügheimer, Abstr., 1874, 894), which forms a viscous, colourless, fragrant liquid, b. p.  $236-237^\circ/750$  mm.,  $D^{18}_D$  1.007 (Rügheimer gives 1.008), does not solidify in solid carbon dioxide, and on oxidation forms phenylpropionic acid, m. p.  $47.5^\circ$ . M. A. W.

**Benzoyl Nitrate.** FRANCIS E. FRANCIS (*Ber.*, 1906, 39, 3798—3804).—This is an amplification of work previously described (*Trans.*, 1906, 89, 1). As prepared, benzoyl nitrate always contains 15—20 % of benzoic anhydride, and has  $D^{20}_D$  1.3.

*Butyryl nitrate* is a light yellow liquid which detonates when heated.

Benzoyl nitrate reacts readily with thiophen, *m*-xylene, mesitylene, anisole, phenetole, or veratrole, forming *o*-nitro-derivatives; in some cases dilution with carbon tetrachloride is necessary. The reaction takes place less easily with bromobenzene, benzoyl chloride, or benzoyl cyanide, only traces of the *p*-nitro-derivatives being obtained. With  $\alpha$ - and  $\beta$ -naphthol, 2:4-dinitro- $\alpha$ -naphthol and 1:6-dinitro- $\beta$ -naphthol respectively are formed; better yields are obtained with  $\alpha$ -naphthol ethyl ether, which yields the 4-nitro- with only traces of the 1:2-dinitro-derivative, and  $\beta$ -naphthol methyl and ethyl ethers which yield the corresponding 1-nitro-derivatives.

Benzaldehyde, anisaldehyde, salicylaldehyde, and *o*-methoxybenzaldehyde are oxidised by benzoyl nitrate, forming the corresponding acids; only with anisaldehyde and salicylaldehyde are traces of nitro-derivatives obtained. Mandelonitrile is readily converted into the *nitro*-derivative,  $NO_2 \cdot CPh(OH) \cdot CN$ , m. p.  $77-78^\circ$ , and is decomposed by

water or alkali hydroxides, forming benzoic, nitrous, and hydrocyanic acids.

3-Nitrovanillin, 5-nitrocoumarin, and a dinitro- $\beta$ -naphthaldehyde, m. p. 194—195°, are formed quantitatively by the action of benzoyl nitrate on vanillin, coumarin, and  $\beta$ -naphthaldehyde respectively, whilst piperonal forms only small amounts of 6-nitropiperonal, being simultaneously oxidised.

In some cases, benzoyl nitrate acts as an oxidising agent; thiophenol is oxidised to diphenyl disulphide, hydrazobenzene to azobenzene.

G. Y.

**Reactions of Benzoyl Nitrate with Amines.** THOMAS H. BUTLER (*Ber.*, 1906, 39, 3804—3807. Compare Francis, *Trans.*, 1906, 89, 1; and preceding abstract).—Benzoyl nitrate reacts with primary aromatic amines, *m*-chloroaniline, *p*-chloroaniline, *m*-nitroaniline, *p*-anisidine, *o*-toluidine, and 1:3:4-xylidine, to form the substituted anilides together with the nitrate of the base. Phenylhydrazine forms *s*-benzoylphenylhydrazine. The secondary bases of the fatty series react with benzoyl nitrate in the same manner, forming disubstituted benzamides.

Benzoyldiamylamine is obtained as an oil, b. p. 300—319°, which is hydrolysed by concentrated hydrochloric acid, yielding benzoic acid and diamylamine hydrochloride.

The action of benzoyl nitrate on diphenylamine leads to the formation of only a small amount of benzodiphenylamide, or on ethylaniline to impure phenylethylnitroamine, whilst with methyl-*p*-toluidine, *p*-tolyl-methylnitroamine,  $C_7H_7 \cdot NMe \cdot NO_2$ , is formed in almost quantitative yields. When treated with concentrated sulphuric and glacial acetic acids, this is converted into 3-nitro-4-methylaminotoluene.

The action of benzoyl nitrate on acetanilide in carbon tetrachloride solution at low temperatures leads to the formation of a small amount of a white, crystalline substance which may be the nitroamine,  $NO_2 \cdot NPhAc$ ; it explodes violently if rubbed when dry, and gradually changes into *o*-nitroacetanilide; this is formed also if the action of benzoyl nitrate on acetanilide takes place at a slightly higher temperature.

*o*-Nitrophenacetin is obtained without formation of an explosive intermediate compound when phenacetin is treated with benzoyl nitrate in carbon tetrachloride solution.

G. Y.

**Action of Ammonium Sulphide on  $\alpha\alpha$ -Dichloroamides and on  $\alpha$ -Ketoamides.** CELSO ULPANI and G. CHIEFFI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 511—516. Compare Ulpiani and Ciancarelli, *Abstr.*, 1904, i, 162).—Although hydrogen sulphide acts on  $\alpha$ -ketoamides giving trithiodiamides (*loc. cit.*), it does not react with the similarly constituted  $\alpha\alpha$ -dichloroamides, probably on account of the hydrogen chloride formed. With ammonium sulphide, however,  $\alpha\alpha$ -dichloroamides give pentathiotetramides,  $S(S \cdot CHR \cdot CO \cdot NH_2)_4$ . This reaction takes place in two stages, the action of hydrogen sulphide on the  $\alpha\alpha$ -dichloroamide forming trithiodiamide, which is converted into pentathiotetramide by ammonia.



*Pentathiotetraphenylacetamide*,  $S(S \cdot CHPh \cdot CO \cdot NH_2)_4$ , prepared by the interaction of ammonium sulphide and  $\alpha$ -dichlorophenylacetamide or of ammonia and trithiodiphenylacetamide or of ammonium sulphide and benzoylformamide, crystallises with  $2H_2O$  in microscopic, rectangular plates, m. p.  $235^\circ$ .

*Pentathiotetracetamide*,  $S(S \cdot CH_2 \cdot CO \cdot NH_2)_4$ , obtained by the action of ammonium sulphide on dichloroacetamide, separates from water in crystals, m. p.  $146-148^\circ$ .

*Pentathiotetrapropionamide*,  $S(S \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2)_4$ , prepared from ammonium sulphide and  $\alpha$ -dichloropropionamide, crystallises from alcohol or water in rectangular plates, m. p.  $187-188^\circ$ .

When heated with a solution of potassium hydroxide (6 mols.), (1) pentathiotetraphenylacetamide yields a substance,



m. p.  $215^\circ$ , forming microscopic, elongated, rectangular crystals; (2) pentathiotetraglycollamide, a substance which, on oxidation with ferric chloride, gives dithioglycollic acid; and (3) pentathiotetrapropionamide, which, with ferric chloride, yields dithiolactic acid. T. H. P.

### Velocity of the Addition of Bromine to Cinnamic Acid.

WALTER HERZ and BRUNO MYLIUS (*Ber.*, 1906, **39**, 3816—3820).—The authors propose to study the velocity of the addition of halogens to ethylene linkings, with special reference to the influence of various solvents and of catalysts, and finally to investigate from a chemical physical standpoint the usual "addition of iodine" method of estimating fats.

The results of two series of experiments in which cinnamic acid was heated with pure bromine in chloroform solution at  $25^\circ$ , in the second series with addition of bromoform, when calculated for a bimolecular reaction gave satisfactorily steady constants. Iodine, if present, acts as a catalytic agent as the constant is greatly increased, being about ten times as large with 0.0102 gram of iodine for 2.0235 millimols. of cinnamic acid. In this case the constant decreases markedly with the time, in consequence probably of the formation of di-iododihydrocinnamic acid taking place in presence of bromine. This decrease of the constant becomes more marked in experiments with large proportional quantities of iodine. With impure bromine, the value of the velocity constant is less steady, pointing to by-reactions, and is three to four times as large; the increase in the value of the constant is still greater, as are also its variations, when "technical" bromine is employed. In all these experiments the first value for the velocity is unsatisfactory.

With carbon tetrachloride as solvent, a constant of higher value but less steadiness is obtained. G. Y.

**Unsaturated Compounds. III. Addition of Free Hydroxylamine to Homologues of Cinnamic Acid. Constitution of and Derivatives of  $\beta$ -Hydroxylamino- $\beta$ -p-tolylpropionic Acid.** THEODOR POSNER and H. OPPERMANN (*Ber.*, 1906, **39**, 3705—3713. Compare Abstr., 1904, i, 160; Abstr., 1906, i, 955).— *$\beta$ -Hydroxylamino- $\beta$ -p-tolylpropionic acid*,  $C_6H_4Me \cdot CH(NH \cdot OH) \cdot CH_2 \cdot CO_2H$ , obtained by the action of hydroxylamine on *p*-methylcinnamic acid,

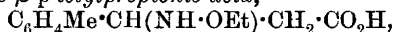
crystallises in leaflets, m. p. 195°. In the cold it reduces both Fehling's solution and ammoniacal silver nitrate; it forms a *diacetyl derivative*,  $C_6H_4Me \cdot CH(NAc \cdot OAc) \cdot CH_2 \cdot CO_2H$ , m. p. 194°. When acted on by ammoniacal silver nitrate the acid forms 3-*p-tolylisooxazole-*

5-one,  $C_6H_4Me \cdot C \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{N} \text{---} \text{O} \end{smallmatrix}$ , which separates from light petroleum in

silky needles, m. p. 133°. It is readily soluble in sodium carbonate and in alkalis and is reprecipitated by acids. Its constitution is determined by its behaviour with nitrous acid when 4-*isonitroso-*

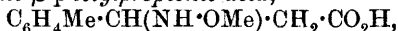
3-*p-tolylisooxazole-5-one*,  $C_6H_4Me \cdot C \begin{smallmatrix} C(:N \cdot OH) \cdot CO \\ \text{N} \text{-----} \text{O} \end{smallmatrix}$ , is formed.

*β-Ethoxylamino-β-p-tolylpropionic acid*,



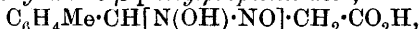
prepared by alkylating *β*-hydroxylamino-*β-p*-tolylpropionic acid with ethyl alcohol and hydrochloric acid, separates from light petroleum in colourless needles, m. p. 87°. The alkyl group is readily eliminated by the addition of potassium hydroxide. The acid readily reduces Fehling's solution and ammoniacal silver nitrate, and is converted by the latter into the *p*-tolylisooxazolone.

*β-Methoxylamino-β-p-tolylpropionic acid*,



separates from light petroleum in colourless needles, m. p. 92°.

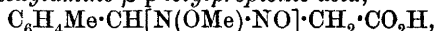
*β-Nitrosohydroxylamino-β-p-tolylpropionic acid*,



m. p. 122°, is obtained by the action of nitrous acid on *β*-hydroxylamino-*β-p*-tolylpropionic acid. When its solution in benzene is heated, nitrous fumes are evolved and 2-*hydroxy-3-p-tolylisooxazolidone*,

$C_6H_4Me \cdot CH \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{N(OH)} \cdot \text{O} \end{smallmatrix}$ , m. p. 141°, is formed.

*β-Nitrosomethoxylamino-β-p-tolylpropionic acid*,

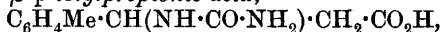


m. p. 53°, is obtained by the action of nitrous acid on *β*-methoxylamino-*β-p*-tolylpropionic acid. It readily decomposes with the formation of

2-*methoxy-3-p-tolylisooxazolidone*,  $C_6H_4Me \cdot CH \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{N(OMe)} \cdot \text{O} \end{smallmatrix}$ , which melts at 118°.

*β-Amino-β-p-tolylpropionic acid (β-amino-p-methylhydrocinnamic acid)*,  $C_6H_4Me \cdot CH(NH_2) \cdot CH_2 \cdot CO_2H$ , obtained by the prolonged boiling of an alcoholic solution of *β*-hydroxylamino-*γ-p*-tolylpropionic acid with free hydroxylamine, crystallises in leaflets, m. p. 226°. Its *copper* salt crystallises with 4H<sub>2</sub>O. The *benzoyl* derivative separates from alcohol in leaflets, m. p. 210°.

*β-Carbamido-β-p-tolylpropionic acid*,



m. p. 210°, is converted by the action of nitrous acid into *β-hydroxy-β-p-tolylpropionic acid*,  $C_6H_4Me \cdot CH(OH) \cdot CH_2 \cdot CO_2H$ , m. p. 185°, which forms a *barium* salt containing 1H<sub>2</sub>O.

A. McK.

**Acylated Allylamines.** OTTO DIELS and ERICH BECCARD (*Ber.*, 1906, 39, 4125—4132. Compare Kay, *Abstr.*, 1894, i, 76).—*Salicylallyl-*

amide,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ , formed by heating salicylic acid with allylthiocarbimide at  $140^\circ$  for twenty hours, crystallises from light petroleum in long needles, m. p.  $52^\circ$  (corr.). The aqueous solution, which has acid properties, gives with ferric chloride a violet coloration. The dibromide crystallises from ethyl acetate in slender white needles, m. p.  $187^\circ$  (corr.), but is decomposed by hot methyl or ethyl alcohol. When salicylallylamine is heated with hydrochloric acid at  $100^\circ$  under pressure, the hydrochloride of 2-o-hydroxyphenyl-5-methyl-4:5-dihydro-oxazole,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{N}-\text{CH}_2 \\ \text{O}-\text{CHMe} \end{smallmatrix}$ , is formed, and is precipitated from its alcoholic solution by ether in slender, white needles, m. p.  $161^\circ$  (corr.). The potassium salt crystallises in compact, white needles, and the platinichloride in fine, yellow leaflet. The base is a yellow oil with a characteristic faint odour.

Hippurallylamine,  $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ , prepared by heating allylthiocarbimide and the corresponding acid at  $130^\circ$  for six hours, crystallises from acetone in aggregates of small, white, irregular plates, m. p.  $138.5^\circ$  (corr.). The hydrobromide,  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2\cdot\text{HBr}$ , precipitated either by mixing acetic acid solutions of hydrogen bromide and amide, or by passing the gas through a chloroform solution of the amide, forms white crystals, m. p.  $140^\circ$ , unstable in moist air and completely decomposed by water into its components. Hippuro- $\beta$ -bromopropylamide, prepared by heating the amide in a saturated solution of hydrogen bromide in acetic acid under pressure at  $60^\circ$ , crystallises from ethyl acetate in rectangular plates, m. p.  $128^\circ$  (corr.). The hippuro-dibromopropylamide, m. p.  $121^\circ$  (corr.), crystallises from acetone in short, compact needles. Hippurobromoallylamine,

$\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CH}_2$ , m. p.  $167^\circ$  (corr.), formed by heating sodium ethoxide and the dibromide on the water-bath, separates from alcohol in slender, white plates. The benzoylglycylglycine (m. p.  $206^\circ$ ) first described by Curtius (Abstr., 1881, 1144) is obtained in good yield when a paste of hippurobromoallylamine in water is treated with ozone at  $40\text{--}50^\circ$  (compare also E. Fischer, Abstr., 1905, i, 263). W. R.

**Carbon Monoxide Scission from Ethyl  $\alpha$ -Bromo- $\alpha$ -phenylacetoacetate.** OTTO DIMROTH and MAX EBLE (*Ber.*, 1906, 39, 3928—3929. Compare Abstr., 1903, i, 631).—Just as ethyl  $\alpha$ -bromopropionylphenylacetate, when distilled with steam, is converted into methylatropic acid, hydrogen bromide, and carbon monoxide, ethyl  $\alpha$ -bromo- $\alpha$ -phenylacetoacetate undergoes decomposition into ethyl atropate, hydrogen bromide, and carbon monoxide. The latter action, which does not, however, take place with the same ease as the former, is represented by the equation



1-Phenyltetronic acid is contained in the residue from the distillation in steam; it separates from dilute alcohol in leaflets, m. p.  $254^\circ$ . Its constitution was established by boiling it with baryta when phenylacetic acid and glycollic acid were formed. A. McK.

**Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. IV. Synthesis of 1-isoPropylcyclohexane-2-one and of *m*-Menthane-2-one from cycloHexanone.** ARTHUR KÖTZ and A. MICHELS (*Annalen*, 1906, 350, 204—216. Compare Abstr., 1906, i, 667).—Instances are given of steric hindrance in the formation of the semicarbazones of cyclohexanones and of their carboxylic esters.

Ethyl cyclohexane-2-one-1-carboxylate is obtained from cyclohexanone, sodium ethoxide, and ethyl oxalate (compare Dieckmann, Abstr., 1901, i, 539).

cycloHexane-2-one-1-oxalic acid,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , obtained from the initial product of condensation in the preceding reaction, m. p. 121°, dissolves in water; the ethyl ester has b. p. 165°/17 mm.

Ethyl 1-methylcyclohexane-2-one-1-carboxylate, b. p. 113°/11 mm., prepared from methyl iodide and ethyl sodiocyclohexane-2-one-1-carboxylate, forms a semicarbazone, m. p. 152°.

Ethyl 1-isopropylcyclohexane-2-one-1-carboxylate, prepared in a similar manner, has b. p. 132°/15 mm., and forms a semicarbazone, m. p. 151°.

1-isoPropylcyclohexane-2-one, obtained from the preceding ester and methyl alcoholic potash, is a colourless liquid with the odour of menthone, b. p. 92°/15 mm.; it forms an additive compound with sodium hydrogen sulphite and a semicarbazone, m. p. 187°.

Ethyl 1-methylcyclohexane-2-one-1:3-dicarboxylate, b. p. 160°/10 mm., prepared from sodium ethoxide, ethyl oxalate, and ethyl 1-methylcyclohexane-2-one-1-carboxylate, forms a semicarbazone, m. p. 239°.

Ethyl 3-isopropyl-1-methylcyclohexane-2-one-1:3-dicarboxylate, obtained from the sodium derivative of the preceding compound and iso-propyl iodide, is a colourless and odourless liquid, b. p. 165°/10 mm., does not form a semicarbazone, and by boiling methyl alcoholic potash is converted into *m*-menthane-2-one (Abstr., 1906, i, 666). C. S.

**Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. V. Synthesis of 1-Methyl-3-isopropylcyclopentane-2-one (Dihydrocamphophorone or Dihydropulegone) from Ethyl cycloPentane-2-one-1-carboxylate.** ARTHUR KÖTZ and PAUL SCHÜLER (*Annalen*, 1906, 350, 217—228).—Methyl cyclopentane-2-one-1-carboxylate, obtained by Dieckmann's method (Abstr., 1901, i, 539), is converted into the metallic derivative by treatment with potassium and sodium in xylene, then treated with 100 % excess of isopropyl iodide and heated at 130—140° for thirty-five hours, when it gives a 55 % yield of methyl 1-isopropylcyclopentane-2-one-1-carboxylate,  $\begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CPr}^s \cdot \text{CO}_2\text{Me}$ , b. p. 112°/11 mm., which does

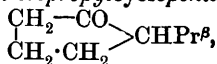
not give a coloration with ferric chloride, and forms a semicarbazone, m. p. 193—194°. The corresponding ethyl ester has b. p. 119°/12 mm.

Methyl  $\alpha$ -isopropyladipate, b. p. 132—133°/15 mm., is obtained from the preceding methyl ester and sodium methoxide; treatment with sodium leads to the formation of methyl 3-isopropylcyclopentane-2-one-1-carboxylate, b. p. 116—125°/11 mm., which forms a semicarbazone

azone, m. p. 134—135°. The corresponding *ethyl* ester has b. p. 128—129°/12 mm.

*Ethyl* 1-methyl-3-isopropylcyclopentane-2-one-1-carboxylate, b. p. 130—135°/12 mm., obtained from the metallic derivatives of the preceding ester and methyl iodide, does not give a blue coloration with ferric chloride.

By treatment with barium hydroxide, ethyl 1-isopropylcyclopentane-2-one-1-carboxylate yields isopropylcyclopentane-2-one,

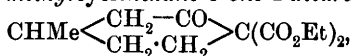


b. p. 175—176°, which forms a *semicarbazone*, m. p. 183—184°.

1-Methyl-3-isopropylcyclopentane-2-one (dihydrocamphorophorone or dihydropulegone) (compare Semmler, Abstr., 1902, i, 385; Wallach, Abstr., 1903, i, 567), b. p. 181—186°, is obtained in a similar manner to the preceding ketone, and forms a *semicarbazone*, m. p. 193—194·5°.

C. S.

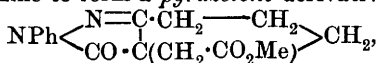
**Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. VI. Dicarboxylic Esters of Cyclic Monoketones.** ARTHUR KÖTZ (*Annalen*, 1906, 350, 229—246).—[With ALBERT HARZER.]—*Ethyl* 1-methylcyclohexane-3-one-4-dicarboxylate,



obtained from ethyl chlorocarbonate and ethyl sodio-1-methylcyclohexane-3-one-4-carboxylate, is a yellow oil, b. p. 232°/17 mm. and 221°/11 mm., does not form a semicarbazone, and yields with phenylhydrazine, Hesse's pyrazolone derivative, m. p. 242°. The ester is decomposed by concentrated sodium hydroxide into 3-methylcyclohexane-1-one.

[With PAUL SCHÜLER.]—*Ethyl* cyclopentane-2-one-1-acetate-1-carboxylate,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{C}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p. 162—163°/14 mm.,

obtained from ethyl bromoacetate and ethyl cyclopentane-2-one-1-carboxylate, does not give a blue coloration with alcoholic ferric chloride, and forms a *semicarbazone*, m. p. 148—149°. The corresponding *methyl* ester, b. p. 153—154°/12 mm. and 157—158°/17 mm., forms a *semicarbazone*, m. p. 180—181°. The methyl ester reacts with methylalcoholic ammonia to form the *amide*,  $\text{C}_8\text{H}_{12}\text{O}_3\text{N}_2$ , m. p. 162—163°, and with phenylhydrazine to form a *pyrazolone* derivative,

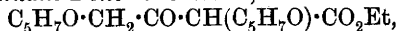


m. p. 146—147°.

cyclopentane-2-one-1-acetic acid,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.

50—51°, is prepared by hydrolysing ethyl cyclopentane-2-one-1-carboxylate-1-acetate with hydrochloric acid. By esterification with alcohol and hydrogen chloride it yields the *ethyl* ester, b. p. 129—130°/18 mm., which has the odour of ethyl acetate, forms a *semicarbazone*, m. p. 173—174°, and by treatment with sodium yields

*ethyl  $\alpha$ -dicyclopentane-2-one-acetoacetate*,



b. p. 240—260°/20 mm.; this forms a *semicarbazone*, m. p. 191—192°.

When ethyl *cyclopentane-2-one-1-carboxylate-1-acetate* is heated with sodium ethoxide, it is converted into *ethyl pentane- $\alpha\beta\epsilon$ -tricarboxylate*,  $\text{C}_{14}\text{H}_{24}\text{O}_6$ , b. p. 188—189°/18 mm.; the *methyl* ester has b. p. 180—181°/18 mm. Hydrolysis of the esters by hydrochloric acid, followed by keeping in a vacuum over sulphuric acid, yields an *anhydride*,  $\text{C}_8\text{H}_{10}\text{O}_5$ , m. p. 95°, which by treatment with water yields the *acid*,  $\text{C}_8\text{H}_{12}\text{O}_6$ , m. p. 81—84°.

[With ARTHUR BIEBER.]—*Ethyl 1-methylcyclohexane-3-one-4-carboxylate-4-acetate*, b. p. 194—195°/12 mm., is obtained from ethyl sodio-1-methylcyclohexane-3-one-4-carboxylate and ethyl chloro- or bromoacetate; the *semicarbazone* has m. p. 126—127°.

[With GUSTAV KAYSER.]—*Ethyl 1-methylcyclohexane-3-one-4-acetate*, b. p. 145—155°/0 mm., is obtained by hydrolysing the preceding ester and esterifying the resulting acid, and forms a *semicarbazone*, m. p. 116°.

*Ethyl  $\beta$ -methylhexane- $\alpha\epsilon\zeta$ -tricarboxylate*, b. p. 215—218°/0 mm., obtained by decomposing ethyl 1-methylcyclohexane-3-one-4-acetate-4-carboxylate with sodium ethoxide; when hydrolysed, yields the *acid*,  $\text{C}_{10}\text{H}_{16}\text{O}_6$ , m. p. 120°. C. S.

#### Esterification of Unsymmetrical Di- and Poly-basic Acids.

**XV. Esterification of 4-Nitrophthalic Acid.** RUDOLF WEGSCHEIDER (*Monatsh.*, 1906, 27, 777—779. Compare Wegscheider and Kailan, *Abstr.*, 1906, ii, 340; Goldschmidt and Sunde, *Abstr.*, 1906, ii, 219).—In view of the uncertainty attached to Goldschmidt's measurements of the velocity of esterification previously utilised (Wegscheider and Lipschitz, *Abstr.*, 1901, i, 32; Wegscheider and Bondi, *Abstr.*, 1905, i, 895) in the discussion of the esterification of 4-nitrophthalic acid, the esterification of *m*-nitrobenzoic acid by means of hydrogen chloride and alcohol has been repeated and found to take place more slowly than that of *p*-nitrobenzoic acid under similar conditions. This shows that the formation of 1-ethyl hydrogen 4-nitrophthalate, by partial hydrolysis of ethyl 4-nitrophthalate, and not that by esterification of 4-nitrophthalic acid with hydrogen chloride and alcohol, is the irregular action. G. Y.

**Direct Comparison of the Diphenyladipic Acids with the Truxillic Acids.** HEINRICH JESSEN (*Ber.*, 1906, 39, 4089—4092).—As the two  $\beta\gamma$ -diphenyladipic acids obtained by Henle on reduction of methyl cinnamate (*Abstr.*, 1906, i, 669) closely resemble the truxillic acids, the author has compared some derivatives of the  $\beta\gamma$ -diphenyladipic acid, which crystallises with  $\text{C}_2\text{H}_6\text{O}$ , m. p. 276° (270°, Henle, *loc. cit.*), with the corresponding derivative of  $\alpha$ -truxillic acid, m. p. 274°, and found them not to be identical.

Methyl  $\beta\gamma$ -diphenyladipate, m. p. 173—174°, and methyl  $\alpha$ -truxillate, m. p. 173—174°, give distinctly different figures on analysis. *Ethyl  $\beta\gamma$ -diphenyladipate*,  $\text{C}_{22}\text{H}_{26}\text{O}_4$ , crystallises in glistening prisms, m. p. 114°; ethyl  $\alpha$ -truxillate, m. p. 146°. *Calcium  $\beta\gamma$ -diphenyladipate*  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Ca}$ , forms a delicate, crystalline precipitate; *calcium  $\alpha$ -truxil-*

late,  $C_{18}H_{14}O_4Ca, H_2O$ , crystallises in needles. *Barium  $\beta$ -diphenyladipate*,  $C_{18}H_{16}O_4Ba, 3H_2O$ , forms short, glistening prisms; *barium  $\alpha$ -truxillate*,  $C_{18}H_{14}O_4Ba, 8\frac{1}{2}H_2O$ , crystallises in large prisms which rapidly effloresce.

The action of concentrated nitric acid on  $\beta$ -diphenyladipic acid leads to the formation of two dinitro-derivatives,  $C_{18}H_{16}O_8N_2$ , m. p.  $318^\circ$  and  $218^\circ$  respectively. The latter dinitro-acid forms an *ethyl ester*,  $C_{22}H_{24}O_8N_2$ , which crystallises in light yellow needles, m. p.  $169-172^\circ$ .  
G. Y.

**Derivatives of Truxillic Acid.** HEINRICH JESSEN (*Ber.*, 1906, 39, 4086—4089).—Homans, Stelzner, and Suckow's  $\alpha$ -dinitro  $\alpha$ -truxillic acid (*Abstr.*, 1891, 1495) is the *pp*-dinitro-acid, as the corresponding diamino-acid yields *p*-aminocinnamic acid when distilled.

*Di-p-acetyl-amino- $\alpha$ -truxillic acid*,  $C_4H_4(C_6H_4 \cdot NHAc)_2(CO_2H)_2$ , prepared by boiling the diamino-acid with sodium acetate and acetic anhydride, crystallises in needles, m. p.  $276^\circ$ . *Ethyl di-p-amino- $\alpha$ -truxillate*,  $C_4H_4(C_6H_4 \cdot NH_2)_2(CO_2Et)_2$ , formed by the action of ethyl iodide on the silver salt, crystallises in leaflets.

*Di-p-chloro- $\alpha$ -truxillic acid*,  $C_4H_4(C_6H_4Cl)_2(CO_2H)_2$ , prepared from diazotised di-*p*-amino- $\alpha$ -truxillic acid by Sandmeyer's reaction, is difficult to purify, m. p. about  $278-280^\circ$ .

*Dinitro-di-p-hydroxy- $\alpha$ -truxillic acid*,  $C_4H_4[C_6H_3(NO_2) \cdot OH]_2(CO_2H)_2$ , obtained by treating the di-*p*-hydroxy-acid with concentrated nitric acid, dissolves in much hot alcohol and could not be crystallised. The *ethyl ester*,  $C_{22}H_{22}O_{10}N_2$ , crystallises in glistening needles, m. p.  $294^\circ$ .

The action of potassium nitrate on di-*p*-nitro- $\alpha$ -truxillic acid in hot concentrated sulphuric acid solution leads to the formation of *tetranitro- $\alpha$ -truxillic acid*,  $C_4H_4[C_6H_3(NO_2)_2]_2(CO_2H)_2$ , which crystallises in glistening, yellow prisms, m. p.  $262^\circ$ , and is stable towards potassium permanganate. The *ethyl ester*,  $C_{22}H_{20}O_{12}N_4$ , crystallises from alcohol in glistening, flat prisms or from acetone in aggregates of needles, m. p.  $146^\circ$ . *Tetra-amino- $\alpha$ -truxillic acid*, obtained by reduction of the tetranitro-acid by means of tin and hydrochloric acid, is isolated in the form of its *hydrochloride*,  $C_{18}H_{20}O_4N_4, 2HCl$ ; this crystallises in white, glistening needles. The *hydrochloride* of ethyl tetra-amino- $\alpha$ -truxillate,  $C_{22}H_{28}O_4N_4, 2HCl$ , prepared by reduction of the tetranitro-ester, crystallises in delicate leaflets and is almost insoluble in all organic solvents.

The oxidation of the tetra-substitution products of  $\alpha$ -truxillic acid leads to the formation of derivatives of benzoic acid or undefined resins, and not of tetramethylene derivatives.  
G. Y.

**Hydramides.** ARTUR FÜRTH (*Monatsh.*, 1906, 27, 839—847. Compare Fulda, *Abstr.*, 1903, i, 199; Ofner, *Abstr.*, 1904, i, 818; Ott, *Abstr.*, 1905, i, 376).—The formation of mixed hydramides by the expulsion of two of the aldehyde groups of a hydramide by another aldehyde failed, as the reaction continues to the complete substitution of the one aldehyde by the other.

Hydrobenzamide, m. p.  $102^\circ$  ( $110^\circ$ , Laurent, *Annalen*, 1837, 21, 130).

Trimethyl-*p*-amarine (Gattermann, Abstr., 1906, i, 589) crystallises with  $\frac{1}{2}$  H<sub>2</sub>O, sinters at 119—120°, and, although a meniscus is formed at 126—127°, is not melted completely below 136°.

Hydrotri-*p*-nitrobenzamide, C<sub>21</sub>H<sub>15</sub>O<sub>6</sub>N<sub>5</sub>, prepared by the action of concentrated aqueous ammonia on *p*-nitrobenzaldehyde, is flocculent, darkens at 160—170°, and does not melt on further heating.

When boiled with *m*-nitrobenzaldehyde in ethereal solution in a reflux apparatus, hydrobenzamide, hydro-*p*-toluamide (Gattermann, *loc. cit.*), hydrosalicylamide, or hydroanisamide yields hydrotri-*m*-nitrobenzamide, N<sub>2</sub>(CH·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>)<sub>3</sub>, m. p. 160° (Bertagnini, *Annalen*, 1851, 79, 272).

Furfuraldehyde, piperonal, anisaldehyde, and salicylaldehyde do not react in this manner with hydrobenzamide or hydro-*p*-toluamide.

G. Y.

**Leuco-derivatives of Hydroxy-ketones.** BERTHOLD KÖNIG and STANISLAUS VON KOSTANECKI (*Ber.*, 1906, 39, 4027—4031).—When benzo-resorcinol (Abstr., 1894, i, 506) is methylated with 1 gram-mol. of methyl sulphate, it yields the *monomethyl ether*, (2-hydroxy-4-methoxybenzophenone), C<sub>6</sub>H<sub>3</sub>(OH)(OMe), m. p. 66°; with a large excess of methyl sulphate it yields 2:4-dimethoxybenzophenone, m. p. 87—88°, which may also be prepared from benzoyl chloride and resorcinol dimethyl ether. The leuco-derivative of the dimethoxy-compound is an oil.

3:4-Dimethoxybenzophenone (Brüggemann, Abstr., 1896, i, 356), m. p. 103—104°, when reduced with zinc dust and alcoholic potash yields 3:4-dimethoxybenzhydrol, OH·CHPh·C<sub>6</sub>H<sub>3</sub>(OMe)<sub>2</sub>, which crystallises from dilute alcohol in colourless prisms, m. p. 99°.

3:4:3':4'-Tetramethoxybenzhydrol, C<sub>17</sub>H<sub>20</sub>O<sub>5</sub>·H<sub>2</sub>O, m. p. 95°, obtained by reducing the corresponding ketone (this vol., i, 75), and dissolves in concentrated sulphuric acid to a magenta-red solution.

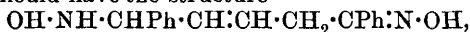
2:5:3':4'-Tetramethoxybenzophenone, m. p. 101—102°, obtained from quinol dimethyl ether and veratroyl chloride; the corresponding leuco-compound has m. p. 132—133°.

2:4:3':4'-Tetramethoxybenzophenone, m. p. 107°, prepared from veratroyl chloride and resorcinol dimethyl ether; its leuco-compound has m. p. 108°. The leuco-derivatives are readily oxidised to the ketones by means of cold chromic acid solution.

J. J. S.

**Action of Hydroxylamine on Ketones of the Type, CHR:CH:CH:CH·CO·R.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 455—459).—With cinnamylideneacetophenone, hydroxylamine gives mainly a hydroxylamineoxime derivative, whilst with cinnamylideneacetone it yields only the ordinary oxime (compare Harries, Abstr., 1904, i, 427; 1905, i, 245).

Hydroxylaminocinnamylideneacetophenoneoxime, which, according to Thiele's law, should have the structure



crystallises from alcohol in colourless needles, m. p. 161°; its acetic acid solution gives with concentrated nitric acid a green coloration with a blue fluorescence. On reduction with sodium and amyl alcohol it



yields a product, the *benzoyl* derivative of which,  $C_{17}H_{19}N_2Bz$ , crystallises from alcohol in minute needles, m. p.  $226^\circ$ .  
T. H. P.

**Synthesis of Euxanthone.** FRITZ ULLMANN and LÉON PANCHAUD (*Annalen*, 1906, 350, 108—117. Compare Graebe, Abstr., 1889, 886; von Kostanecki, Abstr., 1892, 504).—2:6-Dinitrotoluene is converted by a series of reactions into 2-*chloro*-6-methoxybenzoic acid, which forms white needles, m. p.  $141^\circ$ , and by heating with sodium phenoxide and copper at  $180$ — $190^\circ$  yields 2-phenoxy-6-methoxybenzoic acid, which without being isolated is converted by warm concentrated sulphuric acid into 1-methoxyxanthone, m. p.  $138^\circ$ , which forms a blue, fluorescent solution in alcohol. 1-Hydroxyxanthone, m. p.  $147^\circ$ , and obtained from the methyl ether and aluminium chloride in toluene, is identical with Michael's salicylresorcinol ether (Abstr., 1884, 310).

Euxanthone dimethyl ether, m. p.  $149.5^\circ$ , obtained in a similar manner from chloromethoxybenzoic acid and sodium *p*-methoxyphenoxide, is identical with Graebe and Aders' ether obtained from natural euxanthone (Abstr., 1902, i, 42), and is converted by aluminium chloride in benzene or toluene into a substance having m. p.  $240^\circ$  and identical with euxanthone from natural sources.  
C. S.

**Condensation of *o*- and *p*-Nitrobenzoyl Chloride and Acetylacetone.** H. MECH (*Compt. rend.*, 1906, 143, 751—753).—Di-*p*-nitrobenzylacetylacetone,  $C(COMe)_2(CH_2 \cdot C_6H_4 \cdot NO_2)_2$ , obtained by the action of sodioacetylacetone and *p*-nitrobenzyl chloride in absolute alcoholic solution, is a crystalline powder, m. p.  $229^\circ$ . From the mother liquor of the preceding preparation,  $\delta$ -*p*-nitrophenyl- $\beta$ -butanone,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot COMe$ , can be isolated; it forms long, colourless, thin needles, m. p.  $40$ — $41^\circ$ , and is probably formed by the hydrolysis of a monosubstituted derivative of acetylacetone,  
 $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(COMe)_2 + NaOH = MeCO_2Na +$

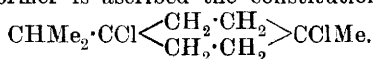
$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot COMe$ ;  
the *oxime*,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CMe:NOH$ , crystallises in needles, m. p.  $120^\circ$ , reduces Fehling's solution and again yields the ketone when dissolved in hydrochloric acid.

Di-*o*-nitrobenzylacetylacetone, prepared similarly to the *para*-compound, forms prismatic crystals, m. p.  $123^\circ$ .  
M. A. W.

**Oxidations with Silver Peroxide. III. Oxidation of *p*-Benzoquinone.** R. KEMPF (*Ber.*, 1906, 39, 3715—3727. Compare Abstr., 1906, ii, 24, 25).—When *p*-benzoquinone is oxidised by silver peroxide, maleic acid and carbon dioxide are the main products, whilst formic acid and carbon monoxide are formed in smaller amounts. When maleic acid itself was oxidised, carbon dioxide was formed together with traces of formic acid, but mesotartaric acid was not detected.

The mechanism of the oxidation of *p*-benzoquinone is discussed. The quantitative methods, by which the proportions of the various oxidation products were estimated, are described. *p*-Benzoquinone and quinol are much more readily oxidised by silver peroxide than by sodium or ammonium persulphate.  
A. McK.

**Terpenes and Ethereal Oils. LXXXII. Compounds, Purification, and Constitution of Terpinene.** OTTO WALLACH (*Annalen*, 1906, 350, 141—179).—Terpinene forms crystalline additive compounds with 2 mol. of halogen acid which exist in *cis*- and *trans*-modifications; the former has the lower melting point and has not been examined further. The *trans*-isomeride is best obtained from sabinene or the terpineol in majorana oil, or less readily from the crude terpinene resulting from the action of dilute sulphuric acid on terpine hydrate. The *hydrochloride*,  $C_{10}H_{16} \cdot 2HCl$ , has m. p. 51—52°, the *hydrobromide*, 58—59°, and the *hydriodide*, 76°. These constants are very near those of the corresponding dipentene derivatives; the method of "mixed" melting points is employed to ascertain whether a halogen compound belongs to the terpinene or to the dipentene series. To the former is ascribed the constitution



Chemically pure terpinene is obtained from the hydrochloride or the hydrobromide by means of aniline, b. p. 179—181°,  $D_D^{20}$  0.846,  $n_D^{20}$  1.4789.

Most carefully purified dipentene has b. p. 178—180°, which is somewhat higher than that of the active limonenes, a fact which requires further investigation.

When terpinene dihydrobromide is treated at 0° with silver acetate in glacial acetic acid,  $\alpha$ -terpineol and *cis*- and *trans*-terpines, m. p. 117° and 156—157° respectively, are obtained; this indicates that the terpinene compound has changed completely in the acetic acid solution into dipentene dihydrobromide.

[With FRIEDRICH BOEDECKER.]—The following hydrochlorides were treated with excess of 2% aqueous potash at 50—60°. Active limonene hydrochloride yields active  $\alpha$ -terpineol. *trans*-Dipentene dihydrochloride yields dipentene,  $\alpha$ -terpineol, *cis*- and *trans*-terpines; the method is very convenient for the preparation of the last-mentioned substance. *cis*-Dipentene dihydrochloride yields the same products as its isomeride with the exception of *trans*-terpine.

Terpinene dihydrochloride, after fifteen hours the temperature being raised to 100°, yields terpinene,  $\alpha$ -terpineol, *cis*- and *trans*-terpine, and a *terpineol* and a *terpine*. The terpineol,  $C_{10}H_{18}O$ , b. p. 90°/11 mm. and 212—214°/760 mm.,  $D_D^{20}$  0.9290,  $n_D^{20}$  1.4803, and differs from other terpineols in its less pleasant odour and in its combination with hydrogen chloride to re-form terpinene dihydrochloride. The terpine,  $C_{10}H_{18}(OH)_2$ , is more soluble than the isomerides, separates from ethyl acetate and light petroleum in glistening leaflets, m. p. 136.5—137.5°, and forms terpinene dihydrobromide with hydrogen bromide in glacial acetic acid.

It is represented by the formula  $CHMe_2 \cdot C(OH) \left\langle \begin{array}{c} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{array} \right\rangle C(OH)Me$ .

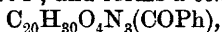
With halogen acids, terpineols behave as follows:  $\alpha$ -terpineol ( $\Delta^1$ -menthene-8-ol), whether active or inactive, yields the dipentene derivative;  $\beta$ -terpineol ( $\Delta^{8(9)}$ -menthene-1-ol) yields the same and also 8-*chloromenthane*-1-ol,  $CMe_2Cl \cdot CH \left\langle \begin{array}{c} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{array} \right\rangle CMe \cdot OH$ , which crystallises in needles, m. p. 74—75°, and is converted into *cis*-terpine by 2%.

aqueous potash;  $\gamma$ -terpineol ( $\Delta^{4(8)}$ -menthene-1-ol) yields the dihydrochlorides of dipentene and of terpinene (compare Baeyer, Abstr., 1894, i, 252). To separate this mixture, it is shaken at  $50^\circ$  for two hours with 2% aqueous potash, whereby the dipentene dihydrochloride is converted into dipentene and  $\alpha$ -terpineol.

Sabinene is converted into *trans*-terpinene dihydrohalide by halogen acids in glacial acetic acid (contrast Kondakoff and Skworzoff, Abstr., 1904, i, 438) and into terpinene by boiling dilute sulphuric acid.  $\alpha$ -Thujene is also converted into the dihalide compounds of terpinene by halogen acids (contrast Kondakoff and Skworzoff (*loc. cit.*); Tschugaeff, 1904, i, 515).

Cardamom and majorana oils each contain the terpineol of the terpinene series, which by oxidation by 1% solution of potassium permanganate yields a *glycerol*,  $C_{10}H_{17}(OH)_3$ , m. p.  $114-116^\circ$ ,  $[a]_D^{22} + 21-24^\circ$ , containing water of crystallisation which is lost at  $130^\circ$ , the residue subliming in crystals and having m. p.  $129^\circ$ , and is not oxidised by chromic acid to a keto-lactone.

When terpinene nitrosite is treated with an equivalent quantity of sodium methoxide or ethoxide, or alcoholic or aqueous potash, the alkali nitrite is formed together with a *substance*,  $C_{20}H_{31}O_4N_3$ , which separates from acetone and water in needles, is insoluble in acids or alkalis, has m. p.  $163-164^\circ$ , and forms a *benzoyl* derivative,



m. p.  $127^\circ$  (compare Semmler, Abstr., 1901, i, 330).

The paper concludes with a brief discussion on the constitution of terpinene. C. S.

**Essential Oils.** HEINRICH HAENSEL (*Chem. Centr.*, 1906, ii, 1495-1496; from *Geschäftsber.*, April-Sept. 1906. Compare Abstr., 1906, i, 524).—The leaves and flowers of the alpine rose yield 0.123% of a yellow oil with a pungent, aromatic odour; it has  $D^{20}_D 0.8620$  and  $\alpha_D^{16.5} - 4.33^\circ$ ; the woody stems of the plant give 0.0097% of the same oil. The terpene, described by Wolpian as hydrocuminene, which occurs together with cymene in cumin oil, has  $D > 0.880$ , and does not yield a crystalline nitrosochloride, hydrochloride, or hydrobromide. The fruit of a species of *Heracleum* known as "semence de panais" yields 1.7% of a greenish-yellow oil of an unpleasant odour having  $D^{20}_D 0.8508$ ,  $\alpha_D^{21.5} - 0.19^\circ$ , acid number 1.3, and saponification number 228.1; the chief alcoholic constituent of this oil is octyl alcohol. *Laserpitium* oil, obtained in 1.87%, yield from the fruits of a plant belonging to that genus, is a dark green oil with an odour resembling that of aniseed and caraway, it has  $D^{20}_D 0.9538$ , acid number 3.2, saponification number before acetylation 15.5, and 28.5 after; it contains limonene, eugenol or dihydroeugenol methyl ether, and a paraffin, m. p.  $57-58^\circ$ . *Oil of rue* on saponification with alkali yields formic and butyric acids. *Sandal oil*, obtained from African sandal wood, is a brown oil of  $D^{20}_D 0.9589$ ,  $[a]_D - 40.6^\circ$ , acid number 1.7, saponification number 17.9, or after acetylation 88.3; it contains a sesquiterpene of b. p.  $260-261.5^\circ$ ,  $D^{20}_D 0.9238$ ,  $\alpha_D^{18} - 39.62^\circ$ , which does not give a solid hydrochloride. The oil, after saponification and drying, condenses with phenylcarbimide, forming diphenylcarbamide, but does

not react in benzene solution with phthalic anhydride. The leaves of *Cyclopia genistoides* on distillation give 0.101% of a light brown, strongly smelling oil having  $D^{15}$  0.8737 and  $\alpha_D + 0.36^\circ$  (in 10% solution in benzene); at ordinary temperatures, it contains crystals of a paraffin, heptacosane, m. p. 53—54°. P. H.

**Essential Oils.** SCHIMMEL & Co. (*Chem. Centr.*, 1906, ii, 1496—1498; from *Geschäftsber.*, Oct. 1906. Compare Abstr., 1906, i, 524).—The dried umbel of the bear's wort from which the fruits have been removed yields 0.08% of a brownish-yellow oil having an odour distinct from that of the fruits; it has  $D^{15}$  0.9273,  $\alpha_D - 0.48'$ , acid number 16.2, ester number 148.6 before acetylation and 195.9 after. The fruits yield 0.9 to 1.21% of an oil having  $D^{15}$  0.8744—0.8798,  $\alpha_D + 0.38'$ — $+1.6'$ , acid number 15.9—7.3, ester number 215.4—242.4 or 285.3—276.3 after acetylation. The dried ripe fruits of *Heracleum giganteum* give 3.6% of a colourless oil with a peculiar odour resembling that of the oil from ordinary bear's wort; it has  $D^{15}$  0.8722,  $\alpha_D + 1.14'$ , acid number 1.6, ester number 288.3 or 314.2 after acetylation. *Basilicum* oil distilled in Germany had  $D^{15}$  0.9038,  $\alpha_D - 9.15'$ ,  $n_D^{20}$  1.48132, acid number 21, ester number 11.6; on dissolving in 80% alcohol it deposited small crystals of paraffin. A sample of oil of *Calamintha Nepeta*, having  $D^{15}$  0.9271,  $\alpha_D + 6.49'$ , ester number 13, contained both pulegone and methone, from which it appears probable that the ketone, calaminthone, described by Genvresse and Chablay, is not a simple substance. The oil from the blossoms of *Champaca* has  $D^{15}$  0.8861,  $\alpha_D - 11.10'$ , acid number 10, ester number 21.6, or 150.1 after acetylation; it has a faint blue fluorescence in alcoholic solution, and therefore appears to contain methyl anthranilate as well as linalool. Oil of Seville oranges should have the following physical properties:  $D^{15}$  0.854—0.857,  $\alpha_D^{20} + 90$ — $+93^\circ$ ;  $\alpha_D$  of the first 10% of the distillate should be higher than that of the original oil; residue 3—5%. Sweet orange oil should have  $D^{15}$  0.848—0.853,  $\alpha_D^{20} + 95$ — $98^\circ$ ;  $\alpha_D$  of the first 10% of distillate should be only very slightly lower than that of the original oil; 2—4% residue. The oil distilled from Algerian *Pinus halepensis* is colourless,  $D^{15}$  0.8643,  $\alpha_D - 3.22'$ , acid number 1.3, ester number 21.2 corresponding with 7.4 of bornyl acetate. A yield of rather less than 1% of camphor oil was obtained from the leaves or branches of camphor trees growing in German East Africa; the oil deposits camphor at the ordinary temperature; the filtrate from this camphor is a golden-yellow oil which has  $D^{15}$  0.9236,  $\alpha_D + 39.20'$ ; its odour is different from that of ordinary camphor oil and it solidifies on freezing; it contains 75% of camphor, traces of a phenolic substance smelling of carvacrol and still smaller quantities of borneol, but no eugenol or safrole such as are found in Japanese camphor oil. From the dried fruits of *Pastinaca sativa* 1.47% of a light yellow oil was obtained,  $D^{15}$  0.8736,  $\alpha_D - 0.9'$ ,  $n_D^{20}$  1.43007, acid number 4.4, ester number 240.6, or 276 after acetylation; the dried umbels of the same plant gave 0.3% of a dark brown oil with an odour faintly resembling that of musk seed oil,  $D^{15}$  1.0168,  $\alpha_D - 0.50'$ ,  $n_D^{20}$  1.50049, acid number 4.2, and ester number 62.9, or after acetylation 86.2; it dissolves in 80% alcohol and deposits paraffin; the dried roots yielded 0.35% of a light yellow oil with

an odour resembling that of vetiver oil,  $D^{15}$  1.0765,  $\alpha_D$  -0°10',  $n_D^{20}$  1.52502, acid number 3.9, ester number 12.6 and 33.7 after acetylation. "Essence d'avocatier" obtained from *Persea gratissima* is a light yellowish-green oil having a bitter taste and an odour resembling that of aniseed,  $D^{15}$  0.956,  $\alpha_D$  +2°22',  $n_D^{20}$  1.51389, ester number 3.8 or after acetylation 18.9; it consists chiefly of methylchavicol,  $\alpha$ -pinene, and a paraffin of m. p. 53—54°. The turpentine, obtained from *Pinus Sabiniana*, which contains abietene, yielded on steam distillation 8.44% of a clear, colourless oil,  $D^{15}$  0.6962,  $\alpha_D$  -0°9'; the chief fraction obtained from this, which boiled at 98.5—99°, was optically inactive, had  $D^{15}$  0.6880, and was identical with *n*-heptane, described by Thorpe as being obtained from the same source. A Spanish hop oil obtained from *Origanum Smyrnaeum* was found to contain cedar camphor; this is, however, not a normal constituent, and may have been introduced by adulteration with cedar oil.

The following oils are described for the first time. A yellowish-green, mobile oil obtained from *Evodia simplex*; it has a pleasant smell,  $D^{15}$  0.9737,  $\alpha_D$  -13°4', acid number 2.1, ester number 16.4 or after acetylation 63.3; it contains methoxyeugenol and a paraffin of m. p. 80—81°. Pilea oil obtained from *Pilea*, species not stated, is a very limpid, clear oil smelling of turpentine; it has  $D^{15}$  0.8533,  $\alpha_D$  +33°53',  $n_D^{20}$  1.46862, ester number 5.1 or after acetylation 24.2; it contains pinene, but the chief constituent was not identified. Oil of white dittany from Algiers, probably obtained from *Amaricus Dictamnus* (*Origanum Dictamnus*), has a yellow colour; it contains 85% of pulegone, of which it smells strongly, and has  $D^{15}$  0.9331 and  $\alpha_D$  +3°.

As phenylcarbimide is not always suitable for identifying alcohols, the authors have experimented with  $\alpha$ -naphthylcarbimide, and have prepared the following carbamates. *Geranyl  $\alpha$ -naphthylcarbamate*, prisms from dilute methyl alcohol, m. p. 47—48°. *Dihydrocuminyl  $\alpha$ -naphthylcarbamate*, prisms from methyl alcohol, m. p. 146—147° (?). The  *$\alpha$ -naphthylcarbamate* obtained from terpineol (m. p. 35°) separates from dilute alcohol in feathery prisms, m. p. 147—148°; the corresponding derivative obtained from terpineol (m. p. 32°) separates from alcohol in prisms, m. p. 83—84°. *Linalyl  $\alpha$ -naphthylcarbamate*, needles from dilute alcohol, m. p. 53°. Nerol and citronellol give only oily naphthylcarbamates, which could not be made to crystallise.

P. H.

**American Copals.** CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1906, [iii], 35, 1143—1150).—Demerara copal has  $D^{19}$  1.047, m. p. 180, acid number 97.7, and Köttsdorfer number 102.4.

Columbian copal has  $D^{19}$  1.054, m. p. > 300°, acid number 118.8, and Köttsdorfer number 155.7.

Brazilian copal has  $D^{19}$  1.053, m. p. 100°, acid number 123, and Köttsdorfer number 133.3.

The solubilities of these three copals in twelve organic solvents are tabulated in the original, which also gives descriptions of the three resins.

T. A. H.

**Vicianin, a new Cyanogenetic Glucoside contained in the Seeds of Vetch.** GABRIEL BERTRAND (*Compt. rend.*, 1906, 143 832—834).—The cyanogenetic principle observed in the seeds of *Vicia angustifolia* by Bruynning and Van Haarst (*Abstr.*, 1900, ii, 160) is a glucoside *vicianin* which is present to the extent of 0.9%, and can be obtained in a crystalline form by extracting the powdered seeds with alcohol at the ordinary temperature, evaporating the solution in a vacuum, extracting the residual syrup several times with ether, and finally filtering the insoluble residue and washing with cold water, then with alcohol. *Vicianin* crystallises from hot water in tufts of brilliant, colourless needles, m. p. 160°,  $[\alpha]_D^{18-12} - 20.7^\circ$  in saturated aqueous solution; it contains 3.2% of nitrogen which is liberated in the form of hydrogen cyanide by the action of emulsin. The seeds of *Vicia angustifolia*, which are capable of furnishing 0.75 gram hydrogen cyanide per kilo., are not a suitable food-stuff for domestic animals.

M. A. W.

**Crystalline Substances of Prickly Ash Bark.** HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1906, 28, 1649—1657).—The isolation of a crystalline substance "xanthoxylin" from the bark of the northern prickly ash (*Xanthoxylum fraxineum* syn. *X. Americanum*) was first accomplished by Staples (*Amer. J. Pharm.*, 1829, 163), and later by Lloyd (*Amer. J. Pharm.*, 1890, 229) and Eberhardt (*Amer. J. Pharm.*, 1890, 231). Another crystalline substance was obtained by Colton (*Amer. J. Pharm.*, 1890, 191) from the southern prickly ash (*X. Carolinianum* syn. *X. Clava-Herculis*), but was shown by Eberhardt (*loc. cit.*) to differ from that yielded by *X. fraxineum*. A third "xanthoxylin" was extracted by Stenhouse from *X. piperatum* (*Annalen*, 1854, 89, 257; 1857, 104, 236), which is quite different from the two former substances, and is isomeric with cantharidin. It is now proposed to retain the name "xanthoxylin" for the last-mentioned substance, and to designate the products of the northern and southern prickly ash as "xanthoxylin N" and "xanthoxylin S" respectively.

Xanthoxylin N,  $C_{14}H_{11}O_3(OMe)$ , m. p. 132.5°, crystallises in white needles, is optically inactive, and gives a red coloration with sulphuric acid. The *dibromide*,  $C_{15}H_{14}O_4Br_2 \cdot H_2O$ , m. p. 171°, crystallises in white aggregates, and becomes yellow on prolonged exposure to the light. On reducing xanthoxylin N with hydrogen iodide, *dihydro-xanthoxylin N*,  $C_{15}H_{16}O_4$ , m. p. 142—143°, is obtained, which forms white needles. Xanthoxylin N does not yield a benzoyl derivative or an anilide. When the substance is dissolved in excess of potassium hydroxide and titrated with acid, it does not exhibit acid properties with methyl-orange, but acts with phenolphthalein as a monobasic acid. With resorcinol it behaves like the anhydride of a dibasic acid and gives a brilliant phthalein reaction.

Xanthoxylin S,  $C_{14}H_{12}O_4$ , m. p. 119—120°, forms snow-white crystals, does not contain a methoxyl group, and is possibly an alcohol or phenol of which xanthoxylin N is the methyl ether.

E. G.

**Chlorophyll. I. Separation and Characterisation of Chlorophyll Derivatives.** RICHARD WILLSTÄTTER and WALTER MIEG (*Annalen*, 1906, 350, 1—47).—Of the products obtained chiefly by Schunck and Marchlewski from chlorophyll by the regulated action of acids and alkalis, only phylloporphyrin has been purified with certainty by means of its sparingly soluble zinc salt; alkachlorophyll, phylloxanthin, phyllocyanin, and phyllotaonin, have not been obtained pure, and it is doubtful whether they are all individual substances. The authors have submitted extracts of chlorophyll to the action of acids and alkalis, and have obtained mixtures of substances which can be separated by means of their varying acidity. These substances are arranged into two classes: (1) *phytochlorins*, which dissolve in neutral solvents to olive-green or green solutions, and in acid solvents to blue or greenish-blue solutions; (2) *phytorhodins*, which form blue or green solutions in acid, and red solutions in neutral, solvents. The various members are denoted by the letters *a*, *b*, *c*, &c.

Phytochlorins and phytorhodins are insoluble in water, but dissolve in organic solvents, alkali and ammonium hydroxides, and sodium hydrogen carbonate; they do not contain phenolic hydroxyl, but an acid group is present, in virtue of which esters can be obtained; they are weak bases forming salts which are decomposed by water.

To obtain the chlorophyll extracts, the dried leaves of the stinging-nettle are treated with light petroleum to remove yellow pigments, and are then either boiled with alcohol or ethyl acetate, or extracted with cold alcohol.

To obtain phytochlorin *a* and *b*, and phytorhodin *f*, the extract obtained by the first method is dissolved in 96% alcohol, sufficient alcoholic potash added to make a 2% solution, and the mixture boiled for fifteen minutes. After diluting with water and neutralising, the solution is extracted with ether; from the ethereal solution after special treatment, alcoholic hydrogen chloride of 3% strength extracts phytochlorin *b*, of 6% strength extracts phytochlorin *a*, and of 11% strength extracts phytorhodin *f*.

Phytochlorin *c* and *d* are obtained by treating *a* or *b* with concentrated alcoholic hydrogen chloride in darkness for twenty-five days; *c* and *d* are extracted from ether by 0.5% and 1.5% alcoholic hydrogen chloride respectively.

To obtain phytorhodins, the cold alcoholic extract of the dried leaves is treated with potassium hydroxide, whereby a greenish-black salt of an alkachlorophyll is precipitated; alcoholic calcium chloride causes the separation of a calcium compound of the substance still remaining in the mother liquor. The finely-powdered potassium salt or the calcium compound is heated with 20% alcoholic hydrogen chloride for seven hours; from the reaction products phytorhodin *a* and its ethyl ester, phytorhodin *b* and its ester, and phytorhodins *c*, *d*, and *e* are ultimately isolated.

*Phytochlorin a*,  $C_{28}H_{38}O_5N_3$ , is obtained by the slow evaporation of its benzene or alcoholic solution in characteristic rosettes of slender blue-black needles, olive-brown by transmitted light, m. p. 181—182°, decomposing. By repeated crystallisation or by heating in a toluene bath, it appears to lose  $\frac{1}{2}H_2O$ , becomes insoluble in ether, and then has

m. p.  $>200^{\circ}$ . Very characteristic of phytochlorin *a* is the splendid blue colour of its solution in glacial acetic acid. The substance has weak basic and pronounced acid properties, and is readily attacked by oxidising or reducing agents.

*Phytochlorin b*,  $C_{28}H_{33}O_5N_3$ , separates from alcohol and benzene in a blue-black, metallic-looking, crystalline mass of prisms and plates, sinters at  $168^{\circ}$ , m. p.  $183-190^{\circ}$ , decomposing. It dissolves in alkalis, forms a copper salt, and is a stronger base than phytochlorin *a*. Assuming the substance to be a monobasic acid, the analysis of the caesium salt indicates a molecular weight of 488. By heating for one to two hours with methyl alcoholic hydrogen chloride, phytochlorin *b* is converted partially into a substance,  $C_{58}H_{68}O_9N_6$ , devoid of acid character, which separates from methyl alcohol in aggregates of steel-blue, rectangular plates and prisms, m. p.  $140^{\circ}$ , yields phytochlorin *b* by hydrolysis, and seems to be the methyl ester resulting from 2 mols. of the latter by loss of 1 mol.  $H_2O$ .

Phytochlorin *a* is converted into *b* by concentrated alcoholic alkali hydroxide.

*Phytochlorin c*,  $C_{28}H_{33}O_6N_3$ , forms by slow separation from methyl alcohol elongated crystals, which acquire an S shape by rapid separation. It differs from phytochlorin *a* and *b* in its more pronounced basic character and in the colour of its solutions.

*Phytochlorin d*,  $C_{28}H_{35}O_6N_3$ , is the strongest base of the series, and is characterised by the magnificent colour of its solutions; the aqueous solution is violet with a strong red fluorescence. The sodium salt is dissociated hydrolytically in dilute solution. From ether, the substance separates in tufts of needles, and in twinned, truncated prisms from alcohol; although comparatively stable towards reagents, it readily loses water, forming a mixture of weaker bases. When strongly heated, it evolves a vapour having the odour of tobacco and giving the pyrrole test with a pine shaving.

*Phytorhodin a*,  $C_{28}H_{35}O_6N_3$ , is obtained in tufts of needles by the slow evaporation of its ethereal solution. It is blue-black by reflected, reddish-brown by transmitted, light, has m. p.  $130-140^{\circ}$ , and dissolves in dilute alkalis or acids. The *ethyl* ester,  $C_{30}H_{37}O_6N_3$ , forms microscopic prisms, is insoluble in alkalis, melts indefinitely below  $100^{\circ}$ , decomposes at higher temperatures, and yields phytorhodin *a* by hydrolysis. The ester is formed with elimination of  $H_2O$ .

*Phytorhodin b*,  $C_{28}H_{33}O_4N_3$ , forms rhombic plates which are frequently twinned and appear reddish-brown by transmitted light, decomposes by heating, and forms solutions with characteristic colours. Sodium hydroxide (0.01% solution) precipitates an acid sodium salt from the ethereal solution, whereas stronger solutions of the alkali (0.1 to 1%) form a soluble salt, which, however, is precipitated by an 8% solution. The *ethyl* ester,  $C_{30}H_{37}O_4N_3$ , crystallises well from benzene or ether in plates, m. p.  $76-80^{\circ}$ , decomposing, yields phytorhodin *b* by hydrolysis with 13% hydrogen chloride, a more basic substance with concentrated hydrogen chloride, and a substance similar to, but less basic than, phytorhodin *a* with boiling alcoholic potash. The ester is decomposed by heating, forming a vapour which distinctly reddens shavings moistened with hydrochloric acid.



*Phytorhodin c*,  $C_{56}H_{68}O_9N_6$ , separates from ether in tufts of slender needles and dissolves in 1% sodium hydroxide solution.

*Phytorhodin d*,  $C_{56}H_{80}O_{11}N_6$ , and *phytorhodin e*,  $C_{28}H_{31}O_4N_3$ , resemble one another closely, but differ in the colour of their solutions. Both are separated from chloroform solution by ether in radiating groups of prisms.

*Phytorhodin f*,  $C_{26}H_{29}O_5N_3$ ,  $C_{28}H_{29}O_6N_3$  or  $C_{26}H_{29}O_5N_3 \cdot 1.5H_2O$ , forms rosettes of black prisms, is sparingly soluble in ether, and exhibits great stability, not being affected by a short boiling with methyl alcoholic potash.

When alcoholic solutions of phytochlorins or of phytorhodins are treated with alcoholic zinc or copper acetates, intensely coloured complex double salts are obtained, which are insoluble in ether, but by treatment with excess of hydrochloric or acetic acid are rendered soluble. The compounds (but not those of the esters) are soluble in alkali hydroxides; the zinc salts are decomposed by 10–20% alcoholic hydrogen chloride, whereas the copper compounds dissolve unchanged in the concentrated acid. C. S.

**Composition of Chlorophyll.** RICHARD WILLSTÄTTER (*Annalen*, 1906, 350, 48–82).—The author criticises adversely Stoklasa's "lecithin" theory of the constitution of chlorophyll (compare Abstr., 1896, ii, 266; 1897, ii, 116), since chlorophyll from fresh stinging nettle or grass contains only 0.0108% and 0.0746% of phosphorus respectively, and that from the dried nettle, purified by the colloidal process, does not contain any.

The crude chlorophyll extracted by methyl or ethyl alcohol or acetone from dried nettle leaves is to some extent purified by two methods: (1) Kraus's method (compare Sorby, *Proc. Roy. Soc.*, 1873, 21, 442), in which the author uses methyl alcohol and gasoline in the place of ethyl alcohol and benzene respectively; (2) the colloidal process, in which an alcoholic or acetone solution of chlorophyll is diluted with 3 vols. of water and treated with ether, which extracts carotin and other impurities; the aqueous-alcoholic or aqueous-acetone solution is now treated with calcium chloride, after which ether extracts the chlorophyll from the solution. The purified chlorophyll is a dark green substance of the consistency of wax, which dissolves in neutral solvents, forming solutions with a brilliant bluish-green colour and pronounced red fluorescence.

The ash of chlorophyll purified by the first process is 1.84%, containing 1.67% of magnesium oxide; chlorophyll purified by the colloidal process leaves 3.14–3.36% of ash containing 1.51–1.71% of magnesium oxide; in neither case is iron present. Nitric acid of D 1.4 converts chlorophyll into a colourless oil.

As an ester, chlorophyll is hydrolysed by alkalis, yielding an *alcohol* having the approximate composition  $C_{20}H_{30}O$  and *chlorophyllin*, a complex substance of acid character, containing magnesium, stable to alkalis, but decomposed by acids.

Chlorophyllin is obtained by treating the alcoholic extract of the nettle or of grass with cold methyl alcoholic potash for twenty-four hours,

diluting the solution with water to dissolve the precipitated potassium salt, adding ether to extract impurities, acidifying most carefully with phosphoric acid and finally with monosodium phosphate, and extracting the chlorophyllin with ether. Two methods of purification are adopted. In virtue of its acid character chlorophyllin is separated from weaker acid and from neutral impurities by extracting the ethereal solution with sodium hydrogen carbonate or disodium phosphate, the chlorophyllin in the latter case being liberated again by the addition of monosodium phosphate. Chlorophyllin, the yield of which is 0.15% of the weight of leaf extracted, is a glistening, metallic-looking substance which contains 3.54% of magnesium oxide, and forms an intensely bluish-green ethereal solution with a strong red fluorescence which disappears by dilution; chlorophyllin prepared at higher temperatures exhibits fluorescence in extremely dilute solution. Chlorophyllin is decolorised by nitric acid of D 1.4 without the separation of an oil, whilst concentrated alcoholic hydrogen chloride changes it into an unstable basic substance (compare preceding abstract). The *barium* and *potassium* salts are precipitated by treating the ethereal solution with the corresponding hydroxides. The alkali salts of chlorophyllin prepared in the cold dissolve in water, forming green solutions without fluorescence, whereas the potassium salt of chlorophyllin prepared by boiling alcoholic potash forms a violet or red fluorescent aqueous solution, somewhat resembling that of alchorophyll; the author regards the last-mentioned substance as a mixture of the chlorophyllins obtained by the action of cold and of boiling alkali on chlorophyll. C. S.

**Filicitannic Acid.** W. WOLLENWEBER (*Arch. Pharm.*, 1906, 244, 466—486. Compare Reich, *Abstr.*, 1901, i, 212).—By extracting the powdered *Filix* rhizomes with absolute alcohol, distilling off the alcohol under diminished pressure, and shaking the residue with ether, the filicitannic acid is obtained as an insoluble residue in yield of 7.8%. This is the natural, or *proto*-, *filicitannic acid*; it has the composition  $C_{41}H_{44}O_{24}N, 2H_2O$ , is very soluble in water, yielding a solution that lathers, has an astringent taste, tans leather, precipitates gelatin and albumin, reduces ammoniacal silver and alkaline copper solutions, gives a transient green coloration with ferric chloride, and reddens a deal splint that has been moistened with hydrochloric acid. At 100° it loses  $2H_2O$ ; the residue is still soluble in water. When heated at 125°, or when it is precipitated with lead acetate and the precipitate is decomposed with hydrogen sulphide, it is converted into *filicitannic anhydride*,  $C_{41}H_{36}O_{18}N$ , which is insoluble in water. At 148° this yields a *second anhydride*,  $C_{41}H_{32}O_{16}N$ .

The acid has a molecular weight of about 470 (determined cryoscopically in aqueous solution), corresponding with half the formula given above, and it diffuses through parchment-paper much more rapidly than tannin, but yet as a single substance, the percentage of nitrogen being the same in the portion which has diffused as in that which has not yet diffused. The barium salt,  $(C_{41}H_{33}O_{18}N)_2Ba_3$ , obtained as a reddish-brown, amorphous precipitate when barium chloride is added to an aqueous solution of the acid mixed with

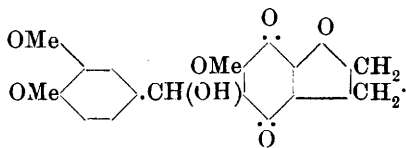
ammonia, is derived from the anhydride. The bromine derivative,  $C_{41}H_{40}O_{24}NBr_8$ , obtained by the action of bromine on a concentrated aqueous solution of the acid, is identical with that obtained by the action of bromine on a solution of the acid in dilute aqueous potassium hydroxide. When the acid is mixed with soda-lime and zinc dust and heated in a current of hydrogen gas, the distillate obtained resembles impure pyrrole.

C. F. B.

**Catechin.** STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1906, 39, 4007—4014. Compare *Abstr.*, 1902, i, 553, 637; A. G. Perkin, *Trans.*, 1902, 81, 1160).—The authors are of the opinion that catechin contains a coumaran and not a chroman group and that the six-carbon ring has one unsubstituted hydrogen, since a monobromo-derivative only can be obtained. The catechol residue is therefore presumably attached to the benzene and not to the furan ring of the coumaran radicle by means of a secondary alcoholic group. The formula,  $C_6H_3(OH)_2 \cdot CH(OH) \cdot C_6H(OH)_2 \langle \begin{smallmatrix} O \\ CH_2 \end{smallmatrix} \rangle CH_2$ , appears to be in harmony with the known behaviour of catechin.

*Pentamethyl catechin*,  $C_{15}H_9O(OMe)_5$ , is formed as a by-product in the preparation of the tetramethyl ether and is readily prepared by the action of a large excess of methyl sulphate on the latter. It crystallises from alcohol in colourless needles, m. p.  $95^\circ$ , and cannot be acetylated. Monobromocatechin tetramethyl ether (*Abstr.*, 1902, i, 637) crystallises in colourless needles, m. p.  $173$ — $174^\circ$ , and is most readily obtained by bromination in sunlight. When oxidised with permanganate, it yields veratric acid and hence probably contains the bromine atom in the six-membered carbon ring of the coumaran molecule; it cannot be oxidised by chromic acid to a catechone derivative. The pentamethyl ether yields a *bromo*-derivative,  $C_{15}H_8OBr(OMe)_5$ , m. p.  $142$ — $144^\circ$ .

Catechone trimethyl ether, when oxidised with cold permanganate, yields veratric acid and hence probably has the constitution

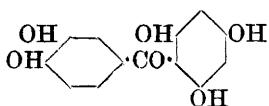


*Catechone tetramethyl ether*,  $C_{19}H_{20}O_7$ , obtained by oxidising catechin pentamethyl ether with an acetic acid solution of chromic acid, crystallises from alcohol in yellow needles, m. p.  $174$ — $175^\circ$ .

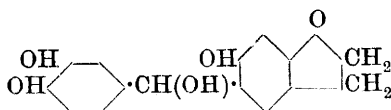
Nitrotrimethylcatechone (Karnowski and Tambor, *Abstr.*, 1902, i, 637), when oxidised with cold permanganate, yields Tiemann and Matsumoto's 6-nitroveratric acid (compare Zincke, *Abstr.*, 1897, i, 59).

J. J. S.

**Maclurin.** STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1906, 39, 4014—4021. Compare Ciamician and Silber, *Abstr.*, 1894, i, 471; 1895, i, 538; König and Kostanecki, *ibid.*, 1894, i, 534; Komarowsky and Kostanecki, *ibid.*, 1894, i, 506).—If catechin has the constitution assigned to it in the preceding abstract, it is the coumaran derivative of leucomaclurin:



Maclurin.



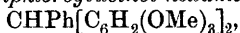
Catechin.

Maclurin pentamethyl ether, 2:4:6:3':4'-pentamethoxybenzophenone (W. H. Perkin, junr., and Robinson, *Proc.*, 1906, **22**, 305), may be obtained by methylating maclurin with hot concentrated potassium hydroxide solution and an excess of methyl sulphate. It is identical with Ciamician and Silber's veratroylphloroglucinol trimethyl ether (*Abstr.*, 1892, 873). When reduced with alcoholic potash and zinc dust, the ether yields *leucomaclurin pentamethyl ether* (2:4:6:3':4'-pentamethoxybenzhydrol),  $C_6H_3(OMe)_2 \cdot CH(OH) \cdot C_6H_2(OMe)_3$ , which crystallises from alcohol in brilliant, prismatic needles, m. p. 109—110°. It dissolves in concentrated sulphuric acid to a red solution, and when oxidised with chromic acid yields 2:6-dimethoxybenzoquinone and veratric acid.

2:4:6-*Trimethoxybenzhydrol* (*leucobenzophloroglucinol trimethyl ether*),  $OH \cdot CHPh \cdot C_6H_2(OMe)_3$ , obtained by reducing benzophloroglucinol trimethyl ether, crystallises in large prisms, m. p. 124—126°, and when oxidised yields 2:6-dimethoxybenzoquinone together with benzaldehyde and benzoic acid.

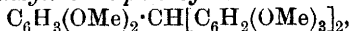
Benzhydrol ethers are readily obtained by boiling solutions of benzhydrol in various alcohols with hydrochloric acid. The *methyl ether*,  $CHPh_2 \cdot OMe$ , has b. p. 270—271°, the *ethyl ether* 288°.

Attempts to methylate leucobenzophloroglucinol trimethyl ether give rise to *benzylidenediphloroglucinol hexamethyl ether*,



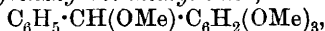
which crystallises in colourless prisms, m. p. 181—182°. The same compound is readily synthesised by condensing benzaldehyde with trimethylphloroglucinol and when oxidised yields dimethoxybenzoquinone, benzaldehyde, and benzoic acid.

3:4-Dimethoxybenzylidenediphloroglucinol hexamethyl ether,



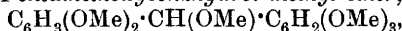
obtained by boiling an alcoholic solution of leucopentamethylmaclurin with a few drops of hydrochloric acid, crystallises in colourless prisms, m. p. 145—146°.

2:4:6-*Trimethoxybenzhydrol methyl ether*,



may be prepared by heating trimethoxybenzhydrol with acetic anhydride and sodium acetate and crystallising the product from methyl alcohol, it forms colourless prisms, m. p. 79—80°; the corresponding *ethyl ether*,  $C_6H_5 \cdot CH(OEt) \cdot C_6H_2(OMe)_3$ , m. p. 72—73°.

2:4:6:3':4'-*Pentamethoxybenzhydrol methyl ether*,



m. p. 94—96°. When oxidised, these ethers yield the same products as the methoxybenzhydrols themselves. Many of the compounds give characteristic purple colorations when the solutions containing hydrochloric acid are exposed to sunlight.

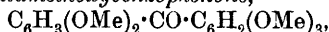
J. J. S.

**Synthesis of Maclurin Pentamethyl Ether.** STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1906, 39, 4022—4027).—Maclurin pentamethyl ether (2:4:6:3':4'-pentamethoxybenzophenone; preceding abstract), has been synthesised by a method identical with that used by W. H. Perkin, junr., and Robinson (*Proc.*, 1906, 22, 305).

2:4:6:4'-Tetramethoxybenzophenone,  $C_{17}H_{18}O_5$ , obtained by Friedel-Craft's synthesis from anisoyl chloride and phloroglucinol trimethyl, crystallises from alcohol in short, colourless prisms, m. p. 146°. The ether corresponding *leuco*-compound,  $C_6H_2(OMe)_3 \cdot CH(OH) \cdot C_6H_4 \cdot OMe$ , m. p. 103°; its concentrated sulphuric acid solution has an orange-yellow colour, and its alcoholic solution yields a purple colour with hydrochloric acid when exposed to sunlight.

2:4:6:3':4':5'-Hexamethoxybenzophenone,  $C_{19}H_{22}O_7$ , m. p. 122°, is obtained from trimethylgalloyl chloride and phloroglucinol trimethyl ether; its *leuco*-compound,  $C_{19}H_{24}O_7$ , has m. p. 124—125°.

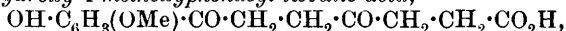
3:4:3':4':5'-Pentamethoxybenzophenone,



obtained from trimethylgalloyl chloride and veratrole, has m. p. 118°. Anisoyl chloride and veratrole yield 3:4:4'-trimethoxybenzophenone,  $C_{16}H_{16}O_4$ , m. p. 98—99°; the same compound may be obtained by condensing veratroyl chloride with anisole, whence its constitution.

3:4:3':4'-Tetramethoxybenzophenone,  $C_{17}H_{18}O_5$ , m. p. 145°, is obtained from veratroyl chloride and veratrole. J. J. S.

*o*-Hydroxyfurfurylidene-acetophenones. ST. COURANT and STANISLAUS VON KOSTANECKI (*Ber.*, 1906, 39, 4031—4034).—*o*-Hydroxychalkones, when boiled with mineral acids, are readily converted into flavanones; the corresponding *o*-hydroxyfurfurylidene-acetophenones, when boiled with mineral acids, combine with water (2 mol.), yielding hydroxyphenacyl-lævulic acids (Marckwald, *Abstr.*, 1888, 135, 677; Kehler, 1901, i, 389). *Furfurylidenepaeonol*,  $OH \cdot C_6H_3(OMe) \cdot CO \cdot CH:CH \cdot C_4OH_8 [CO:OH:OMe = 1:2:4]$ , obtained by the condensation of paeonol with furfuraldehyde in the presence of alcohol and 50% sodium hydroxide solution, crystallises from alcohol in long, yellow needles, m. p. 112°; it yields a sparingly soluble sodium salt, and when boiled with aqueous alcoholic hydrochloric acid yields 2-hydroxy-4-methoxyphenacyl-lævulic acid,

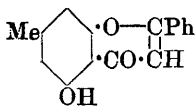


which crystallises from dilute alcohol in long, colourless needles, m. p. 165—166°.

*Furfuryliden-2-hydroxy-5-methoxyacetophenone* forms orange-red needles, m. p. 75°, and yields 2-hydroxy-5-methoxyphenacyl-lævulic acid, m. p. 125°. J. J. S.

**Synthesis of 1-Hydroxy-3-methylflavone.** S. LUDWINOWSKY and JOSEF TAMBOR (*Ber.*, 1906, 39, 4037—4041).—Rasinski's oracetophenone is shown to be 1:6-dihydroxy-4-methylacetophenone. The dimethyl ether,  $C_6H_2Me(OMe)_2 \cdot COMe$ , may be prepared by Friedel-Craft's synthesis from orcinol dimethyl ether; it crystallises from dilute alcohol in colourless prisms, m. p. 89°, b. p. 222°/720 mm., and condenses with ethyl benzoate in the presence of sodium, yielding 2:6-dimethoxy-4-methylbenzoylacetophenone,  $C_6H_2Me(OMe)_2 \cdot CO \cdot CH_2 \cdot COPh$ , which

crystallises from concentrated alcohol in tabular prisms, m. p. 98—99°. When boiled with hydriodic acid, D 2.0, the ketone yields 1-hydroxy-3-methylflavone, in the form of yellow, lustrous needles, m. p. 143°. It forms a sparingly soluble sodium salt and is thus shown to be a 1-hydroxyflavone. The acetyl derivative,  $C_{15}H_8MeO_2 \cdot OAc$ , m. p. 132°.



J. J. S.

**Derivative of Dihydroisobenzofuran. Part IV.** ALFRED GUYOT and J. CATEL (*Bull. Soc. chim.*, 1906, [iii], 35, 1124—1135. Compare Abstr., 1906, i, 761).—Most of the facts recorded in this paper have already been given in Abstr., 1905, i, 540. *o*-Benzhydryltriphenylcarbinol is formed when phenylphthalide reacts with an excess of magnesium phenyl bromide in ether, but if the phenylphthalide is in excess the principal product is 2-hydroxy-1 : 2-diphenyl-1 : 2-dihydroisobenzofuran,  $C_6H_4 \begin{array}{c} \text{CHPh} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{CPh} \quad \text{CPh} \end{array} \text{OH}$ .

The product formed by the dehydration of the latter is now shown to be 1 : 2-diphenylisobenzofuran,  $C_6H_4 \begin{array}{c} \text{CPh} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{CPh} \quad \text{CPh} \end{array}$ , which on solution in benzene or alcohol and exposure to light in the absence of air polymerises,

forming a substance,  $C_6H_4 \begin{array}{c} \text{CPh} \quad \text{CPh} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{CPh} \quad \text{CPh} \quad \text{CPh} \quad \text{CPh} \end{array} C_6H_4$ ; this occurs in small,

faintly yellow crystals, is scarcely soluble in organic solvents, and when heated regenerates 1 : 2-diphenylisobenzofuran.

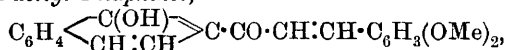
Similar solutions of the latter on exposure to air in the dark furnish *o*-dibenzoylbenzene, and the same transformation takes place when the solutions are exposed to the joint action of air and light.

*o*-Dibenzhydrylbenzene,  $C_6H_4(CHPh \cdot OH)_2$ , produced by reducing 2-hydroxy-1 : 2-diphenyl-1 : 2-dihydroisobenzofuran or *o*-dibenzoylbenzene with sodium amalgam, forms small, faintly yellow crystals, and when dehydrated by sulphuric acid (Abstr., 1906, i, 761) furnishes phenylanthracene.

When hydrochloric acid is used as the dehydrating agent, 1 : 2-diphenyl-1 : 2-dihydroisobenzofuran is produced, which forms small, faintly yellow crystals, m. p. 95°, is soluble in most organic solvents and, on treatment with sulphuric acid, is converted into phenylanthracene.

T. A. H.

**3' : 4'-Dihydroxy- $\alpha$ -naphthaf flavonol.** P. BIGLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1906, 39, 4034—4037).—3' : 4'-Dimethoxybenzylidene-2-acetyl-1-naphthol,

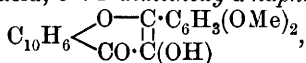


obtained by the condensation of veratraldehyde with 2-acetyl-1-naphthol in the presence of aqueous alcoholic sodium hydroxide, crystallises in red prisms with a violet lustre, m. p. 134.5°. Its solution in concentrated sulphuric acid has a violet-red colour. The acetyl derivative,  $OAc \cdot C_{10}H_6 \cdot CO \cdot CH : CH \cdot C_6H_3(OMe)_2$ , crystallises from alcohol in yellow plates, m. p. 139.5°. When boiled with

aqueous alcoholic hydrochloric acid, the naphthol derivative yields 3':4'-dimethoxy- $\alpha$ -naphthaflavanone,  $C_{10}H_6 \begin{smallmatrix} O-CH \cdot C_6H_3(OMe)_2 \\ CO \cdot CH_2 \end{smallmatrix}$ , which crystallises from alcohol in colourless needles, m. p. 135°, and is soluble in concentrated sulphuric acid to an orange-coloured solution.

The isonitroso-derivative,  $C_{10}H_6 \begin{smallmatrix} O-CH \cdot C_6H_3(OMe)_2 \\ CO \cdot C:N \cdot OH \end{smallmatrix}$ , forms long, yellow needles melting and decomposing at 156°. It dissolves in dilute sodium hydroxide solution, dyes orange with cobalt mordants, but yellow with uranium, cadmium, and lead mordants.

When an acetic acid solution of the isonitroso-compound is boiled with 10% sulphuric acid, 3':4'-dimethoxy- $\alpha$ -naphthaflavonol,



is formed. It crystallises from alcohol in yellow needles, m. p. 224°, and dissolves in concentrated sulphuric acid to a yellow solution with a green fluorescence. The sodium salt is sparingly soluble and the acetyl derivative is colourless, m. p. 191—192°.

3':4'-Dihydroxy- $\alpha$ -naphthaflavonol, m. p. 286°, forms yellow, glistening needles containing water of crystallisation. It becomes opaque on exposure to the air. The triacetyl derivative forms needles, m. p. 215°. J. J. S.

**Optical Isomerides of Arginine and Ornithine.** OTTO RIESSER (*Zeit. physiol. Chem.*, 1906, 49, 210—246. Compare Kutscher, *Abstr.*, 1901, i, 561).—Full details are given for the preparation of *d*-arginine by a modification of E. Fischer's method (*Ber.*, 1905, 38, 4187). One of the simplest methods of purification is by means of the picrate.

*d*-Arginine nitrate,  $C_6H_{14}O_2N_4 \cdot HNO_3 \cdot \frac{1}{2}H_2O$ , has m. p. 126° (not 175° as stated by Gulewitsch, *Abstr.*, 1899, 833), and the dinitrate, m. p. about 250° (Kanitz, *Zeit. physiol. Chem.*, 1906, 47, 491). The picrolonate (Stendel, *Abstr.*, 1903, i, 431), m. p. 231°, contains  $1H_2O$ , and its solubility in water at 16° is 0.05. The  $\beta$ -naphthalene sulphone derivative,  $C_6H_{13}O_2N_4 \cdot SO_2 \cdot C_{10}H_7$ , forms a colourless powder, m. p. 88—89°.

A 50% yield of the racemic modification of arginine may be obtained by heating *d*-arginine sulphate with 50% sulphuric acid for thirty-three hours at 160—180°; *r*-ornithine is formed at the same time. *r*-Arginine carbonate is harder and more hygroscopic than the *d*-isomeride. The *r*-picrate crystallises in anhydrous, glistening prisms, m. p. 200—201°, and its solubility in water at 16° is 0.22, whereas that of the isomeric *d*-compound is 0.5. The nitrate is sparingly soluble, m. p. 217° (not 211° as stated by Kutscher). A dinitrate,  $C_6H_{14}O_2N_4 \cdot 2HNO_3$ , forms large crystals, readily soluble in water; m. p. 151°. The *r*-cupric nitrate derivative,  $2C_6H_{14}O_2N_4 \cdot Cu(NO_3)_2 \cdot 3H_2O$ , has m. p. 228—229°. The silver nitrate derivative,

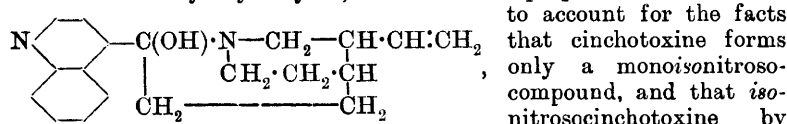
$(C_6H_{14}O_2N_4 \cdot HNO_3)_2 \cdot AgNO_3 \cdot \frac{1}{2}H_2O$ , has m. p. 170—172°, and the *r*-picrolonate, m. p. 248°, is anhydrous, and its solubility in water at 16° is 0.03. The  $\beta$ -naphthalene sulphone derivative,  $C_6H_{13}O_2H_4 \cdot SO_2 \cdot C_{10}H_7 \cdot \frac{1}{2}H_2O$ , has not a sharp melting point.

*l*-Arginine may be obtained from the *r*-compound by means of arginase (Kossel and Dakin, Abstr., 1904, ii, 425), which transforms *d*-arginine into *d*-ornithine and carbamide. The picrate, nitrate, dinitrate, cupric nitrate, silver nitrate, picrolonate, and naphthalene sulphone derivative have been prepared and resemble the corresponding derivatives of the *d*-base.

*β*-Naphthalene sulphone-*d*-ornithine,  $C_5H_{10}O_2N_2(SO_2 \cdot C_{10}H_7)_2$ , m. p. 189°, is less soluble in water or alcohol than the corresponding arginine derivative.

*r*-Ornithine picrate,  $C_5H_{12}O_2N_2 \cdot 2C_6H_3O_7N_3 \cdot 2\frac{1}{2}H_2O$ , crystallises in ochre-yellow plates, m. p. 183—184°, decomposing. *β*-Naphthalene sulphone-*r*-ornithine is anhydrous, m. p. 195—196°. J. J. S.

**Cinchona Alkaloids.** I. PAUL RABE (*Annalen*, 1906, 350, 180—203. Compare Rabe and Ritter, Abstr., 1905, i, 811).—Koenigs' formula of cinchonine (Abstr., 1906, i, 762) explains the formation of cinchene by hydrolysis; the author proposes the formula,



to account for the facts that cinchotoxine forms only a monoisosnitroso-compound, and that *iso*-nitrosocinchotoxine by the Beckmann transformation yields cinchoninic acid and meroquininenitrile.

[With KARL RITTER.]—The nitrile of *N*-methylmeroquinene has b. p. 162°/49 mm., 252—255°/741 mm.,  $D_4^{20}$  0.9505,  $n_D^{20}$  1.4803,  $[\alpha]_D^{20}$  17.11°. Hydrolysis by barium hydroxide and subsequent acidification leads to the formation of *N*-methylmeroquinene, of which the *picrate*,  $C_{16}H_{20}O_9N_4$ , decomposes at 218°, and the *picrolonate*,  $C_{20}H_{25}O_7N_5$ , at 210°; the *ethyl ester*, b. p. 147—148°/22 mm., forms a *hydrochloride*, m. p. 177°; *aurichloride*, m. p. 128—130°; *picrate*, m. p. 102—104°, and *picrolonate*, m. p. 152—154°.

*iso*-Nitrosoethylcinchotoxine,  $C_{21}H_{25}O_2N_3$ , prepared from ethylcinchotoxine, sodium ethoxide, and amyl nitrite, separates from alcohol in slender, white needles, m. p. 136°, and by treatment with phosphorus pentachloride in dry chloroform yields cinchoninic acid and *N*-ethylmeroquininenitrile,  $C_{11}H_{18}N_2$ , which is a liquid, b. p. 268°/750 mm., has the odour of piperidine, and is volatile in steam; the *methiodide*,  $C_{12}H_{21}N_2I$ , decomposes at 230—233°. Hydrolysis of the nitrile yields *N*-ethylmeroquinene, derivatives of which have been described by Koenigs (*loc. cit.*).

*Meroquininenitrile*,  $C_9H_{14}N_2$ , obtained from *isonitrosocinchotoxine* in 6—8% yield, b. p. 147—150°/12 mm., is volatile in steam and forms a *picrolonate* decomposing at 215—217°. C. S.

**Quinine Formates.** HUNKIARBÉYENDIAN LACROIX (*J. Pharm. Chim.*, 1906, [vi], 24, 493—494. See Abstr., 1905, i, 716).—Normal quinine formate loses formic acid towards 50° and yields quinine when heated at 95°; it is dissociated in cold aqueous solution into formic acid and basic quinine formate, m. p. 109° (not 132° as previously stated)  $[\alpha]_D^{20}$  -144.2°, which is not affected even by boiling water; it loses,



however, the greater part of the acid when heated to just below its melting point. E. F. A.

**Alkaloids of Ergot.** GEORGE BARGER and HENRY H. DALE (*Arch. Pharm.*, 1906, 244, 550—555).—Kraft's "hydroergotinine" (*Abstr.*, 1906, i, 979) has already been described as ergotoxine (Barger and Carr, *Chem. News*, 1906, 94, 89). This alkaloid has the composition  $C_{26}H_{30}O_3N_4$  or  $C_{27}H_{32}O_3N_4$ , and although itself amorphous, forms crystalline salts. Very small doses induced contraction of the pupil, bladder, and uterus in the case of cats, accompanied by abortion if the animal was pregnant; a comparatively large dose induced gangrene in the case of a fowl.

Ergotinine probably has the formula,  $C_{28}H_{32}O_4N_4$ ; it may be the acetyl derivative of ergotoxine. C. F. B.

**Alkaloids of Pareira Root.** MAX SCHOLTZ (*Arch. Pharm.*, 1906, 244, 555—560. Compare *Abstr.*, 1896, i, 710; 1899, i, 92).—Bebeerine has again been isolated from *Radix Pareirae* and also from a commercial specimen of "bebeerinum purum." It had the same melting point and solubility as that obtained previously, but it exhibited dextrorotation, equal in magnitude to the laevorotation of the older specimen, of which it was obviously the optical isomeride. The *benzyl iodide*,  $C_{18}H_{21}O_3N, CH_2PhI$ , is crystalline and melts at  $225^\circ$ .

When bebeerine, in the process of preparation, is extracted with ether from the crude mass of alkaloid, a resinous mass remains. By extracting this with pyridine and precipitating the solution with methyl alcohol, a small quantity was obtained of an amorphous powder that exactly resembles active bebeerine in composition and reactions, but has m. p.  $300^\circ$  (instead of  $214^\circ$ ), and is less soluble in the usual solvents. This substance is precipitated when chloroform solutions of *d*- and *l*-bebeerine are mixed; it is evidently the racemic modification, *r*-bebeerine.

In action on the heart, *d*-bebeerine surpasses *l*-bebeerine greatly. A dose of 0.45 gram of crystalline *d*-bebeerine injected subcutaneously into a rabbit was without effect, whereas the same dose of amorphous *r*-bebeerine killed the animal. C. F. B.

**The Phosphorus Haloid Method of Decomposing Pyrrolidine.** JULIUS VON BRAUN and ERICH BESCHKE (*Ber.*, 1906, 39, 4119—4125. Compare *Abstr.*, 1905, i, 596).—This method of decomposing cyclic imines serves as a convenient means of obtaining various dihalogenated paraffins having the substituents attached to the terminal carbon atoms, and the investigation has been extended to pyrrolidine, the simplest five-membered ring compound.

1-Benzoylpyrrolidine,  $NBz \begin{smallmatrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{smallmatrix}$ , prepared by benzoylating pyrrolidine in cold alkaline solution, is a colourless liquid like glycerol, not miscible with water or dilute acids, b. p.  $190-191^\circ/12$  mm.

The products of the interaction of phosphorus pentachloride and 1-benzoylpyrrolidine depend on the conditions of experiment. *Benzo-δ*

*chlorobutylamide*,  $\text{NHBz} \cdot [\text{CH}_2]_3 \cdot \text{CH}_2\text{Cl}$ , is obtained when the mixture is boiled for one hour, and crystallises from ether in snow-white spears, m. p. 48–49°. If, however, the mixture is distilled, a mixture of benzonitrile and  $\alpha\delta$ -dichlorobutane is formed. The latter is a colourless liquid of agreeable aromatic odour, b. p. 53–54°/12 mm., 161–163°/760 mm.

*Benzo- $\delta$ -iodobutylamide*,  $\text{NHBz} \cdot [\text{CH}_2]_3 \cdot \text{CH}_2\text{I}$ , is obtained from the corresponding chloro-derivative by digestion with sodium iodide in alcoholic solution. It crystallises from a mixture of ether and light petroleum in slender, colourless needles, m. p. 58°.

The interaction of phosphorus pentabromide and 1-benzoylpyrrolidine gives benzonitrile and  $\alpha\delta$ -dibromobutane, b. p. 82°/12 mm. (compare Hamonet, Abstr., 1901, i, 247).

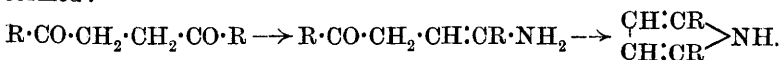
An improved method of preparing pyrrolidine in large quantities is described (compare Gabriel, Abstr., 1892, i, 131); in the course of this preparation a by-product,  $\lambda$ -phenoxybutyramide,  $\text{OPh} \cdot [\text{CH}_2]_3 \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 80°, crystallising from dilute alcohol in white plates, was isolated.

W. R.

**Condensation Products of Pyrroles.** GIUSEPPE PLANCHER and ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 447–454. Compare Abstr., 1902, i, 640; 1905, i, 298).—When 2-methylpyrrole is condensed by means of zinc acetate in acetic acid solution, it yields 2:4-dimethylindole. The first stage in the change probably consists in the hydrolysis of the 2-methylpyrrole into lævulinaldehyde, which then reacts with a further quantity of 2-methylpyrrole (1 mol.), giving 2:4-dimethylindole and 2 mols. of water. 2:4-Dimethylindole is also obtained by the condensation of acetone with *m*-tolylhydrazine in presence of zinc chloride and is probably identical with that prepared by Dennstedt (Abstr., 1889, 400).

T. H. P.

**Formation of Pyrrole from 1:4-Diketones.** **Action of Ammonia on Ethyl  $\alpha\beta$ -Diacylcarboxylic Acids.** WALTHER BORSCHKE and ALBERT FELS (*Ber.*, 1906, 39, 3877–3886).—It is probable that in the conversion of 1:4-diketones into pyrrole derivatives by means of ammonia, unsaturated 1:4-amino-ketones are first formed:



Knorr and Rabe (Abstr., 1901, i, 163) have isolated ethyl  $\beta$ -amino- $\Delta^{\beta}$ -hexene-3-one- $\gamma\delta$ -dicarboxylate from ethyl diacetosuccinate, and the authors have isolated ethyl  $\gamma$ -amino- $\alpha$ -acetyl- $\gamma$ -phenyl- $\Delta^{\beta}$ -butenoate,  $\text{NH}_2 \cdot \text{CPh} : \text{CH} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$ , from ammonia and ethyl phenacylacetoacetate in ethereal solution and ethyl  $\gamma$ -amino- $\alpha$ -benzoyl- $\Delta^{\beta}$ -pentenoate,  $\text{NH}_2 \cdot \text{CMe} : \text{CH} \cdot \text{CHBz} \cdot \text{CO}_2\text{Et}$ , from ammonia and ethyl acetonylbenzoylacetate.

*Ethyl  $\gamma$ -amino- $\alpha$ -acetyl- $\gamma$ -phenyl- $\Delta^{\beta}$ -butenoate* separates from a mixture of benzene and ether in colourless crystals, m. p. 125–127°. Even when kept in a desiccator water is eliminated and the melting point rapidly falls. When warmed with water or left in contact with dilute

alkalis it is partially hydrolysed to ammonia and ethyl phenacylacetate and partially condensed to ethyl 5-phenyl-2-methylpyrrole-3-carboxylate (Paal, Abstr., 1885, 516), which is also formed as a by-product in the preparation of the amino-compound. It is most readily formed by heating the dry amino-compound at 150° or by gently warming with *N*/4 sulphuric acid. When the aminoketone is gently boiled with a 2% solution of sodium hydroxide it yields the

*lactam*, 
$$\begin{array}{c} \text{OH} \cdot \text{CMe} \cdot \text{C} - \text{CO} \\ | \\ \text{HC} : \text{CPh} \end{array} > \text{NH},$$
 together with phenylcyclopentenone (Abstr., 1906, i, 509). The lactam crystallises in greenish-yellow plates, m. p. 158°, decomposing, and is only sparingly soluble in ether. Its benzoyl derivative melts and decomposes at 195°.

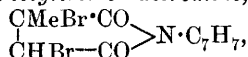
Ethyl  $\gamma$ -amino- $\alpha$ -benzoyl- $\Delta^{\beta}$ -pentenoate forms large colourless, transparent crystals, m. p. 127—128°, and in contact with water is readily hydrolysed. When warmed with dilute sulphuric acid it yields ethyl

5-phenyl-2-methylpyrrole-4-carboxylate, 
$$\begin{array}{c} \text{CO}_2\text{Et} \cdot \text{C} : \text{CPh} \\ | \\ \text{HC} : \text{CMe} \end{array} > \text{NH},$$
 in the form

of colourless plates, m. p. 81°. The corresponding acid, m. p. 145°, is extremely unstable and readily loses carbon dioxide yielding 5-phenyl-2-methyl-pyrrole. The *lactam*, 
$$\begin{array}{c} \text{OH} \cdot \text{CPh} : \text{C} - \text{CO} \\ | \\ \text{HC} : \text{CMe} \end{array} > \text{NH},$$
 is obtained to

gether with phenylcyclopentenone by boiling the amino-ester with 2% sodium hydroxide solution. It crystallises in yellow needles, m. p. 129—130°. J. J. S.

**Unsaturated Acids.** FRITZ FICHTER (*J. pr. Chem.*, 1906, [ii], 74, 297—339. Compare Fichter, Enz-nauer, and Uellenberg, Abstr., 1900, i, 312; Fichter and Preiswerk, Abstr., 1902, i, 443).—I. *Citraconic acid dibromide and aromatic amines*.—[With ERNST TSCHUDIN.]—*Citracon-p-tolylimide dibromide*,

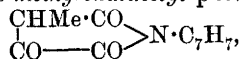


prepared by the action of bromine on citracon-*p*-tolylimide in glacial acetic solution at 5°, crystallises from alcohol; m. p. 149°.

*Bromocitracon-p-tolylimide*, 
$$\begin{array}{c} \text{CMe} \cdot \text{CO} \\ || \\ \text{CBr} - \text{CO} \end{array} > \text{N} \cdot \text{C}_7\text{H}_7,$$
 prepared by heating

mesaconic acid dibromide with *p*-toluidine in aqueous solution on the water-bath, crystallises in small, yellow needles, m. p. 140°. *p*-Tolu-

*idinocitracon-p-tolylimide*, 
$$\begin{array}{c} \text{CMe} \cdot \text{CO} \\ || \\ \text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{C} - \text{CO} \end{array} > \text{N} \cdot \text{C}_7\text{H}_7,$$
 formed by adding citracon-*p*-tolylimide to fused *p*-toluidine at 200°, crystallises in yellow needles, m. p. 177°; when heated with 60% sulphuric acid on the water-bath it yields methylloxalacetyl-*p*-tolylimide,



which crystallises from carbon tetrachloride in almost colourless, microscopic needles, m. p. 198—200°, and forms a *silver* salt,  $\text{C}_{12}\text{H}_{10}\text{O}_3\text{NAg}$ , crystallising in yellow needles.

*p*-Toluidinosuccin-*p*-tolylimide,  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_2$ , prepared by reduction of *p*-toluidinocitracon-*p*-tolylimide with aluminium amalgam in ethereal

solution, crystallises in colourless needles, m. p.  $200^{\circ}$ . The *stereoisomeride* of this substance which melts at a lower temperature could not be isolated from the mother liquors.

*Citracon-o-tolylimide*,  $C_{12}H_{11}O_2N$ , crystallises from methyl alcohol in plates, m. p.  $64^{\circ}$ , and is volatile in a current of steam. *Citracon-o-tolylimide dibromide*,  $C_{12}H_{11}O_2NBr_2$ , forms colourless plates, m. p.  $84^{\circ}$ . *Bromocitracon-o-tolylimide*,  $C_{12}H_{10}O_2NBr$ , crystallises in slightly yellow needles, m. p.  $119^{\circ}$ . *o-Toluidinocitracon-o-tolylimide*,  $C_{19}H_{18}O_2N_2$ , separates from alcohol in delicate, yellow, granular crystals, m. p.  $138^{\circ}$ . *o-Toluidinosuccin-o-tolylimide* crystallises from dilute acetic acid in colourless, microscopic needles, m. p.  $144^{\circ}$ . The *stereoisomeride* of this substance, which melts at a lower temperature, remains in the mother liquors.

*Citracon-p-dimethylaminoanil*,  $C_{13}H_{14}O_2N_2$ , crystallises in reddish-yellow, glistening needles, m. p.  $161.5^{\circ}$ . *Bromocitracon-p-dimethylaminoanil*,  $C_{13}H_{13}O_2N_2Br$ , crystallises in slender, yellowish-red needles, m. p.  $125^{\circ}$ . *p-Dimethylaminoanilnocitracon-p-dimethylaminoanil*,  $C_{21}H_{24}O_2N_4$ , crystallises in brownish-red prisms, m. p.  $263-264^{\circ}$ .

*p-Dimethylaminoanilnocitraconanil*,  $C_{19}H_{19}O_2N_3$ , crystallises in red needles, m. p.  $163^{\circ}$ .

*Citracon-a-naphthylimide dibromide*,  $C_{15}H_{11}O_2NBr_2$ , forms a colourless crystalline mass, m. p.  $161.5-162^{\circ}$ . *Bromocitracon-a-naphthylimide*,  $C_{15}H_{10}O_2NBr$ , crystallises from alcohol in glistening, golden spangles, m. p.  $169^{\circ}$ .

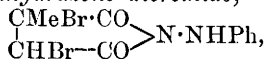
*Citracon-β-naphthylimide dibromide* forms colourless crystals, m. p.  $169.5-170^{\circ}$ . *Bromocitracon-β-naphthylimide* crystallises from alcohol in light yellow spangles, m. p.  $185^{\circ}$ . *β-Naphthylaminocitracon-β-naphthylimide*,  $C_{25}H_{18}O_2N_2$ , forms silky, yellow needles, m. p.  $203^{\circ}$ .

II. *Citraconic and mesaconic acid dibromides and aromatic hydrazines*.—[With REINHARD VORTISCH.]—The action of aromatic hydrazines on citraconic and mesaconic acid dibromides leads to the formation of 1-aryl-4-methyl-3-pyrazolones (compare Stolz, Abstr., 1905, i, 942). The following pyrazolones together with the corresponding 4-arylaazo-1-aryl-3-methyl-5-pyrazolones have been prepared by this reaction. 1-*p-Tolyl-4-methyl-3-pyrazolone*,  $C_{11}H_{12}ON_2$ , crystallises in stout needles, m. p.  $217^{\circ}$ . A product, m. p.  $242^{\circ}$ , was obtained also from citraconic acid dibromide.

1-*p-Bromophenyl-4-methyl-3-pyrazolone*,  $C_{10}H_9ON_2Br$ , crystallises in white needles, m. p.  $245-246^{\circ}$ . 4-*p-Bromophenylazo-1-p-bromophenyl-3-methyl-5-pyrazolone*, m. p.  $229-230^{\circ}$ , is identical with Eibner and Lane's azo-compound, m. p.  $227^{\circ}$  (Abstr., 1906, i, 613).

1-*p-Nitrophenyl-4-methyl-3-pyrazolone*,  $C_{10}H_9O_3N_3$ , crystallises in glistening, slightly brown leaflets, m. p.  $266^{\circ}$ , and dissolves in dilute sodium hydroxide, forming an intensely red solution.

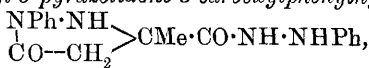
III. *Action of phenylhydrazine on citraconic acid*.—[With GUSTAV FÜEG.]—*Citraconphenylhydrazone dibromide*,



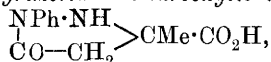
prepared by the action of bromine on citraconphenylhydrazone, crystallises from carbon tetrachloride in yellow aggregates of small needles, m. p.  $144^{\circ}$ . It readily loses hydrogen bromide, forming *bromocitracon-*

phenylhydrazine,  $\begin{array}{c} \text{CMe} \cdot \text{CO} \\ | \\ \text{CBr} \cdot \text{CO} \end{array} > \text{N} \cdot \text{NHPh}$ , which separates from carbon tetrachloride in yellow crystals, m. p. 136°.

1-Phenyl-3-methyl-5-pyrazolidone-3-carboxylphenylhydrazide,



prepared by boiling citraconic anhydride with 2 mols. of phenylhydrazine in aqueous solution, crystallises in glistening, white leaflets, m. p. 144°. It is hydrolysed by much boiling hydrochloric acid, forming 1-phenyl-3-methyl-5-pyrazolidone-3-carboxylic acid,



which crystallises from benzene in broad, colourless needles, m. p. 139°, and is oxidised by ferric chloride to pyrazole blue. The silver salt,  $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}_2\text{Ag}$ , is crystalline and forms a silver mirror when heated with a solvent. The action of an excess of nitrous acid on the carboxylic acid leads to the formation of 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone.

Duden's phenylhydrazinesuccinyldihydrazide (Abstr., 1893, i, 231) is considered to be the phenylhydrazide of 1-phenyl-5-pyrazolidone-3-carboxylic acid.

Citracon-p-tolylhydrazine,  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$ , separates from alcohol in yellow crystals, m. p. 169. 1-p-Tolyl-3-methyl-5-pyrazolidone-3-carboxyl-p-tolylhydrazide,  $\text{C}_{19}\text{H}_{22}\text{O}_2\text{N}_4$ , crystallises from alcohol in glistening, white leaflets, m. p. 204—206° with slight decomposition. 1-p-Tolyl-3-methyl-5-pyrazolidone-3-carboxylic acid,  $\text{C}_{12}\text{H}_{14}\text{O}_3\text{N}_2$ , forms colourless needles, m. p. 148°, and when treated with nitrous acid yields 4-isonitroso-1-p-tolyl-3-methyl-5-pyrazolone.

Citracon-2 : 4-xyllylhydrazine,  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ , separates from alcohol in orange-red crystals, m. p. 129°.

Citracon-p-nitrophenylhydrazine,  $\text{C}_{11}\text{H}_9\text{O}_4\text{N}_3$ , crystallises in brownish-red needles, m. p. 205°.

IV. Iodophenylhydrazines.—[With KARL PHILIPP.]—5-Iodo-2-acetylaminotoluene,  $\text{C}_9\text{H}_9\text{ONI}$ , prepared by the action of iodine chloride on o-acetotoluidide, crystallises in long, glistening, silky needles, m. p. 168°. 5-Iodo-2-aminotoluene,  $\text{C}_7\text{H}_7\text{NI}$ , forms stout, colourless crystals, m. p. 88°. 5-Iodotolyl-2-hydrazine,  $\text{C}_7\text{H}_9\text{N}_2\text{I}$ , prepared from diazotised 5-iodo-2-aminotoluene by conversion into potassium 5-iodo-toluene-2-diazosulphonate and reduction of this with stannous chloride and hydrochloric acid, crystallises in colourless plates, m. p. 98°.

4-Iodophenylbenzylidenehydrazine,  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{I}$ , formed from benzaldehyde and 4-iodophenylhydrazine (Neufeld, Abstr., 1889, 251), crystallises in almost colourless leaflets, m. p. 121°.

Phenyl-4-iodobenzylidenehydrazine crystallises in silvery leaflets, m. p. 90°.

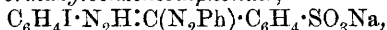
2 : 4-Di-iodophenylbenzylidenehydrazine,  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{I}_2$ , forms colourless plates, m. p. 104°.

5-Iodo-o-tolylbenzylidenehydrazine,  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{I}$ , crystallises in silvery plates, m. p. 102—103°.

4'-Iodoformazylbenzene,  $\text{C}_{19}\text{H}_{15}\text{N}_4\text{I}$ , formed by the action of diazo-

benzene on 4-iodophenylbenzylidenehydrazine, crystallises from alcohol or light petroleum, m. p. 185—186°.

*Sodium 4'-iodoformazylbenzenesulphonate*,



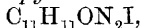
forms a red, crystalline powder and dyes silk a bluish-red.

2':4'-*Di-iodoformazylbenzene*,  $\text{C}_{19}\text{H}_{14}\text{N}_4\text{I}_2$ , crystallises in dark red needles, m. p. 186°.

5'-*Iodo-o-tolylformazylbenzene*,  $\text{C}_{20}\text{H}_{17}\text{N}_4\text{I}$ , forms glistening, black needles, m. p. 167°.

1-*p-Iodophenyl-3-methyl-5-pyrazolone*,  $\text{C}_{10}\text{H}_9\text{ON}_2\text{I}$ , formed from 4-iodophenylhydrazine and ethyl acetoacetate, crystallises from alcohol in colourless needles, m. p. 196°. The 4-isonitroso-derivative,  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_3\text{I}$ , forms yellow needles, m. p. 189°.

1-*Iodophenyl-2:3-dimethyl-5-pyrazolone* (*p-iodoantipyrene*),



crystallises in colourless needles, m. p. 126°.

1-*op-Di-iodophenyl-3-methyl-5-pyrazolone*,  $\text{C}_{10}\text{H}_8\text{ON}_2\text{I}_2$ , separates from toluene in a slightly yellow, crystalline crust, m. p. 153°.

1-*Iodo-o-tolyl-3-methyl-5-pyrazolone*,  $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{I}$ , m. p. 194°, forms a golden-yellow isonitroso-derivative,  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_3\text{I}$ , crystallising in leaflets, m. p. 181°.

1-*p-Iodophenyl-4-methyl-3-pyrazolone* or 5-*pyrazolone*,  $\text{C}_{10}\text{H}_9\text{ON}_2\text{I}$ , formed from 4-iodophenylhydrazine and mesaconic acid dibromide, crystallises in glistening, silvery leaflets, m. p. 126—127°.

V. *Crotonyltolylenediamine* (compare Autenrieth and Pretzell, Abstr., 1903, i, 474).—[With ERNST PREISWERK.]—*Crotonyl-p-toluidide*,  $\text{C}_{11}\text{H}_{13}\text{ON}$ , formed by heating crotonic acid with *p*-toluidine in a reflux apparatus and distilling the product in a vacuum, crystallises from benzene; m. p. 132°; an excess of *p*-toluidine leads to the formation of  $\beta$ -*p-toluidinobutryryl-p-toluidide*,  $\text{C}_{18}\text{H}_{22}\text{ON}_2$ , which crystallises from a mixture of benzene and light petroleum; m. p. 101°. *Dibromobutryryl p-toluidide*,  $\text{C}_{11}\text{H}_{13}\text{ONBr}_2$ , forms slender, white needles, m. p. 171°.

*Crotonyl-3-nitro-p-toluidide*,  $\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_2$ , formed by the action of nitric acid, D 1.45, on crotonyl-*p*-toluidide, crystallises in yellowish-red needles, m. p. 111°. When reduced with tin and hydrochloric acid under cooling, it yields 3-*amino-4-crotonylaminotoluene*,  $\text{C}_{11}\text{H}_{14}\text{ON}_2$ , which forms white needles, m. p. 148°. Energetic reduction of the nitro-compound or boiling of the preceding compound with hydrochloric acid leads to a partial intramolecular change, resulting in the formation of 4-*amino-3-crotonylaminotoluene*; this separates from benzene in stout crystals, m. p. 182°.

1-*Crotonyl-5-methyl-1:2:3-benzotriazole*,



prepared by the action of nitrous acid on 3-amino-4-crotonylaminotoluene, crystallises in white needles, m. p. 148°.

1-*Crotonyl-6-methyl-1:2:3-benzotriazole*,  $\text{C}_{11}\text{H}_{11}\text{ON}_3$ , prepared from 4-amino-3-crotonylaminotoluidine, crystallises in broad, flat needles, m. p. 186°.

2-*Cinnamenyl-5-methylbenziminazole* (Bamberger and Berlé, Abstr.,

1893, i, 435) is formed by heating cinnamic acid with tolylene-3 : 4-diamine and distilling the product in a vacuum ; it crystallises with  $\frac{1}{2}\text{H}_2\text{O}$ , m. p. 108—110°, loses  $\frac{1}{2}\text{H}_2\text{O}$  at 130° ; the anhydrous base crystallises from dry toluene ; m. p. 164—165°. When treated with bromine in chloroform solution, the base forms an orange-yellow *perbromide* which is converted by boiling alcohol into *bromocinnamemethylbenziminazole hydrobromide*,  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{Br}\cdot\text{HBr}$ , crystallising in colourless needles. The free *bromo-base*,  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{Br}$ , forms colourless crystals, m. p. 195°.

VI. *Methylbenziminazoles from fatty acids*.—[With GEORGE ROSENBERGER.]—Whilst methylbenziminazoles are formed by distillation of acyltolylene-3 : 4-diamines or of tolylene-3 : 4-diamine with  $\alpha$ -methyl- $\Delta^8$ -pentoic acid or cinnamic acid (compare preceding section), only resinous substances are obtained on heating crotonyl- or dimethylacryl-tolylene-3 : 4-diamines.

*Butyryl-p-toluidide*,  $\text{C}_{11}\text{H}_{15}\text{ON}$ , forms white, glistening needles, m. p. 73—74°. *3-Nitrobutyryl-p-toluidide*,  $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}_2$ , crystallises in yellow needles, m. p. 62°. *3-Amino-4-butyrylamino-toluene*,  $\text{C}_{11}\text{H}_{16}\text{ON}_2$ , forms white leaflets, m. p. 140°. *1-Butyryl-5-methyl-1 : 2 : 3-benzotriazole*,  $\text{C}_{11}\text{H}_{13}\text{ON}_3$ , m. p. 40°. *5-Methyl-2-propylbenziminazole*,  $\text{C}_{11}\text{H}_{14}\text{N}_2$ , crystallises from water in flat, white needles, m. p. 156—157°.

*isoValeryl-p-toluidide*,  $\text{C}_{12}\text{H}_{17}\text{ON}$ , forms flat, white needles, m. p. 110°, and on nitration yields *3-nitro-isovaleryl-p-toluidide* (Friederici, Abstr., 1879, 311). *3-Amino-4-isovaleryl-amino-toluene*,  $\text{C}_{12}\text{H}_{15}\text{ON}_2$ , forms white leaflets, m. p. 154°. *1-isoValeryl-5-methyl-1 : 2 : 3-benzotriazole*,  $\text{C}_{12}\text{H}_{15}\text{ON}_3$ , forms white, nacreous leaflets, m. p. 54°. *5-Methyl-2-isobutylbenziminazole* crystallises in white needles, m. p. 160° (145—146°, Hübner, Abstr., 1882, 180).

*isoHeptoyl-p-toluidide*,  $\text{C}_{14}\text{H}_{21}\text{ON}$ , crystallises from alcohol in white needles, m. p. 75°. *3-Nitroisoheptoyl-p-toluidide*,  $\text{C}_{14}\text{H}_{20}\text{O}_3\text{N}_2$ , forms yellow or colourless needles, m. p. 62°. *3-Amino-4-isoheptoyl-amino-toluene*,  $\text{C}_{14}\text{H}_{22}\text{ON}_2$ , crystallises in white leaflets, m. p. 130°. *5-Methyl-1-isoheptoyl-1 : 2 : 3-benzotriazole*,  $\text{C}_{14}\text{H}_{19}\text{ON}_3$ , forms white needles, m. p. 52°. *5-Methyl-2-isoheptylbenziminazole*,  $\text{C}_{14}\text{H}_{20}\text{N}_2$ , crystallises from alcohol in white needles, m. p. 119°.

*Dimethylacryl-p-toluidide*,  $\text{C}_{12}\text{H}_{15}\text{ON}$ , crystallises in flat, white needles, m. p. 102°. The *3-nitro-derivative*,  $\text{C}_{12}\text{H}_{14}\text{O}_3\text{N}_2$ , forms yellowish-red needles, m. p. 131°. *3-Amino-4-dimethylacrylamino-toluene*,  $\text{C}_{12}\text{H}_{16}\text{ON}_2$ , crystallises in white leaflets, m. p. 133°. *1-Dimethylacryl-5-methyl-1 : 2 : 3-benzotriazole*,  $\text{C}_{12}\text{H}_{13}\text{ON}_3$ , separates from alcohol in long needles, m. p. 129°.

*Cinnamoyl-3-nitrotoluidide*,  $\text{C}_{16}\text{H}_{14}\text{O}_3\text{N}_2$ , forms yellow leaflets, m. p. 147°. *3-Amino-4-cinnamoylamino-toluene*, crystallises in light yellow needles, m. p. 201°. *1-Cinnamoyl-5-methyl-1 : 2 : 3-benzotriazole*,  $\text{C}_{16}\text{H}_{13}\text{ON}_3$ , m. p. 156°.

$\alpha$ -*Methyl- $\Delta^8$ -pentenoyl-p-toluidide*,  $\text{C}_{13}\text{H}_{17}\text{ON}$ , crystallises in white leaflets or scales, m. p. 73°, and on nitration yields a mixture of products (compare Fichter and Pfister, Abstr., 1904, i, 547). *5-Methyl-2- $\alpha$ -methyl- $\Delta^8$ -butenylbenziminazole*,  $\text{C}_{13}\text{H}_{16}\text{N}_2$ , m. p. 145°, crystallises from water and forms a deep yellow *picrate*.

VII. *Diphenylvinylacetic acid*.—[With WILHELM LATZKO.]—Whilst

the relative stabilities of  $\gamma$ -phenylcrotonic and  $\gamma$ -phenylvinylacetic acids towards sodium hydroxide are the converse of those of the  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -unsaturated fatty acids in general (Fittig and Luib, Abstr., 1895, i, 223),  $\beta\gamma$ -diphenyl-crotonic and -vinylacetic acids behave in the normal manner (compare Thiele, Abstr., 1899, i, 217, 612).

$\beta\gamma$ -Diphenylvinylacetic acid,  $\text{CHPh}:\text{CPh}:\text{CH}_2\cdot\text{CO}_2\text{H}$ , is prepared by heating a mixture of sodium phenylsuccinate, benzaldehyde, and acetic anhydride in a reflux apparatus at  $125$ — $130^\circ$ ; it crystallises from a mixture of benzene and light petroleum in slender needles, m. p.  $172$ — $173^\circ$ , and decolorises alkaline potassium permanganate instantaneously. The calcium ( $4\text{H}_2\text{O}$ ) and barium ( $\frac{1}{2}\text{H}_2\text{O}$ ) salts are described.

$\gamma$ -Bromo- $\beta\gamma$ -diphenylbutyric acid,  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{Br}$ , formed by the action of hydrogen bromide on the preceding acid in glacial acetic acid solution, crystallises from a mixture of ether and light petroleum in needles, m. p.  $139^\circ$ , and when boiled with water yields  $\beta\gamma$ -diphenylvinylacetic acid together with traces of a neutral substance.

$\beta\gamma$ -Diphenylcrotonic acid ( $\beta$ -benzylcinnamic acid),  $\text{C}_{16}\text{H}_{14}\text{O}_2\cdot\text{H}_2\text{O}$ , formed by boiling  $\beta\gamma$ -diphenylisocrotonic acid with 40 mols. of sodium hydroxide in  $20\%$  solution, crystallises from water in glistening leaflets, and loses  $\text{H}_2\text{O}$  at  $125^\circ$ ; the anhydrous acid crystallises from a mixture of ether and light petroleum in needles, m. p.  $130$ — $131^\circ$ , and decolorises alkaline potassium permanganate instantaneously.

allo- $\beta\gamma$ -Diphenylvinylacetic acid,  $\text{C}_{16}\text{H}_{14}\text{O}_2$ , formed together with  $\beta\gamma$ -diphenylvinylacetic acid by condensation of ethyl phenylsuccinate and benzaldehyde in presence of sodium ethoxide in absolute ethereal solution, crystallises from a mixture of ether and light petroleum, m. p.  $142^\circ$ , is an extremely weak acid which cannot be titrated sharply (compare Sudborough and Lloyd, Trans., 1898, 73, 81), decolorises alkaline potassium permanganate instantaneously, and yields  $\beta$ -benzylcinnamic acid when boiled with aqueous sodium hydroxide; the calcium salt,  $(\text{C}_{16}\text{H}_{13}\text{O}_2)_2\text{Ca}\cdot\text{C}_{16}\text{H}_{14}\text{O}_2\cdot 7\text{H}_2\text{O}$ , crystallises in needles.

VIII. *Benzylcrotonic acid*.—[With EUGEN ALBER.]—When carefully distilled,  $\beta$ -hydroxy- $\alpha$ -benzylbutyric acid yields  $\alpha$ -benzylcrotonic acid and  $\alpha$ -phenyl- $\Delta^{\beta}$ -butylene.

$\alpha$ -Benzylcrotonic acid,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHMe}$ , crystallises from hot water in long, silky, white needles, m. p.  $99^\circ$ , and is slightly volatile in a current of steam. The magnesium, calcium, and barium salts are amorphous and readily soluble.  $\alpha$ -Benzylcrotonyl chloride, b. p.  $139^\circ/12$  mm.  $\alpha$ -Benzylcrotonamide,  $\text{C}_{11}\text{H}_{13}\text{ON}$ , crystallises from alcohol in slender needles, m. p.  $117$ — $118^\circ$ . The anilide,  $\text{C}_{17}\text{H}_{17}\text{ON}$ , forms white needles, m. p.  $90$ — $91^\circ$ . The *p*-toluidide,  $\text{C}_{18}\text{H}_{19}\text{ON}$ , crystallises in slender, white needles, m. p.  $107^\circ$ .  $\beta$ -Bromo- $\alpha$ -benzylbutyric acid,  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{Br}$ , m. p.  $52$ — $55^\circ$ , formed by the action of hydrogen bromide on  $\alpha$ -benzylcrotonic acid in glacial acetic acid solution, could not be purified and yields  $\alpha$ -phenyl- $\Delta^{\beta}$ -butylene and  $\alpha$ -benzylcrotonic acid when boiled with sodium carbonate solution.

When fused with hydrated potassium hydroxide at  $230^\circ$ ,  $\alpha$ -benzylcrotonic acid undergoes isomeric changes, forming  $\alpha$ -benzylidenebutrylic (phenylangelic) acid, m. p.  $104$ — $105^\circ$ , together with traces of hydrocinnamic acid.  $\alpha$ -Benzylidenebutryl chloride forms a yellow oil, b. p.



142°/14 mm; the *anilide*,  $C_{17}H_{17}ON$ , crystallises in white needles, m. p. 128—129°; the *p-toluidide*,  $C_{18}H_{19}ON$ , forms slender, white needles, m. p. 111°.  $\beta$ -Bromo- $\beta$ -phenyl- $\alpha$ -ethylpropionic acid,  $C_{11}H_{13}O_2Br$ , formed by the action of hydrogen bromide on  $\alpha$ -benzylidenebutylric acid, crystallises in glistening, fatty leaflets, m. p. 135—137°, and yields chiefly  $\alpha$ -phenyl- $\Delta^{\beta}$ -butylene and  $\alpha$ -benzylidenebutylric acid when boiled with aqueous sodium carbonate. The *magnesium* ( $3H_2O$ ), *calcium* ( $4H_2O$ ), and *barium* ( $3H_2O$ ) salts of  $\alpha$ -benzylidenebutylric acid are described.

When boiled with 10 vols. of 20% alcoholic potassium hydroxide  $\alpha$ -phenyl- $\Delta^{\beta}$ -butylene is converted almost quantitatively into  $\alpha$ -phenyl- $\Delta^{\alpha}$ -butylene.

$\gamma$ -Phenylvinylacetic acid is formed in a 50—55% yield by boiling phenylacetaldehyde with malonic acid and pyridine in a reflux apparatus, or by heating phenylacetaldehyde with ethyl malonate and glacial acetic acid on the water-bath; in both methods a small amount of phenylcrotonic acid is formed.

G. Y.

**Palladium Halides.** ALEXANDER GUTBIER and M. WOERNLE (*Ber.*, 1906, 39, 4134—4139. Compare Abstr., 1905, i, 584, 876; ii, 534; 1906, i, 12, 244, 402, 805).—The authors have prepared pyridinium,  $\alpha$ -picolinium, and quinolinium tetrahalogen palladium salts and examined their behaviour towards water.

The salts in question are sparingly soluble in alcohol, and may be crystallised from the corresponding halogen acids without undergoing decomposition. Their aqueous solutions undergo slow decomposition at the ordinary temperature and rapid decomposition when warmed with the formation of palladosammines.

The Anderson reaction is always observed when palladous halides unite with halogen hydrates of aromatic bases or of aliphatic diamines to form more complex compounds; the reaction is not, however, noted when the halogen hydrates of aliphatic amines are used.

*Pyridiniumpalladochloride*,  $(C_5H_5N)_2, H_2PdCl_4$ , separates from dilute hydrochloric acid in brownish-yellow needles. By the action of water, it is converted into *palladous pyridine chloride*,  $Pd(C_5H_5N)_2Cl_2$ , which is a yellow, microcrystalline powder. *Pyridiniumpalladichloride*,  $(C_5H_5N)_2, H_2PdCl_6$ , forms red prisms.

*Pyridiniumpalladobromide*,  $(C_5H_5N)_2, H_2PdBr_4$ , crystallises from dilute hydrobromic acid in reddish-brown leaflets and by the action of water is converted into *palladous pyridine bromide*,  $Pd(C_5H_5N)_2Br_2$ , which is a yellow, microcrystalline powder. *Pyridiniumpalladibromide*,  $(C_5H_5N)_2, H_2PdBr_6$ , forms bluish-black prisms.

*$\alpha$ -Picoliniumpalladochloride*,  $(C_5H_4NMe)_2, H_2PdCl_4$ , separates from dilute hydrochloric acid in brown needles and forms with water *palladous  $\alpha$ -picoline chloride*,  $Pd(C_5H_4NMe)_2Cl_2$ , which separates from alcohol in yellow leaflets. The *palladichloride*,  $(C_5H_4NMe)_2, H_2PdCl_6$ , forms red prismatic needles. The *palladobromide*,  $(C_5H_4NMe)_2, H_2PdBr_4$ , separates from dilute hydrobromic acid in brown needles. It is converted by water into *palladous  $\alpha$ -picoline bromide*,  $Pd(C_5H_4NMe)_2Br_2$ , which crystallises in yellowish-red leaflets.

*Quinoliniumpalladochloride*,  $(C_9H_7N)_2, H_2PdCl_4$ , separates from dilute hydrochloric acid in yellowish-brown needles, and is converted by

water into *palladous quinoline chlorine*,  $\text{Pd}(\text{C}_9\text{H}_7\text{N})_2\text{Cl}_2$ , which is a yellow solid.

*Quinolinium palladichloride*,  $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{PdCl}_6$ , forms red prisms.

*Quinolinium palladobromide*,  $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{PdBr}_4$ , crystallises from dilute hydrobromic acid in reddish-brown needles, and with water forms *palladous quinoline bromide*,  $\text{Pd}(\text{C}_9\text{H}_7\text{N})_2\text{Br}$ , which forms reddish-brown leaflets.

*Methylammonium palladichloride*,  $(\text{NH}_2\text{Me})_2\text{H}_2\text{PdCl}_6$ , forms brick-red leaflets and needles; the *palladibromide* forms green needles.

*Ethylammonium palladichloride*,  $(\text{NH}_2\text{Et})_2\text{H}_2\text{PdCl}_6$ , crystallises in scarlet needles.

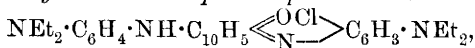
*Ethylammonium palladibromide*,  $(\text{NH}_2\text{Et})_2\text{H}_2\text{PdBr}_6$ , forms green needles. *Propylammonium palladibromide*,  $(\text{NH}_2\text{Pr})_2\text{H}_2\text{PdCl}_6$ , forms brick-red leaflets; the *palladibromide* forms dark bluish-green leaflets and needles.

*iso Butylammonium palladichloride*,  $(\text{C}_4\text{H}_9\cdot\text{NH}_2)_2\text{H}_2\text{PdCl}_6$ , forms leaflets with a bronze lustre; the *palladibromide* separates in bluish-black needles.

A. McK.

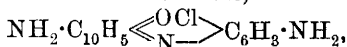
**Oxazine Dyes.** JULIUS FORMÁNEK (*Zeit. Farb. Ind.*, 1906, 5, 433—434).—A preliminary notice. *Diaminophenazoxonium chloride*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\text{N} \begin{smallmatrix} \text{OCl} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_3\cdot\text{NH}_2$ , is prepared by adding *m*-aminophenol to *p*-benzoquinonedichlorodi-imine in glacial acetic acid solution. The analogous methyl, ethyl, dimethyl, and diethylaminophenazoxonium compounds were prepared similarly, using the corresponding alkylaminophenols. *Trimethyldiaminophenazoxonium chloride* when prepared from nitrosomethylaniline and *m*-dimethylaminophenol is always mixed with the tetramethyl compound; it is obtained pure only by the interaction of methylaniline and nitroso-*m*-dimethylaminophenol in acetic acid solution. Similar remarks apply to the analogous triethyldiaminophenazoxonium chloride.

*Diethylaminophenazoxonium chloride* is prepared by gently warming a 1 : 20 solution of nitrosoethylaniline hydrochloride and  $\beta$ -naphthol; if more concentrated solutions are used at a higher temperature the initial product condenses with *p*-phenylenediethyldiamine, formed from the nitrosodiethylaniline, and a greater or less proportion of *diethylumino-diethylanilinouminophenonaphthazoxonium chloride*,

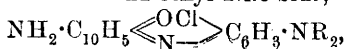


is produced according to the conditions. Similar results are obtained with nitrosodimethylaniline and  $\beta$ -naphthol.

*Diaminophenonaphthazoxonium chloride*,



prepared by warming a concentrated aqueous solution of aminophenonaphthazoxonium chloride with hydroxylamine hydrochloride, forms brown crystals with a bronze reflex and gives fluorescent solutions. Methyl-Nile-blue and ethyl-Nile-blue,

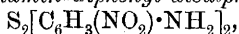


can be readily prepared in a similar way from Meldola's Blue or diethylaminophenonaphthazoxonium chloride respectively by using hydroxylamine.

The spectroscopic relations of the foregoing substances will be dealt with subsequently.

W. A. D.

**Sulphineazo-dyes.** HERMANN A. MÜLLER (*Zeit. Farb. Ind.*, 1906, 5, 357—361).—On reduction with ammonium sulphide, 2:4-dinitro-1-thiocyanobenzene (Austen and Smith, *Abstr.*, 1886, 693) is converted into 2:2'-dinitro-4:4'-diaminodiphenyl disulphide,



which crystallises from alcohol in lustrous red leaflets, m. p. 222°; the nitro-group in the para-position to the thiocyano-radicle is therefore reduced, not that in the ortho-position. It is probable that a mercaptan is the primary product of the reduction, but it undergoes oxidation during the treatment employed. The structure of the product follows from its giving 2:2'-dinitrodiphenyl disulphide (Cleve, *Abstr.*, 1887, 834) on eliminating the amino-groups by the diazo-reaction; the 2:2'-dinitrodiphenyl sulphide was characterised by its giving, on reduction, 2:2'-diaminodiphenyl disulphide and by its conversion into 1-methylbenzothiazole.

2:2'-Dinitro-4:4'-diaminodiphenyl disulphide is used for preparing dyes by diazotising and coupling with bases (French Patent, 337329, 1903). 2:2'-Dinitrodiphenyl disulphide-4:4'-disazo-di- $\beta$ -naphthylamine,  $[\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)]_2\text{S}_2$ , prepared in this way from  $\beta$ -naphthylamine, separates from acetic acid as a dark red crystalline powder.

*p*-Nitrothiocyanobenzene,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CNS}$ , prepared from *p*-nitroaniline by the diazo-reaction, crystallises from carbon tetrachloride in lustrous leaflets, from glacial acetic acid in long, white needles, m. p. 133°. On reduction with ammonium sulphide it gives 4:4'-dinitrodiphenyl sulphide, which is reduced by stannous chloride to the corresponding 4:4'-diamino-compound; this serves to prepare diphenyl-disulphide-4:4'-disazo-di- $\beta$ -naphthylamine,  $[\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_6\text{H}_3]_2\text{S}_2$ , as above; the dye crystallises from toluene in dark red crystals.

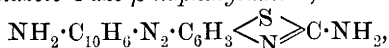
On reduction with stannous chloride and hydrochloric acid, 2:2'-dinitro-4:4'-diaminodiphenyl disulphide gives 2:4-diaminothiophenol hydrochloride; on decomposing this with ammonia, 2:4:2':4'-tetra-aminodiphenyl disulphide,  $\text{S}_2[\text{C}_6\text{H}_3(\text{NH}_2)_2]_2$ , is obtained, which crystallises from benzene or toluene, m. p. 148°. When the reduction of 2:2'-dinitro-4:4'-diaminodiphenyl disulphide is effected by zinc dust in presence of acetic acid and acetic anhydride, 4-acetylaminomethylbenzothiazole,  $\text{NHAc}\cdot\text{C}_6\text{H}_3\langle\text{N}\rangle\text{S}\text{CMe}$ , is obtained; it crystallises from water in nearly colourless needles, m. p. 159°.

On reduction with stannous chloride and hydrochloric acid, 2:4-dinitro-1-thiocyanobenzene gives, not the corresponding diamino-derivative (compare Austen, *Abstr.*, 1889, 700), but the isomeric 1:4-diaminobenzothiazole,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\text{N}\rangle\text{S}\text{C}\cdot\text{NH}_2$ , which crystallises from toluene or benzene in silvery leaflets, m. p. 175°. The reduction of *o*-nitrothiocyanobenzene takes place similarly. *o*-Nitrothiocyano-

benzene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CNS}$ , prepared from diazotised *o*-nitroaniline and potassium thiocyanate, crystallises from carbon tetrachloride in colourless needles, m. p.  $132.5^\circ$ ; on reduction with stannous chloride and hydrochloric acid it gives 1-aminobenzothiazole, the *acetyl* derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{NHAc}$ , of which forms white crystals, m. p.  $185\text{--}186^\circ$ .

1 : 4-*Diacetyldiaminobenzothiazole*, prepared by boiling the corresponding diamino-compound with acetic anhydride and acetic acid, separates from the latter in white crystals containing  $1\frac{1}{2}$  mol. of acetic acid, m. p.  $271^\circ$ . When the acetylation is carried out in alcoholic solution at the ordinary temperature, 1-amino-4-acetylaminobenzothiazole,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{NH}_2$ , m. p.  $259\text{--}261^\circ$ , is formed; it crystallises from acetic acid on adding light petroleum.

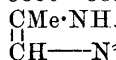
1-Aminobenzothiazole-4-azo- $\beta$ -naphthylamine,



prepared by diazotising 1-4-diaminobenzothiazole and coupling with  $\beta$ -naphthylamine, crystallises from alcohol in dark violet needles with a metallic reflex, from toluene in reddish-yellow leaflets; m. p.  $223^\circ$ .

W. A. D.

**Decomposition of Dextrose by Ammoniacal Zinc Hydroxide in the Presence of Acetaldehyde.** ADOLF WINDAUS (*Ber.*, 1906, **39**, 3886—3891. Compare Abstr., 1905, i, 381).—2 : 4-*Dimethylglyoxaline*,



is formed together with the 4-methyl compound when dextrose is left for some time in contact with an ammoniacal solution of zinc hydroxide and concentrated acetaldehyde solution. The 4-methylglyoxaline only is formed in the absence of acetaldehyde. The two bases are separated by means of their oxalates, as the dimethylglyoxaline oxalate dissolves readily in methyl alcohol. The *picrate*,  $\text{C}_{11}\text{H}_{11}\text{O}_7\text{N}_5$ , crystallises from hot water in deep yellow prisms, m. p.  $142\text{--}143^\circ$ , and is less soluble in water than the picrate of the monomethylglyoxaline. The base has b. p.  $266^\circ/733\text{ mm.}$ , m. p.  $92^\circ$ , and dissolves readily in alcohol or water. The *hydrochloride*,  $\text{C}_5\text{H}_9\text{N}_2\text{Cl}$ , m. p.  $205^\circ$ , is hygroscopic. The *platinichloride* melts and decomposes at  $204^\circ$  and the *nitrate* at  $133\text{--}134^\circ$ . The constitution of the base follows from the fact that it can be obtained by passing Jowett and Potter's 3 : 4-dimethylglyoxaline (*Trans.*, 1903, **83**, 464) through a strongly heated glass tube (compare Wallach, Abstr., 1883, 910).

J. J. S.

**Action of Bromine on  $\alpha$ -Lactylcarbamide and Related Compounds.** II. SIEGMUND GABRIEL (*Annalen*, 1906, **350**, 118—134. Compare Abstr., 1906, i, 634).—The action of bromine on  $\alpha$ -phenylhydantoin does not lead to the formation of products analogous to those obtained from 4-methylhydantoin ( $\alpha$ -lactylcarbamide).

4-Bromo-4-phenylhydantoin,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CBrPh} \\ | \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , obtained from 1 mol

of phenylhydantoin and bromine ( $> 1$  mol.) in glacial acetic acid on the water-bath, forms stout prisms or oblong plates, m. p.  $> 200^\circ$ , decomposing, loss of hydrogen bromide commencing at  $100^\circ$ . The halogen is very readily displaced. Hot water causes the separation of 4-hydroxy-4-phenylhydantoin, which readily reacts with hydrogen bromide to re-form the bromo-compound. The position of the hydroxyl group or of the halogen atom in these compounds is ascertained by decomposing them with hydrochloric acid at  $160^\circ$ , whereby benzoylformic acid is produced.

4-Amino-4-phenylhydantoin sinters at  $160^\circ$ , m. p.  $285^\circ$ , decomposing, dissolves in acids or alkalis, yields the hydroxy-compound with boiling water and forms a sparingly soluble nitrate,  $C_9H_9O_2N_3 \cdot HNO_3$ , m. p.  $199-200^\circ$ .

4-Anilino-4-phenylhydantoin forms slender, flattened needles and has m. p.  $295-300^\circ$ , decomposing.

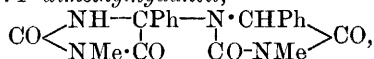
4-Phenyl-1-methylhydantoin by bromination yields the 4-bromo-compound which is converted by hot water into 4-hydroxy-4-phenyl-1-methylhydantoin,  $CO \begin{array}{c} \text{NH}-CPh \cdot OH \\ | \\ NMe \cdot CO \end{array}$ , m. p.  $128-129^\circ$ .

The reaction between alcoholic potash, methylamine hydrochloride, and mandelonitrile at  $70-80^\circ$  yields phenylsarcosinamide, the hydrochloride of which and potassium cyanate yield 4-phenyl-3-methylhydantoin,  $C_{10}H_{10}O_2N_2$ , which separates from hot water in long needles, m. p.  $177^\circ$ , and dissolves in alkali hydroxides. The 4-hydroxy-compound,  $C_{10}H_{10}O_3N_2$ , has m. p.  $167-168^\circ$ . By methylation, the preceding hydantoin yields 4-phenyl-1:3-dimethylhydantoin,  $C_{11}H_{12}O_2N_2$ , which separates from water in short, stout, hexagonal prisms, is insoluble in alkalis, and has m. p.  $108-109^\circ$ .

By treating 4-phenylhydantoin with bromine ( $\frac{1}{2}$  mol.) in glacial acetic acid at  $100^\circ$ , by heating the same substance with its bromo-derivative, or by heating it with its hydroxy-derivative at  $160^\circ$  or in aqueous or acid solution, a substance, diphenylhydantil, is obtained to which is ascribed the constitution  $CO \begin{array}{c} \text{NH} \cdot CPh - N \cdot CHPh \\ | \quad \quad | \\ \text{NH} \cdot CO \quad CO - NH \end{array} CO$ .

It is a microcrystalline powder, m. p.  $336-338^\circ$ , decomposing, sparingly soluble in solvents with high boiling points, but readily in alkalis. Its constitution follows from the decomposition by concentrated hydrochloric acid at  $165^\circ$ , whereby benzoylformic and phenylaminoacetic acids are the characteristic products.

4 : 4'-Diphenyl-1 : 1'-dimethylhydantil,



resulting by the methylation of diphenylhydantil or by the bromination of 4-phenyl-1-methylhydantoin in glacial acetic acid, forms long, white needles, m. p.  $329-334^\circ$ , decomposing, does not dissolve in cold alkalis and is decomposed by boiling potash, yielding benzoylformic acid and 4-phenyl-1-methylhydantoin.

When 4-phenyl-3-methylhydantoin, 4-phenyl-1-methylhydantoin, or 4-phenyl-1:3-dimethylhydantoin is heated with 4-bromo-4-phenylhydantoin in glacial acetic acid at  $100^\circ$ , diphenylhydantil is obtained

contrary to expectation, whilst in the second case diphenyldimethylhydantil is also produced.

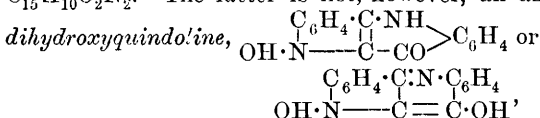
Diphenylhydantil is identical with Pinner's  $\psi$ -phenylhydantoin (compare following abstract), which can be obtained also by exposing an alcoholic solution of 4-phenylhydantoin to atmospheric oxygen.

C. S.

**$\psi$ -Hydantoins.** ADOLF PINNER (*Annalen*, 1906, **350**, 135—140. Compare Abstr., 1888, 1102; preceding abstract).—The author has re-examined the decomposition of 4-phenyl-1-ethyl- $\psi$ -hydantoin by barium hydroxide, and has identified ammonia, ethylamine, benzoylformic and 4-phenyl-1-ethylhydantoic acids in the decomposition products. He agrees with Gabriel that phenyl- $\psi$ -hydantoin is diphenylhydantil; similarly, styryl- $\psi$ -hydantoin is dicinnamylhydantil.

C. S.

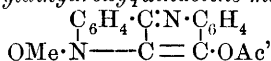
**Quindoline.** FRIEDRICH FICHTER and RUDOLF BOEHRINGER (*Ber.*, 1906, **39**, 3932—3942).—With the view of obtaining cyclic azoxy-compounds, ethyl *bis-o*-nitrobenzylmalonate was acted on by alcoholic sodium hydroxide. The action was a vigorous one, attended with the separation of sodium carbonate and the formation of a dark red sodium salt, which, when decomposed with acids, formed a compound,  $C_{15}H_{10}O_2N_2$ . The latter is not, however, an azoxy-compound, but is



a compound containing both a quinoline and an indene nucleus. Its formation is represented by the equation  $C_{21}H_{22}O_8N_2 = C_{15}H_{10}O_2N_2 + 2CO_2 + 2EtOH$ ; it is assumed that *bis-o*-nitrobenzylmethane is formed as an intermediate product. Dihydroxyquindoline forms a red, crystalline powder which does not melt below  $300^\circ$ ; it is a weak acid, dissolving readily in alkali hydroxides, but with difficulty in sodium carbonate or ammonia. It forms dark red salts which are soluble in water.

The acid character of dihydroxyquindoline is ascribed to the hydroxy-group attached to nitrogen, whilst in the other portion of the molecule the grouping is analogous to that in hydroxy-2-methylquinoline. The

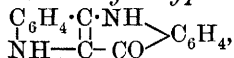
*methyl ether*,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NH} \\ | \quad | \\ \text{OMe} \cdot \text{N} - \text{C} - \text{CO} \end{array} > \text{C}_6\text{H}_4$ , obtained by the action of methyl sulphate on the solution of dihydroxyquindoline in sodium hydroxide, separates in needles, m. p.  $184^\circ$ ; it is insoluble in alkali. When acetylated it forms *acetyldihydroxyquindoline methyl ether*,



which separates from absolute alcohol in greenish-white needles, m. p.  $148^\circ$ . It is readily saponifiable, and is comparable with esters of hydroxyquinaldine.

When dihydroxyquindoline is warmed with phenylhydrazine it loses

one-half of its oxygen and forms *hydroxyquindoline*,



which forms yellow, rhombic crystals and does not melt below  $300^\circ$ ; it is a weak base. The *hydrochloride*,  $(\text{C}_{15}\text{H}_{10}\text{ON}_2)_2\text{HCl}$ , forms yellow, silky needles; the *picrate* is also described. The *acetyl* derivative,  $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4$ ,  $\text{NH} - \text{C} = \text{C} \cdot \text{OAc}$ , separates from absolute alcohol in yellowish-white needles and is readily saponifiable.

*Nitrohydroxyquindoline*,  $\text{NO}_2 \cdot \text{C} \cdot \text{CH} - \text{C} - \text{C} \cdot \text{NH}$ ,  $\text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{NH} \cdot \text{C} - \text{CO}$   $> \text{C}_6\text{H}_4$ , obtained

by nitrating hydroxyquindoline in glacial acetic acid solution, separates from nitrobenzene in glistening, red leaflets. Its solution in concentrated sulphuric acid is red, whilst its solution in alcoholic sodium hydroxide is blue. When reduced by sodium sulphide it forms *amino-hydroxyquindoline*,  $\text{C}_{15}\text{H}_{11}\text{ON}_3$ , which separates in yellow needles, forms a *hydrochloride*, and condenses with benzaldehyde to form *benzylidene-amino-hydroxyquindoline*,  $\text{CHPh} \cdot \text{C} \cdot \text{CH} - \text{C} - \text{C} \cdot \text{NH}$ ,  $\text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{NH} \cdot \text{C} - \text{CO}$   $> \text{C}_6\text{H}_4$ , which crystallises in needles.

*Quindoline*,  $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} -$ ,  $\text{NH} - \text{C} \cdot \text{CH}$   $> \text{C}_6\text{H}_4$ , obtained by the vigorous reduction

of dihydroxyquindoline by phenylhydrazine, or better by heating dihydroxyquindoline with a mixture of hydriodic acid and phosphorus at  $150^\circ$ , separates from alcohol in colourless needles, m. p.  $247-248^\circ$ ; it forms coloured salts. The *hydrochloride*, *hydriodide*, *nitrate*, and *picrate* are described. *Acetylquindoline*,  $\text{C}_{17}\text{H}_{12}\text{ON}_2$ , separates from alcohol in yellowish-white needles, m. p.  $177-178^\circ$ .

*Quindoline methiodide*,  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{I}$ , separates from water in yellow needles. It forms a *periodide*,  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{I}_3$ , obtained as a by-product in the preparation of the methiodide, or by heating dihydroxyquindoline with a mixture of methyl iodide and methyl alcohol at  $130-140^\circ$ , and forms glistening leaflets.

*Quindoline ethiodide*,  $\text{C}_{17}\text{H}_{15}\text{N}_2\text{I}$ , forms yellow needles, m. p.  $222-223^\circ$ ; its *periodide*,  $\text{C}_{17}\text{H}_{15}\text{N}_2\text{I}_3$ , separates from alcohol in greenish-black needles.

When a warm aqueous solution of quindoline methiodide is acted on by an excess of a 10% solution of sodium hydroxide, a product is precipitated which, when crystallised from toluene, is free from iodine. It decomposes at  $260^\circ$ ; it is a *pseudo*-base, forming the yellow quaternary salts with acids, even with carbon dioxide. The compound is possibly *methylquindolanol*,  $\text{C}_{16}\text{H}_{14}\text{ON}_2$  A. McK.

**Basic Triphenylmethane Dyes containing Sulphur.** JULIUS SCHMIDLIN (*Ber.*, 1906, 39, 4204-4216).—When *p*-leucaniline or its homologues (compare D.R.-P. 100556) is treated with fuming sulphuric acid at low temperatures for from eight days to a month and the product is oxidised, best electrolytically, sparingly soluble blue dyes are obtained, which contain two sulphone groups (hence called *rosaniline*-

disulphones), are mono-acid bases, and have two diazotisable amino-groups. *p*-Rosanilinedisulphone, obtained from *p*-leucaniline hydrochloride, forms copper-coloured crystals soluble in acids; the *sulphate*,  $[C_{19}H_{14}N_3(SO_2)_2]_2SO_4 \cdot H_2O$ , was prepared.

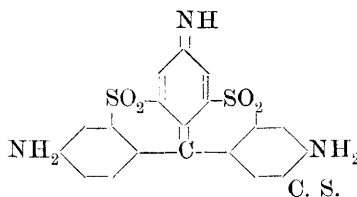
*p*-Rosanilinedisulphone trisulphonic acid,  $C_{19}H_{10}N_3(SO_2)_2(SO_3H)_3 \cdot 4H_2O$ , is obtained when *p*-leucaniline hydrochloride and fuming sulphuric acid (60% of trioxide) are heated to incipient ebullition for two and a half hours. It is a white powder, soluble in warm water to an intensely blue solution, from which concentrated sulphuric acid reprecipitates the hydrated substance in white needles; at 130—140° the water is expelled and the dark brown residue dissolves in water to a blue solution. The alkali salts are colourless. At 170—180° the sulphonic acid absorbs oxygen, changing into a sparingly soluble substance.

Leucaniline hydrochloride yields a similar dye which forms dark blue crystals with red reflex; the *sulphate*,  $[C_{20}H_{16}N_3(SO_2)_2]_2SO_4 \cdot H_2O$ , was prepared.

The leuco-compound of new magenta (triaminotritolylmethane hydrochloride) yields the *sulphate* of *new magenta disulphone*,  $[C_{22}H_{20}N_3(SO_2)_2]_2SO_4 \cdot H_2O$ , which is sparingly soluble in water and separates from 10% sulphuric acid in dark blue crystals with a red reflex. The *base*,  $C_{22}H_{19}N_3(SO_2)_2 \cdot H_2O$ , is a black, microcrystalline powder, insoluble in water. The *hydrochloride*,  $C_{22}H_{19}N_3(SO_2)_2 \cdot HCl$ , forms brown crystals, is sparingly soluble in water, and does not yield triacid salts.

When new magenta disulphone is boiled with hydrochloric acid for two days the blue colour disappears, and a brown, flocculent *substance*,  $C_{22}H_{21}O_8NS_2$ , is obtained, which dissolves sparingly in dilute acids, readily in alkalis. New magenta disulphone sulphate is converted by nitrous acid into a *substance* apparently identical with the preceding; the violet-coloured solution of the diazonium salt is extraordinarily sensitive to light, exposure for a few seconds to sunlight causing the evolution of nitrogen and the formation of the substance mentioned above.

The formula proposed for the rosaniline disulphones is



**Action of Hydroxylamine on *iso*Rosindone and Thio-rosindone, and the Formation of Naphthasafranrol from *iso*-Rosindone.** OTTO FISCHER and K. ARNTZ (*Ber.*, 1906, 39, 3807—3812. Compare Fischer and Hepp, *Abstr.*, 1905, i, 948).—The supposed *isorosindoneoxime* (Fischer and Hepp, *Abstr.*, 1900, i, 461) is now shown to be *s*-amino*isorosindone*,  $C_6H_5O \leq N - C \cdot C_6H_4 \geq C \cdot NH_2$ .

An improved method for the preparation of the substance is described. *Acetylaminosorosindone*,  $C_{24}H_{17}O_2N_3$ , crystallises in steel-blue, glistening needles, dissolves in alcohol, forming a scarlet solution, and gives a bluish-violet coloration with concentrated sulphuric acid. The



*benzylidene* derivative,  $C_{29}H_{19}ON_3$ , formed by heating a molecular mixture of benzaldehyde and aminoisorosindone on the water-bath, is obtained in scarlet crystals, gives a violet coloration with concentrated sulphuric acid, and is hydrolysed by boiling dilute acids, forming its generators. The *p*-nitrobenzylidene derivative,  $C_{29}H_{18}O_3N_4$ , crystallises in red needles. The *o*-hydroxybenzylidene derivative forms scarlet crystals.

When heated with concentrated hydrochloric acid and glacial acetic acid at  $180-190^\circ$  under pressure, aminoisorosindone yields the *hydrochloride* of the corresponding hydroxyisorosindone; this forms dark red, metallic needles and remains unchanged when heated with hydrochloric acid at  $200-220^\circ$  under pressure for twenty hours. *Hydroxyisorosindone*,  $C_{22}H_{14}O_2N_2$ , crystallises from a mixture of benzene and alcohol in glistening, bronze, narrow leaflets, sinters at  $230^\circ$ , and decomposes yielding a red sublimate at  $260^\circ$ . When boiled with alcoholic potassium hydroxide and methyl or ethyl iodide, hydroxyisorosindone yields the corresponding ether of naphthasafran.ol.

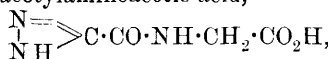
The substance previously described as 7-*o*-tolylisorosindoneoxime (Abstr., 1900, i, 460) must be amino-*o*-tolylisorosindone.

The action of hydroxylamine on thiorosindone leads to the formation of Kehrman and Locher's product,  $C_{22}H_{15}ON_3$  (Abstr., 1899, i, 82), which when treated with concentrated hydrochloric acid at  $200^\circ$  under pressure yields rosindone.

Naphthasafran.ol is formed when isorosindone is heated with glacial acetic and concentrated hydrochloric acids at  $200^\circ$  under pressure for ten to fifteen hours.

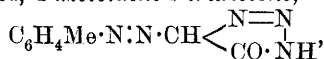
G. Y.

**Formation of 5-Triazolone and of 5-Triazolone Derivatives from Diazoaliphatic Acids.** THEODOR CURTIUS and JAMES THOMPSON (*Ber.*, 1906; **39**, 4140—4144. Compare Abstr., 1906, i, 940, this vol., i, 21).—The authors prove that the compound originally described as *isodiazoacetyl*aminoacetic acid,



is in reality 5-triazolone-1-acetic acid,  $\begin{array}{c} \text{N} \\ \parallel \\ \text{N} \text{---} \text{CH}_2 \cdot \text{CO} \end{array} \text{---} \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ . The isolation of 5-triazolone is described.

When diazoacetamide (1 mol.) is agitated with 2*N*-potassium hydroxide (2 mols.), neither nitrogen nor an appreciable amount of ammonia is evolved. On the addition of a diazotoluene sulphate solution, an orange-coloured solution is obtained, from which, on the addition of acetic acid, 4-azotoluene-5-triazolone,

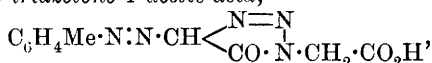


is precipitated; it crystallises from alcohol in yellow needles which deflagrate at  $163^\circ$ .

When an aqueous solution of diazoacetamide is warmed with barium hydroxide, the transformation into triazolone also occurs. After removal of the excess of barium hydroxide, the barium salt

of triazolone is obtained in needles, from which 5-triazolone,  $\text{N}=\text{N}-\text{CH}_2\cdot\text{CO}-\text{NH}$ , itself may be prepared. The latter separates from dilute alcohol in colourless rosettes and decomposes at about  $135^\circ$ . It gives an acid reaction towards litmus. When boiled with moderately concentrated sulphuric acid, it is decomposed with the gradual evolution of nitrogen, and when alkali is then added, ammonia is evolved. When sodium nitrite and acetic acid are added to its aqueous solution, a dark violet coloration is produced. 5-Triazolone is very stable towards alkali, no ammonia being evolved when it is boiled with concentrated sodium hydroxide.

4-Azotoluene-5-triazolone-1-acetic acid,



prepared by coupling 5-triazolone-1-acetic acid, formerly described as isodiazoacetylaminooacetic acid (*loc. cit.*), with diazotoluene sulphate, separates from alcohol in orange-red needles, m. p.  $156^\circ$ , decomposing.

The *amide* separates from alcohol in yellowish-red needles, m. p.  $166^\circ$ , decomposing. Its solution in alkali is yellow. When crystallised from glacial acetic acid, it forms the isomeric compound,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_6$ , which crystallises in colourless needles, m. p.  $231^\circ$ , decomposing, and is insoluble in alkali. A. McK.

**Formation of Derivatives of Oxanilhydroxamic Acid from 4-isoNitroso-1-phenyl-5-triazolone.** OTTO DIMROTH and LUDWIG TAUB (*Ber.*, 1906, **39**, 3912—3920. Compare Abstr., 1903, i, 127).—By the action of nitrous acid on 5-hydroxy-1-phenyl-1:2:3-triazole,

$\text{NPh} \begin{array}{l} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH})\cdot\text{CH} \end{array}$  or on 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylic acid, a compound is formed, which may be formulated either as 4-nitroso-5-hydroxy-1-phenyltriazole,  $\text{NPh} \begin{array}{l} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH})\cdot\text{C}\cdot\text{NO} \end{array}$  or more

probably as 4-isonitroso-1-phenyl-5-triazolone,  $\text{NPh} \begin{array}{l} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{C}\cdot\text{N}\cdot\text{OH} \end{array}$ . It separates from a mixture of ether and light petroleum in silky, orange-coloured needles, which are completely decomposed at  $195^\circ$ ; its *ammonium* salt forms violet plates.

4-isoNitroso-1-phenyl-5-triazolone is of interest on account of the ease with which the ring is broken. When treated with concentrated hydrochloric acid, nitrogen is evolved, and *oxanilhydroxamic chloride*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CCl}\cdot\text{N}\cdot\text{OH}$ , formed; this separates from a mixture of ether and light petroleum in colourless needles and begins to decompose at about  $160^\circ$ .

*Oxanilhydroxamic anilide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{C}\cdot\text{NHPh}\cdot\text{N}\cdot\text{OH}$ , obtained from the preceding chloride and aniline, separates from alcohol in colourless needles, m. p.  $180^\circ$ . Its constitution is established by its conversion into oxanilide and hydroxylamine by the action of fuming hydrochloric acid.

*Oxanilhydroxamic acid*,  $\text{NHPh}\cdot\text{CO}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ , obtained by the

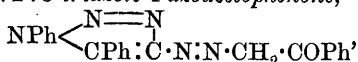
action of water on oxanilhydroxamic chloride, separates from alcohol in colourless needles and decomposes at  $163^{\circ}$ . When heated in a vacuum at a high temperature, it forms diphenylcarbamide, carbon dioxide, and ammonia.

When 4-isonitroso-1-phenyl-5-triazolone is boiled with water, in addition to oxanilhydroxamic acid two colourless, crystalline isomerides,  $C_{16}H_{12}O_4N_4$ , are formed according to the equation  $2C_8H_8O_3N_2 = C_{16}H_{12}O_4N_4 + 2H_2O$ . The constitution of these compounds has not yet been absolutely settled. The one is probably *glyoximeperoxidedicarboxylanilide*,  $\begin{matrix} \text{NHP} \cdot \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{O} \\ \text{NHP} \cdot \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{O} \end{matrix}$ , which may be

obtained either by boiling 4-isonitroso-1-phenyl-5-triazolone with dilute sulphuric acid or by boiling oxanilhydroxamic chloride with aqueous sodium acetate; it separates from alcohol in prisms, m. p.  $187^{\circ}$ ; it is very stable towards oxidising agents, but is readily attacked by reducing agents. The second isomeride is probably 3:6-dioximino-2:5-diketo-1:4-diphenylpiperazine,  $\text{NPh} \begin{matrix} \text{CO} \cdot \text{C}(\text{N} \cdot \text{OH}) \\ \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \end{matrix} \text{NPh}$ ; it is best obtained by warming 4-isonitroso-1-phenyl-5-triazolone with alcohol. It forms glistening, colourless leaflets and decomposes at  $195^{\circ}$ . Its alcoholic solution gives a red coloration with ferric chloride. When acted on by dilute sodium hydroxide, it is converted into oxanilhydroxamic anilide. A. McK.

**Syntheses with Azoimides. VI. Condensation of Phenyl-azoimide with Ketones.** OTTO DIMROTH, ERICH FRISONI, and JOSEPH MARSHALL (*Ber.*, 39, 3920—3928. Compare Abstr., 1903, i, 127).—Since phenylazoimide readily interacts with acid esters,  $\beta$ -ketonic esters, &c., in the presence of sodium ethoxide with the formation of 1:2:3-triazole, it was probable that ketones would undergo condensation in an analogous manner. The authors accordingly investigated the action of phenylazoimide on acetone and on dypnone.

1:5-Diphenyl-1:2:3-triazole-4-azoacetophenone,

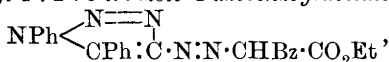


obtained by the interaction of acetophenone, phenylazoimide, and sodium ethoxide, separates from dilute alcohol in yellow leaflets, m. p.  $176^{\circ}$ . It is a weak acid and forms red salts; at the same time, as a triazole derivative, it exhibits basic character in so far as it forms a hydrochloride which is readily decomposed by water. The sodium salt is a brick-red powder; the silver salt is red; the methyl derivative forms colourless crystals, m. p.  $133$ — $135^{\circ}$ ; the acetyl derivative forms colourless crystals, m. p.  $175^{\circ}$ .

4-Amino-1:5-diphenyl-1:2:3-triazole,  $\text{NPh} \begin{matrix} \text{N}=\text{N} \\ \text{CPh} \cdot \text{C} \cdot \text{NH}_2 \end{matrix}$ , obtained

by the reduction of 1:5-diphenyl-1:2:3-triazole-4-azoacetophenone with zinc dust and ammonia in alcoholic suspension, forms colourless needles, m. p.  $124^{\circ}$ . Its constitution follows from its synthesis from

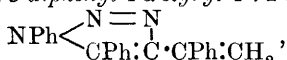
ethyl 1:5-diphenyl-1:2:3-triazole-4-carboxylate,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{N} \\ | \\ \text{CPh}:\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$  (Abstr., 1903, i, 127), which was first converted into its *hydrazide*,  $\text{C}_{15}\text{H}_{13}\text{ON}_5$ ; this separates from water in colourless needles, m. p. 166—167°. The corresponding *azoimide*, m. p. 111—112°, when boiled with alcohol, forms the *urethane*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_4$ , from which 4-amino-1:5-diphenyl-1:2:3-triazole is readily obtained by boiling with concentrated hydrochloric acid. When the base is diazotised and then coupled with ethyl benzoylacetate, it forms the azo-compound, *ethyl 1:5-diphenyl-1:2:3-triazole-4-azobenzoylacetate*,



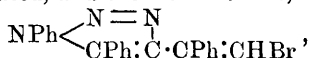
which crystallises in yellow needles, m. p. 148°, from which on boiling with alcoholic potassium hydroxide the carbethoxy-group is eliminated with the formation of a compound identical in all respects with that obtained by the interaction of phenylazoimide with acetophenone.

The mechanism of the formation of 1:5-diphenyl-1:2:3-triazole-4-azoacetophenone from phenylazoimide and acetophenone is discussed; it is assumed that the first phase of the action consists in the formation of a diazoamino-compound.

When phenylazoimide and dyponne are condensed in presence of sodium ethoxide, 1:5-diphenyl-4-*α*-styryl-1:2:3-triazole,



is obtained; it forms yellow prisms, m. p. 127—128°. The action is represented by the equation  $\text{C}_6\text{H}_5\text{N}_3 + \text{C}_{16}\text{H}_{14}\text{O} = \text{C}_{22}\text{H}_{17}\text{N}_3 + \text{H}_2\text{O}$ . The compound is unsaturated, uniting with bromine to form the *dibromide*,  $\text{C}_{22}\text{H}_{17}\text{N}_3\text{Br}_2$ , which crystallises in colourless needles and melts and decomposes at 195°. When boiled with alcohol, hydrogen bromide is quantitatively eliminated, and the *monobromide*,

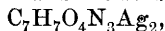


obtained; the latter separates in colourless prisms, m. p. 112—113°. When oxidised by permanganate in the cold, 1:5-diphenyl-4-*α*-styryl-1:2:3-triazole forms 4-benzoyl-1:5-diphenyl-1:2:3-triazole,

$\text{NPh} \begin{smallmatrix} \text{N}=\text{N} \\ | \\ \text{CPh}:\text{C}\cdot\text{Bz} \end{smallmatrix}$ , which separates from alcohol in spear-shaped crystals, m. p. 166°. The same compound may be formed by the condensation of phenylazoimide with dibenzoylmethane in the presence of sodium methoxide.  
A. McK.

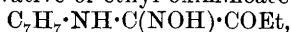
**Compounds containing a previously Unknown Ring. II.**  
MILORAD Z. JOVITSCHITSCH (*Ber.*, 1906, **39**, 3821—3830. Compare Abstr., 1898, i, 93; 1899, i, 239; 1902, i, 202).—After repeated recrystallisations from water, phenyldioxatriazine crystallises in light green needles, commences to decompose above 250°, and forms a gelatinous silver salt. When boiled with an excess of *N*/10 alkali hydroxide solution, phenyldioxatriazine or its ethyl carboxylate yields a deep red solution of the sodium derivative of phenyldihydroxydi

hydrodioxatriazine and not of phenyldioxatriazine as previously supposed. 3 : 6-Dihydroxy-4-phenyldihydro-1 : 2 : 3 : 4 : 6-dioxatriazine,  $\text{C}_6\text{H}_2\cdot\text{N}(\text{OH})\cdot\text{O}$ ,  $\text{NPh}\cdot\text{N}(\text{OH})\cdot\text{O}$ , crystallises in golden scales, m. p.  $205^\circ$ , and is moderately soluble in alcohol. The *monoalkali* salts become yellow on exposure to air; the *dialkali* salts are stable; the *silver* salt,



is reddish-brown.

The *o*-toluidine derivative of ethyl oximinoacetate,



prepared in a quantitative yield by the action of 2 mols. of *o*-toluidine on ethyl chloro-oximinoacetate in ethereal solution, crystallises in white octahedra, m. p.  $88^\circ$ , the *m*-toluidine derivative, m. p.  $123^\circ$ , obtained in the same way, but in poorer yields, crystallises on dilution of its alcoholic solution. The *p*-toluidine derivative, m. p.  $125^\circ$ , crystallises on evaporation of its ethereal solution. The *m*-xylylidine derivative, m. p.  $79^\circ$ , crystallises from dilute alcohol.

Ethyl 4-*o*-tolyldioxatriazine-5-carboxylate,  $\text{C}_6\text{H}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{O}$ ,  $\text{N}(\text{C}_7\text{H}_7)\text{—N}\cdot\text{O}$ , formed

by the action of nitrous acid on the *o*-toluidine derivative of ethyl oximinoacetate in concentrated sulphuric acid, crystallises in silky, matted, voluminous needles, m. p.  $157^\circ$ , decomposes immediately above its melting point, and dissolves in aqueous alkali hydroxides, forming a violet *monoalkali* salt; the *silver* salt is red. 4-*o*-Tolyldioxatriazine, prepared by hydrolysis of the ethyl carboxylate with more than 2 mols. of *N*/10 alkali hydroxide, crystallises from hot water in light yellow needles, commences to blacken at  $240^\circ$ , m. p.  $254^\circ$ , forms a yellow, gelatinous *silver* salt, and when boiled with an acid yields a substance crystallising in white needles, m. p.  $254^\circ$ , and giving an intense yellow coloration with alkali hydroxides. 3 : 6-Dihydroxy-4-*o*-tolyl-dihydrodioxatriazine, formed by boiling the dioxatriazine or its ethyl carboxylate with an excess of *N*/10 alkali hydroxide, crystallises from hot water in slender, golden scales, m. p.  $178^\circ$ , forms *mono*- and *di*-alkali and a *silver* salt, and when boiled with acids yields the white substance, m. p.  $254^\circ$ . Ethyl 4-*m*-tolyl-dioxatriazine-5 carboxylate is formed in the same manner and has properties similar to those of the *o*-tolyl compound.

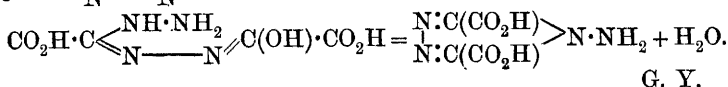
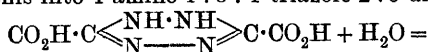
Ethyl 4-*m*-xylyldioxatriazinecarboxylate gives violet to red colorations with alkali hydroxides.

G. Y.

"Dihydrotetrazine." Condensation of 1-Amino-1 : 3 : 4 triazole with Acetylacetone. CARL BÜLOW (*Ber.*, 1906, 39, 4106—4109. Compare *Abstr.*, 1906, i, 905).—As ethyl 1-(1')-triazole-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, like other pyrrole derivatives prepared by condensation of amines with ethyl diacetyl succinate, does not give the characteristic pyrrole reactions, the author has prepared 1-(4')-triazole-2 : 5-dimethylpyrrole,  $\begin{array}{c} \text{N}:\text{CH} \\ \text{N}:\text{CH} \end{array} > \text{N}\cdot\text{N} < \begin{array}{c} \text{CMe}:\text{CH} \\ \text{CMe}:\text{CH} \end{array}$ , by boiling 1-amino-1 : 2 : 4-triazole with acetylacetone in acetic acid solution. This crystallises in long, stout needles, m. p.  $151^\circ$ , is readily soluble in

organic solvents with the exception of light petroleum, and gives Laubenheimer's pyrrole reaction.

Curtius, Darapsky, and Müller's formula for bisdiazooacetic acid (this vol., i, 21) allows of a simple explanation of the conversion of this into 1-amino-1:3:4-triazole-2:5-dicarboxylic acid:



G. Y.

**Electrochemical Reduction of *o*-Nitroacetanilide.** KURT BRAND and EDWARD STOHR (*Ber.*, 1906, **39**, 4058—4068. Compare Brand, *Abstr.*, 1905, i, 770; Bamberger, *Abstr.*, 1895, i, 217; Elbs, *Abstr.*, 1901, i, 74; Willstätter and Pfannenstiel, *Abstr.*, 1905, i, 723; Niementowski, *Abstr.*, 1906, i, 319).—The electrochemical reduction of *o*-nitroacetanilide in a solution of sodium acetate in alcohol, water, and ethyl acetate, with a nickel wire gauze cathode and a current density of 2—3 amperes per square decimetre, in the cold, leads to the formation of *o*-azoacetanilide, in a 25 % yield, and traces of *o*-nitroaniline, *o*-phenylenediamine, and 2-methylbenziminazole. If a mercury cathode is employed, *o*-azoxyacetanilide also is obtained, but only in small quantity as it is readily reduced further to *o*-azoacetanilide.

The principal product of the reduction in mineral acid solution is *o*-phenylenediamine, whilst 2-methylbenziminazole is formed in concentrated acetic acid solution in presence of sodium acetate and stannous chloride.

On reduction in the manner previously described for nitrobenzene (*Abstr.*, 1905, i, 770), but in a solution of sodium acetate in glacial acetic acid and alcohol, and with a current density of 5 amperes per square decimetre, *o*-nitroacetanilide yields *o*-azoxy- and *o*-azo-acetanilide and *o*-hydroxylaminoacetanilide,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$ , which remains in solution, and reduces silver nitrate and Fehling's solutions; it changes gradually in neutral solution into *o*-azoacetanilide or more rapidly in alkaline solution, when *o*-azoxyacetanilide, 2-methylbenziminazole, and *o*-nitroaniline also are formed. Oxidation of *o*-hydroxylaminoacetanilide by means of silver nitrate, copper sulphate, or ferric chloride in sodium acetate solution, leads to the formation of *o*-nitrosoacetanilide,  $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , which crystallises in stout needles or leaflets, m. p. 105—106°, and is converted into *o*-azoxyacetanilide when boiled with alcohol or treated with dilute acids or alkali hydroxides at the ordinary temperature.

*o*-Azoxyacetanilide,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{NHAc})_2$ , is prepared by the action of sodium hydroxide on a molecular solution of *o*-nitrosoacetanilide and *o*-hydroxylaminoacetanilide in alcohol. It crystallises in brownish-orange-yellow leaflets or needles, m. p. 185°, and when boiled with moderately concentrated alcoholic hydrogen chloride, yields *o*-azoxyaniline,  $\text{C}_{12}\text{H}_{12}\text{ON}_4$ , which crystallises in red needles, m. p. 115°; the hydrochloride,  $\text{C}_{12}\text{H}_{12}\text{ON}_4\cdot 2\text{HCl}$ , forms greyish-yellow leaflets, m. p. 220°,

decomposing. The base yields *o*-azoxybenzanilide when benzoylated in pyridine solution.

The action of formaldehyde on *o*-hydroxylaminoacetanilide in neutral solution leads to the formation of the *condensation* product,  $\text{CH}_2(\text{O}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc})_2$ , which is obtained in yellow needles, m. p.  $144^\circ$ , decomposing, is insoluble in almost all organic solvents, and when boiled with alcohol or dilute acids or alkali hydroxides, decomposes to formaldehyde and *o*-azoxyacetanilide.

*Benzylidene-o-aminoacetanilide*,  $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , is formed by reduction of *o*-nitroacetanilide in the same manner as described above for the preparation of *o*-hydroxylaminoacetanilide but with a current density of 10 amperes per square decimetre, and addition of benzaldehyde to the reduced solution. It crystallises in glistening, golden-yellow leaflets, m. p.  $125^\circ$ , forms benzaldehyde on prolonged boiling with water, and yields 2-methylbenziminazole and benzaldehyde when heated with dilute acids. G. Y.

**Change of Colour in Constitutively Unchangeable Substances.** ARTHUR HANTZSCH and W. H. GLOVER (*Ber.*, 1906, 39, 4153—4174).—Solutions of "neutral" substances such as azo-compounds, quinones, and diketones have been examined by green light in Martens and Grünbaum's improved form of König's spectrophotometer. In accordance with Beer's law, the colour intensity is proportional to the concentration. The colour of any one substance depends very largely on the nature of the solvent, those containing oxygen forming solutions of a lighter shade, probably containing a loose molecular compound of solvent and solute. The alkali salts of hydroxyazo-compounds and of quinonedioximes are more intensely coloured than the parent substances; the same is true of the alkyl and acyl derivatives of benzeneazophenol and of tolueneazophenol (compare Kauffmann, *Abstr.*, 1906, i, 577), the colour intensity being independent of the nature of the substituent but proportional to the molecular weight. Of the derivatives of  $\beta$ -naphthaquinonedioxime, the alkyl and acyl compounds are the least coloured, and the alkali salts most intensely coloured.

The new compounds described are: *p*-benzeneazophenyl benzyl ether,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , yellow needles, m. p.  $116^\circ$ ; *tolueneazophenyl benzoate*,  $\text{C}_7\text{H}_7\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ , orange-red prisms, m. p.  $158^\circ$ ; various metallic salts of *o*-benzoquinonedioxime; *benzylloxylaminotribromo-o-benzoquinone*,  $\text{C}_7\text{H}_7\cdot\text{O}\cdot\text{NH}\cdot\text{C}_6\text{Br}_3\text{O}_2$ , orange-yellow needles, m. p.  $170^\circ$ , decomposing; the *benzoyl* derivative of  $\beta$ -naphthaquinonedioxime  $\alpha$ -methyl ether,  $\text{OMe}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NOBz}$ , faintly yellow leaflets, m. p.  $119^\circ$ ;  $\beta$ -naphthaquinonemonooxime benzyl ether,  $\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{OC}_7\text{H}_7$ , golden-yellow prisms, m. p.  $101^\circ$ ;  $\beta$ -naphthaquinonedioxime benzyl ether,  $\text{NOH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{OC}_7\text{H}_7$ , yellow prisms, m. p.  $168^\circ$ , and its *benzoyl* derivative,  $\text{NOBz}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{OC}_7\text{H}_7$ , faintly yellow needles, m. p.  $116^\circ$ . C. S.

**Behaviour of Certain Artificial Dyes with Liquid Sulphur Dioxide.** EUGENE GRANDMOUGIN (*Zeit. Farb. Ind.*, 1906, 5, 383—385).—The colours produced by dissolving azo-dyes in liquid sulphur dioxide are comparable with those given by the same dyes when

dissolved in acetic acid, and different from the colours obtained with concentrated sulphuric acid. It appears that salt formation does not occur and that the liquid sulphur dioxides acts merely as a solvent. The substances examined were : azobenzene, hydroxyazobenzene, aminoazobenzene, benzeneazo- $\beta$ -naphthol, 1:2- and 1:4-benzeneazo- $\alpha$ -naphthols, benzeneazo-salicylic acid, benzeneazo- $\alpha$ -hydroxynaphthoic acid, and benzenedisazo- $\alpha$ -naphthol.

Several of these can be recrystallised from liquid sulphur dioxide.

W. A. D.

**The Chemical Functions of Textile Fibres.** LÉO VIGNON (*Compt. rend.*, 1906, 143, 550—552).—The author has shown previously (Abstr., 1890, 553, 939; *Compt. rend.*, 1898, 127, 872) that from a chemical point of view fabrics of animal origin are to be considered as amino-acids, and those of vegetable origin as alcohols; the present paper contains an account of experiments made on wool, silk, and cotton to determine the partition coefficient of an acid, base, or salt between the fabric and water. The experiments were conducted by immersing skeins of known weight for one hour at the ordinary temperature in 1 or 0.1 per cent solutions of acids, bases, or salts, and determining the amount of acid, base, or salt in the bath both before and after the experiment. Control experiments were also made in which the fabric was replaced by pure pulverised wood charcoal. The results confirm the conclusions of the earlier experiments, and show further that the acidic or basic functions of the textile fibre increase with the dilution of the aqueous solution of the base or acid, and that porous substances such as charcoal are chemically inert.

M. A. W.

**Heat Production and Enzyme Action. I. General.** FRANZ TANGL (*Pflüger's Archiv*, 1906, 114, 1—6). **II. Action of Pepsin.** ROLAND VON LENGYEL (*ibid.*, 7—10). **III. Action of Trypsin.** PAUL HÁRI (*ibid.*, 11—51).—In the enzyme actions investigated, there is no change of potential into other forms of energy and no apparent development of heat.

W. D. H.

**Catalases.** AMEDEO HERLITZKA (*Atti. R. Accad. Lincei*, 1906, [v], 15, ii, 333—341).—The action of catalases on hydrogen peroxide is not a unimolecular reaction, and further, as the partial pressure or concentration of the oxygen has no influence on the action of catalases, the action is not a reversible one.

In presence of small quantities of manganese lactate, hydrogen peroxide prevents the oxidation of guaiacum resin. This apparently paradoxical behaviour is explained according to the views of Bertrand (compare Abstr., 1897, ii, 493; 1898, i, 53), who showed that, the weaker the acid of a manganese salt the greater is the oxidising action of the salt. Further, the weaker the acid, the greater will be the amount of hydrolysis of the manganese salt and hence the greater the concentration of the oxide of manganese formed. But the increased ionising action of hydrogen peroxide over that of water causes considerable dissociation of even weak acids, so that the hydrolysis of the



manganese salt and the formation of oxide of manganese become very limited. If, however, catalase is added, the hydrogen peroxide is destroyed and the guaiacum resin consequently oxidised. T. H. P.

**Studies on Enzyme Action. Lipase II.** HENRY E. ARMSTRONG and ERNEST ORMEROD (*Proc. Roy. Soc.*, 1906, B., 78, 376—385. Compare Abstr., 1906, i, 126).—Experiments made in the hope of discovering an explanation of the selective power displayed by the enzyme, which by preference promotes the hydrolysis of esters of the higher fatty acids, such as occur in natural fats. *Ricinus* lipase alone has very little or no effect on ethyl butyrate. In presence of *N*/5 acetic acid, the butyrate is slowly hydrolysed. The extent of hydrolysis depends both on the amount of enzyme and to a certain point on the proportion of acid present. In the case of natural fats the liberated acids are too feeble and too insoluble materially to affect the process. Glycerol only retards hydrolysis when more than 25 per cent. is present; and the retarding effect of alcohol is approximately proportional to the amount.

Since the ethereal salts hydrolysed under the influence of lipase are all of the type  $R' \cdot CO \cdot OX$ , and both  $R'$  and  $X'$  may be varied within wide limits, it follows that the carboxyl group is the controlling influence. It is suggested that the association of the enzyme with carboxyl may be prevented by hydration, so that salts which are the more attractive of water will be the less readily hydrolysed. This would accord with the fact that the higher members of the acetic acid series are more readily hydrolysed by lipase (although not by ordinary hydrolytic agents) than the lower members which tend to form hydrates (hydrols) such as  $OEt \cdot CMe(OH)_2$ ; and the hypothesis is also strikingly supported by comparative results obtained with ethylic malonate, succinate, malate, and tartrate.

Animal lipase seems to differ from vegetable lipase only in being less active, the superiority of the seed residue being perhaps due to its much greater emulsifying power.

It is important, especially when employing animal lipase, that the esters to be compared should be in solution.

N. H. J. M.

**Hydrolytic Action of the Maltase of Malt.** LUIGI MARINO and G. FIORENTINO (*Gazzetta*, 1906, 36, ii, 395—427).—The maltase of malt decomposes maltose and also those natural and artificial glucosides which are decomposed by emulsin. Of the artificial glucosides, maltase of malt only attacks the  $\beta$ -compounds of dextrose; it is hence supposed that those natural glucosides which are acted on by maltase are also  $\beta$ -derivatives of dextrose. The results indicate that one enzyme alone can produce hydrolysis in cases in which recourse was formerly had to the action of two or more enzymes, and indicate also the general applicability of Fischer's law concerning the relations between the configuration and the action of enzymes. Maltase obtained by the method of Marino and Sericano (Abstr., 1906, i, 125) contains no emulsin, since, when a concentrated solution of it acts on amygdalin, the hydrogen cyanide liberated renders the

maltase almost inactive, and, if the enzyme is recovered, it is found to have only an extremely slight action on maltose or salicin; under identical conditions, the addition of a trace of emulsin to the recovered enzyme leads to the decomposition of at least 75 per cent. of the salicin taken.

Maltase obtained from malt, like that of beer yeast, is able to act synthetically, yielding *isomaltose*, so that it is probable that, if the two maltases were purified, they would be found to be identical.

Benzaldehyde and hydrocyanic acid have no influence on the activity of emulsin. T. H. P.

**Alcoholic Ferment of Yeast-juice. Part II. Co-ferment of Yeast-juice.** ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1906, B, 78, 369—375. Compare Abstr., 1906, i, 470).—The residue obtained by filtering yeast-juice through a Martin gelatin filter can be completely freed from the co-ferment by redissolving in water and filtering; it is then dried for fifteen hours over sulphuric acid in a vacuum. The inactive residue loses its potential activity slowly; after two months the rate of fermentation in presence of boiled yeast-juice was about one-third of that attained with the freshly prepared residue.

Cessation of fermentation in a mixture of the inactive residue and co-ferment may be due to the disappearance of either the one or the other, according to the relative amounts originally present. In absence of dextrose, the co-ferment usually disappears in about forty-eight hours (at 26°); in presence of 10 per cent. of dextrose a small amount of co-ferment remained at the end of four days.

Whilst, as previously shown, soluble phosphates exert a remarkable effect on the fermentation of dextrose by yeast-juice, their addition to a solution of the inactive residue in dextrose does not set up fermentation. N. H. J. M.

**Comparative Investigations of Vegetable Proteolytic Ferments.** EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, 49, 21—25).—Yeast-juice splits glycylglycine and glycyl-*l*-tyrosine. The latter peptide lends itself very well to such experiments because it is readily soluble in water; it is also split by papain, but not by the fluid from the pitchers of *Nepenthes*. W. D. H.

**The Action of Proteolytic Ferments of Germinating Seeds of Wheat and Lupins on Polypeptides.** EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, 49, 26—30).—The juices expressed from the germinating seeds of wheat and lupin seeds split *dl*-leucylglycine, glycylglycine, and dialanyl cystine. In no case was an amino-group eliminated. W. D. H.

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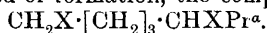
## Organic Chemistry.

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**Melting Points of Hydrocarbons Homologous with Methane.** D. E. TSAKALOTOS (*Compt. rend.*, 1906, 143, 1235—1236).—When the boiling points of the members of a homologous series are plotted against the number of carbon atoms the curve thus obtained is smooth (Young, Abstr., 1905, ii, 231), but the m. p. curve, similarly constructed, shows a number of zigzags (maxima and minima), and in the case of the hydrocarbons of the methane series the curve is irregular from  $C_9H_{20}$  to  $C_{15}H_{32}$ , and then becomes regular up to  $C_{60}H_{122}$ . The melting points of the hydrocarbons between the limits  $C_{16}H_{34}$  and  $C_{60}H_{122}$  can be calculated from the formula  $\Delta n = [85 - 0.01882(n - 1)^2]/(n - 1)$ , where  $\Delta n$  is the difference between the m. p. of one hydrocarbon of the series and that of its next higher homologue and  $n$  is the number of carbon atoms in the molecule. In the original are tabulated the experimental and calculated values of the known hydrocarbons of the methane series between the values  $n = 16$  and  $n = 60$ , and with the exception of the hydrocarbon  $C_{35}H_{72}$ , there is a very close agreement between the two sets of values. M. A. W.

**Preservation of Chloroform.** PIERRE BRETEAU and PAUL WOOG (*Compt. rend.*, 1906, 143, 1193—1195).—Chloroform exposed to air and light decomposes into hydrogen chloride and phosgene; and the latter is very toxic. It is essential for the surgeon that chloroform should be pure, and impurities of the kind indicated are best detected by congo-red, which is turned blue. This succeeds when silver nitrate gives no trace of precipitate. W. D. H.

**Conversion of Conine into Dichloro- and Dibromo-Octanes.** JULIUS VON BRAUN and E. SCHMITZ (*Ber.*, 1906, 39, 4365—4369).—The action of phosphorus penta-chloride or -bromide on benzoylconine leads to the formation of *dichloro-octane*, b. p. 105—107°/16 mm. and of *dibromo-octane*, b. p. 123—129°/11 mm. respectively, which should have, from their method of formation, the composition



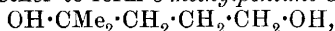
Conine derivatives cannot be re-formed from these substances; only one-half of the halogen is displaced by the action of benzylamine or of potassium cyanide. C. S.

**Synthesis of Halogenated *tert.*-Alcohols by Means of Organo-magnesium Compounds.** Mdle. R. DALEBROUX and HENRI WUYTS (*Bull. Soc. chim., Belg.*, 1906, 20, 156—158. Compare Henry, Abstr., 1906, i, 133, and Süsskind, *ibid.*).—Ethyl chloroacetate (1 mol.) reacts with magnesium ethyl bromide (3 mols.), in presence of ether, to form a complex, which on treatment with water furnishes *chloromethyl-diethylcarbinol*,  $CH_2Cl \cdot C(Et)_2 \cdot OH$ , a slightly viscous liquid, b. p. 70°/20 mm.,  $D_4^{15}$  1.0267. When distilled with a slight excess of

potassium hydroxide it yields *aa-diethylethylene oxide*,  $\text{O} \begin{smallmatrix} \text{CEt}_2 \\ \text{CEt}_2 \end{smallmatrix}$ , a mobile liquid with a slight odour of mint, b. p.  $107^\circ$ ,  $D_4^{15}$  0.8403.

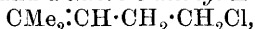
Ethyl  $\beta$ -iodopropionate reacts similarly with magnesium ethyl bromide, forming  $\gamma$ -*iodo-aa-diethylpropyl alcohol*,  $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{CEt}_2 \cdot \text{OH}$ , a slightly viscous liquid with a characteristic odour. This on distillation over potassium hydroxide yields *aa-diethylpropylene oxide*,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CEt}_2 \end{smallmatrix} \text{O}$ , a colourless, mobile liquid with an odour simultaneously recalling those of anise and of mint; b. p.  $128-130^\circ$ . T. A. H.

**Butyrolactone and *as*-Dimethylsuccinic Glycol [ $\delta$ -Methylpentane- $\alpha\delta$ -diol].** LOUIS HENRY (*Compt. rend.*, 1906, 143, 1221—1225. Compare Houben, *Abstr.*, 1904, i, 334).—Butyrolactone (*Abstr.*, 1886, 216) reacts with magnesium methyl iodide in the presence of dry ether to form  *$\delta$ -methylpentane- $\alpha\delta$ -diol*,



which is a viscous, colourless, odourless liquid with a bitter-sweet taste, b. p.  $158^\circ/65$  mm. or  $222^\circ/774$  mm. (corr.). It contains both the tertiary and primary alcoholic groupings, and reacts (1) with acetyl chloride to form the *chloroacetin*,  $\text{CMe}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OAc}$  ( *$\delta$ -chloro- $\delta$ -methylpentyl acetate*), a colourless, mobile liquid with a disagreeable odour, b. p.  $132^\circ/70$  mm. or  $190^\circ/747$  mm. with evolution of hydrogen chloride; and (2) with dilute sulphuric acid (15%) to form its *oxide* (2 : 2-dimethyltetrahydrofuran),  $\text{O} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$ , a colourless, mobile liquid, b. p.  $95^\circ/756$  mm.

Ethyl  $\gamma$ -chlorobutyrate,  $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , yields with magnesium methyl bromide the *chlorohydrin* ( $\alpha$ -chloro- $\delta$ -methylpentane- $\delta$ -ol),  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$ , which decomposes on heating into 2 : 2-dimethyltetrahydrofuran and  $\alpha$ -chloro- $\delta$ -methyl- $\Delta^7$ -amylene,



b. p.  $135^\circ$ ; and is converted by the action of fuming hydrochloric acid or acetyl chloride into the *dichlorohydrin* ( $\alpha\delta$ -dichloro- $\delta$ -methylpentane),  $\text{CMe}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$ , b. p.  $179-180^\circ$ , which does not solidify at  $-80^\circ$ . M. A. W.

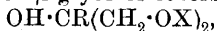
**Influence of Radicles on the Character of the Residual Valencies of Oxygen.** WLADIMIR TSCHELINZEFF (*Compt. rend.*, 1906, 143, 1237—1239. Compare *Abstr.*, 1905, ii, 802; 1906, ii, 334; Blaise, *Abstr.*, 1901, i, 317).—The author has measured the thermal effects  $q$  and  $q'$  corresponding with the combination of an alkyl magnesium iodide with two successive molecular proportions of an

	$q$ .	$q'$ .	$Q$ .	$Q = q + q'$ .
$\text{OEt}_2$ .....	6.63	6.16	12.60	12.79
$\text{EtO} \cdot \text{C}_8\text{H}_7$ .....	6.15	5.93	12.12	12.08
$\text{EtO} \cdot \text{C}_4\text{H}_9(\text{iso})$ .....	5.84	5.37	11.40	11.21
$\text{EtO} \cdot \text{C}_5\text{H}_{11}(\text{iso})$ .....	6.17	5.47	11.73	11.64
$\text{O}(\text{C}_5\text{H}_{11})_2(\text{iso})$ .....	5.91	4.54	10.31	10.45
$\text{PhOMe}$ .....	—	—	—	—
$\text{PhOEt}$ .....	—	—	—	—

ether, also the value  $Q$  of its direct combination with 2 mols. of the ether; the alkyl magnesium iodide employed was  $C_3H_7MgI$ , and the results are tabulated on p. 106.

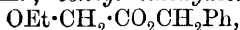
These figures show that in the aliphatic ethers the replacement of one radicle by another (with the exception of the *isoamyl* group) has very little effect on the character of the residual valencies of the oxygen atoms; but in the case of the aromatic radicles the nature of the reaction is quite different, there being practically no thermal effect accompanying the addition of one phenyl group. M. A. W.

**Complex Ether-Oxides.** MARCEL SOMMELET (*Ann. Chim. Phys.*, 1906, [viii], 9, 484—576).—A detailed account of the preparation and properties of the  $\alpha$ -glycol ethers of the types  $OH \cdot CR_2 \cdot CH_2 \cdot OX$  and  $OH \cdot CRR' \cdot CH_2 \cdot OX$ , and of  $\beta$ -glycerol ethers of the type



and of the aldehydes of the respective types  $CR_2H \cdot CHO$ ,  $CRR' H \cdot CHO$ , and  $CH_2 \cdot CR \cdot CHO$  derived from them. Certain of these compounds have already been described in two earlier papers (Behal and Sommelet, *Abstr.*, 1904, i, 222; and Sommelet, this vol., i, 21), and will therefore only be referred to in this present abstract in the cases where their physical constants have been amended or extended.

Alkyl esters of ethoxyacetic acid are readily prepared by the action of the corresponding alcohol on ethoxyacetic acid in the presence of hydrochloric acid; *isobutyl ethoxyacetate*,  $OEt \cdot CH_2 \cdot CO_2C_4H_9$ , b. p.  $186^\circ/755$  mm. (corr.); *isoamyl ethoxyacetate*,  $OEt \cdot CH_2 \cdot CO_2C_5H_{11}$ , b. p.  $204-205^\circ/756$  mm.; *benzyl ethoxyacetate*,



b. p.  $155^\circ/21$  mm.; *phenyl ethoxyacetate*, obtained by the action of phenol on ethoxyacetyl chloride in pyridine solution, b. p.  $139^\circ/18$  mm.; *ethoxyacetic anhydride*,  $(OEt \cdot CH_2 \cdot CO)_2O$ , b. p.  $142-143^\circ/125$  mm.

*Ethoxyacetylacetone*,  $OEt \cdot CH_2 \cdot CO \cdot CH_2 \cdot COMe$ , prepared from acetone and ethyl ethoxyacetate by the Claisen condensation, is a colourless oil, b. p.  $83-84^\circ/13$  mm.; its *copper* derivative forms blue needles, m. p.  $149^\circ$ . *Ethoxyacetyl methylacetone*,  $OEt \cdot CH_2 \cdot CO \cdot CHMe \cdot COMe$ , prepared by the action of methyl iodide on the sodium derivative of ethoxyacetylacetone in sealed tubes at  $125^\circ$ , is a pale yellow liquid, b. p.  $103-105^\circ/15$  mm.; *ethoxyacetyl ethylacetone*, b. p.  $116^\circ/15$  mm.

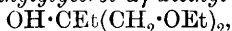
Of the ketones of the type  $R \cdot CO \cdot CH_2 \cdot OEt$  (*Abstr.*, 1904, i, 222), prepared by the action of organomagnesium compounds on the corresponding cyanoalkyloxymethanes (this vol., i, 21), the densities and amended boiling points are given, and the semicarbazones described. *Ethoxyacetone-semicarbazone*,  $OEt \cdot CH_2 \cdot CMe \cdot N \cdot NH \cdot CO \cdot NH_2$ , forms prismatic needles, m. p.  $96^\circ$  (compare Leonardi and Franchis, *Abstr.*, 1903, i, 788).  $\alpha$ -Ethoxybutanone, b. p.  $55^\circ/24$  mm. or  $62.5^\circ/33$  mm.;  $D_4^{16}$  0.914; the *semicarbazone*, m. p.  $87^\circ$ .  $\alpha$ -Ethoxypentanone, b. p.  $60^\circ/11$  mm. or  $64-65^\circ/17$  mm.,  $D_4^{16}$  0.9218; the *semicarbazone*, m. p.  $87^\circ$ .  $\alpha$ -Ethoxy- $\delta$ -methylpentanone, b. p.  $67.5-68.5^\circ/14$  mm. or  $73-74^\circ/20$  mm. and  $D_4^{16}$  0.8912; the *semicarbazone*, m. p.  $119^\circ$ .  $\alpha$ -Ethoxy- $\epsilon$ -methylhexanone, b. p.  $88^\circ/13$  mm.; the *semicarbazone*, m. p.  $89^\circ$ .  $\omega$ -Ethoxyacetophenone

*oxime*,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{Ph} \cdot \text{NOH}$ , crystallises from ether or petroleum in prisms, m. p.  $55^\circ$ ; the *semicarbazone*, m. p.  $128^\circ$ .

The densities of the  $\alpha$ -glycol ethers,  $\text{OH} \cdot \text{CR}_2 \cdot \text{CH}_2 \cdot \text{OX}$ , already described (Abstr., 1904, i, 222), are as follows:  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OEt}$ ,  $D_4^{15}$  0.8786;  $\text{OH} \cdot \text{CEt}_2 \cdot \text{CH}_2 \cdot \text{OEt}$ ,  $D_4^{15}$  0.8961;  $\text{OH} \cdot \text{C}(\text{C}_3\text{H}_7)_2 \cdot \text{CH}_2 \cdot \text{OEt}$ ,  $D_4^{15}$  0.8716;  $\text{OH} \cdot \text{C}(\text{C}_5\text{H}_{11})_2 \cdot \text{CH}_2 \cdot \text{OEt}$ ,  $D_4^{15}$  0.8595;  $\text{OH} \cdot \text{CPh}_2 \cdot \text{CH}_2 \cdot \text{OEt}$ ,  $D_4^{15}$  1.094.

In addition to the  $\alpha$ -glycol ethers of the type  $\text{OH} \cdot \text{CRR}' \cdot \text{CH}_2 \cdot \text{OX}$  previously mentioned (Abstr., 1904, i, 222), the following are described:  $\alpha$ -ethoxy- $\beta$ -methylbutane- $\beta$ -ol,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{C}_2\text{H}_5$ , b. p.  $148$ — $149^\circ/763$  mm.,  $D_4^{16.5}$  0.8825;  $\alpha$ -ethoxy- $\beta$ -methylpentane- $\beta$ -ol,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2 \cdot \text{Et}$ , b. p.  $167$ — $168^\circ$ ,  $D_4^{16.5}$  0.8767;  $\alpha$ -ethoxy- $\beta$ -ethylpentane- $\beta$ -ol, b. p.  $182$ — $183^\circ$  or  $77^\circ/13$ — $14$  mm., and not  $180$ — $184^\circ$  as previously stated,  $D_4^{16.5}$  0.8786;  $\alpha$ -ethoxy- $\delta$ -methyl- $\beta$ -ethylpentane- $\beta$ -ol,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CEt}(\text{OH}) \cdot \text{CH}_2 \text{Pr}^a$ , b. p.  $97^\circ/26$  mm. or  $93^\circ/22$  mm.,  $D_4^{16.5}$  0.8731;  $\alpha$ -ethoxy- $\beta$ -methyloctane- $\beta$ -ol, b. p.  $102$ — $105^\circ/11$ — $12$  mm.,  $D_4^{16.5}$  0.8665;  $\alpha$ -ethoxy- $\beta$ -methylnonane- $\beta$ -ol, b. p.  $118$ — $119^\circ/11$  mm.,  $D_4^{16.5}$  0.8685;  $\alpha$ -ethoxy- $\beta$ -methylundecane- $\beta$ -ol,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{C}_9\text{H}_{19}$ , b. p.  $152$ — $153^\circ/19$  mm.,  $D_4^{16.5}$  0.8623.

$\beta$ -Glycerol ethers of the type  $\text{OH} \cdot \text{CR}(\text{CH}_2 \cdot \text{OX})_2$  are prepared by the condensation of the ethereal salt of the corresponding acid and the chloromethyl alkyl ether in the presence of magnesium and a little mercuric chloride.  $\beta$ -Ethylglycerol  $\alpha$ -diethyl ether,

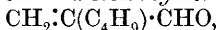


b. p.  $84$ — $86^\circ/20$  mm. or  $195^\circ/765$  mm. (corr.),  $D_4^{16.5}$  0.9503.  $\beta$ -Propylglycerol  $\alpha$ -diethyl ether,  $\text{OH} \cdot \text{CPr}^a(\text{CH}_2 \cdot \text{OEt})_2$ , b. p.  $97^\circ/16$  mm. or  $210^\circ/760$  mm.,  $D_4^{16.5}$  0.9195.  $\beta$ -isobutylglycerol  $\alpha$ -diethyl ether,  $\text{C}_4\text{H}_9 \cdot \text{C}(\text{CH}_2 \cdot \text{OEt})_2 \cdot \text{OH}$ , b. p.  $111$ — $112^\circ/23$  mm. or  $215^\circ/760$  mm.,  $D_4^{16.5}$  0.9077.  $\beta$ -isobutylglycerol  $\alpha$ -dipropyl ether,  $\text{C}_4\text{H}_9 \cdot \text{C}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_3\text{H}_7)_2 \cdot \text{OH}$ , b. p.  $139$ — $140^\circ/22$ — $23$  mm.,  $D_4^{16.5}$  0.8938.  $\beta$ -isobutylglycerol  $\alpha$ -diisobutyl ether,  $\text{C}_4\text{H}_9 \cdot \text{C}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_4\text{H}_9)_2 \cdot \text{OH}$ , b. p.  $145$ — $147^\circ/18$  mm.,  $D_4^{16.5}$  0.8766.  $\beta$ -isobutylglycerol  $\alpha$ -diisoamyl ether,  $\text{C}_4\text{H}_9 \cdot \text{C}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_5\text{H}_{11})_2 \cdot \text{OH}$ , b. p.  $162^\circ/12$  mm. or  $178^\circ/25$  mm.,  $D_4^{16.5}$  0.8785.  $\beta$ -n-Amylglycerol  $\alpha$ -diethyl ether,  $\text{C}_5\text{H}_{11} \cdot \text{C}(\text{CH}_2 \cdot \text{OEt})_2 \cdot \text{OH}$ , b. p.  $118$ — $119^\circ/13$  mm.,  $D_4^{16.5}$  0.9029.  $\beta$ -Hexylglycerol  $\alpha$ -diethyl ether,  $\text{C}_6\text{H}_{13} \cdot \text{C}(\text{CH}_2 \cdot \text{OEt})_2 \cdot \text{OH}$ , b. p.  $135$ — $136^\circ/15$  mm.,  $D_4^{16.5}$  0.9013.  $\beta$ -Decenylglycerol  $\alpha$ -diethyl ether,  $\text{C}_{10}\text{H}_{19} \cdot \text{C}(\text{CH}_2 \cdot \text{OEt})_2 \cdot \text{OH}$ , b. p.  $180^\circ/12$  mm.,  $D_4^{16.5}$  0.9.  $\beta$ -Octylglycerol  $\alpha$ -diethyl ether,  $\text{C}_8\text{H}_{17} \cdot \text{C}(\text{CH}_2 \cdot \text{OEt})_2 \cdot \text{OH}$ , b. p.  $160^\circ/15$  mm.,  $D_4^{16.5}$  0.8949.  $\beta$ -Benzylglycerol  $\alpha$ -diethyl ether,  $\text{CH}_2\text{Ph} \cdot \text{C}(\text{CH}_2 \cdot \text{OEt})_2 \cdot \text{OH}$ , b. p.  $174^\circ/14$  mm.,  $D_4^{16.5}$  1.0091.

In addition to the aldehydes of the types  $\text{CR}_2\text{H} \cdot \text{CHO}$  and  $\text{CRR}'\text{H} \cdot \text{CHO}$  previously mentioned (Abstr., 1904, i, 222), certain of their derivatives and some new members of the series are described.  $\alpha$ -Ethylbutaldehyde *oxime*, has b. p.  $95^\circ/34$  mm., and the *semicarbazone*, m. p.  $93$ — $94^\circ$ .  $\alpha$ -Propylvaleraldehyde has  $D_4^{15}$  0.8347, the *oxime*, b. p.  $126^\circ/47$  mm., and the *semicarbazone*, m. p.  $100$ — $101^\circ$ .  $\alpha$ -isoAmylisoheptaldehyde has  $D_4^{15}$  0.8261, the *oxime* b. p.  $153^\circ/29$  mm.  $\alpha$ -Ethylisohexaldehyde,  $\text{C}_7\text{H}_{13} \cdot \text{CHEt} \cdot \text{CHO}$ , b. p.  $154$ — $155^\circ$ ; the *semicarbazone*, m. p.  $97$ — $98.5^\circ$ .  $\alpha$ -Methyloctaldehyde,  $\text{C}_8\text{H}_{15} \cdot \text{CHMe} \cdot \text{CHO}$ , b. p.  $82$ — $83^\circ/20$  mm.; the *semicarbazone*, m. p.  $78$ — $80^\circ$ .

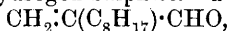
The following  $\alpha$ -alkylacraldehydes were obtained by the action of anhydrous oxalic or pure (crystallisable) formic acid on the corresponding  $\beta$ -alkylglycerol  $\alpha\gamma$ -dialkyl ethers.

$\alpha$ -Ethylacraldehyde,  $\text{CH}_3\cdot\text{CET}\cdot\text{CHO}$ , yields a crystalline semicarbazone, m. p.  $192\cdot5^\circ$ .  $\alpha$ -Propylacraldehyde,  $\text{CH}_3\cdot\text{CP}_1\alpha\cdot\text{CHO}$ , b. p.  $116$ — $118^\circ$ ; the semicarbazone, m. p.  $182^\circ$ .  $\alpha$ -isoButylacraldehyde,



b. p.  $133^\circ$ , forms the semicarbazone, m. p.  $184^\circ$ , and yields isobutylacrylic acid, b. p.  $118$ — $120^\circ/26$  mm., on oxidation with silver oxide.

$\alpha$ -Amylacraldehyde,  $\text{CH}_3\cdot\text{C}(\text{C}_5\text{H}_{11})\cdot\text{CHO}$ , b. p.  $59^\circ/13$  mm.; the semicarbazone, m. p.  $154\cdot5^\circ$ .  $\alpha$ -Hexylacraldehyde,  $\text{CH}_3\cdot\text{C}(\text{C}_6\text{H}_{13})\cdot\text{CHO}$ , b. p.  $78^\circ/15$  mm., yields the semicarbazone, m. p.  $156^\circ$ , and a crystalline compound with sodium hydrogen sulphite.  $\alpha$ -Octylacraldehyde,



b. p.  $104\cdot5$ — $106^\circ/14$  mm., and the semicarbazone m. p.  $147\cdot5^\circ$ .  $\alpha$ -Benzylacraldehyde,  $\text{CH}_3\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{CHO}$ , b. p.  $118$ — $120^\circ/13$  mm., and the semicarbazone, m. p.  $189^\circ$ . M. A. W.

**Esterification of Arsenious Anhydride by Alcohols and Phenol.** VICTOR AUGER (*Compt. rend.*, 1906, 143, 907—909. Compare Abstr., 1902, i, 255).—Arsenious oxide is not volatile in steam, but is volatile in the vapour of methyl alcohol with the formation of methyl arsenite. Owing to the hydrolytic action of the water formed during the esterification the reaction is a balanced one, and the extent to which arsenious oxide is esterified by methyl alcohol and its homologues was determined by heating the alcohol with excess of crystalline arsenious oxide in a sealed tube at  $160$ — $180^\circ$ , and estimating the arsenic in a portion of the cooled liquid by means of iodine, the difference between this quantity and the amount of arsenious oxide dissolved by the same quantity of alcohol in the cold representing approximately the amount of ester formed. In the case of methyl alcohol and arsenious oxide the equilibrium stage is reached in the cold in fourteen hours when  $5\cdot16\%$  of ester is formed; after three hours at  $150^\circ$ ,  $6\cdot5\%$  of ester is formed, but after eighteen hours this has diminished to  $5\%$ . In the case of ethyl alcohol,  $1\cdot2\%$  of ethyl arsenite is formed on heating, and the corresponding numbers for propyl, isopropyl, isobutyl, and isoamyl alcohols are  $1\cdot153$ ,  $0\cdot112$ ,  $0\cdot36$ , and  $0\cdot19$  respectively.

It is possible to isolate the alkyl arsenites, either by fractional distillation in the case of isobutyl or isoamyl alcohol, or by removing the water from the alcohol and aqueous distillate by means of calcium carbide in the case of the other alcohols, and the following alkyl arsenites were thus formed: propyl arsenite,  $\text{As}(\text{OC}_3\text{H}_7)_3$ , b. p.  $217^\circ$ ; n-butyl arsenite,  $\text{As}(\text{OC}_4\text{H}_9)_3$ , b. p.  $263^\circ$ ; and isobutyl arsenite,  $\text{As}(\text{OC}_4\text{H}_9)_3$ , b. p.  $242^\circ$ .

Phenyl arsenite is formed when phenol is heated with excess of arsenious oxide. M. A. W.

**Constitution of the Salts of Glucinum with the Fatty Acids, and the Valency of Glucinum.** BORIS GLASMANN (*Chem. Zeit.*, 1907, 31, 8—9).—According to Tanatar (Abstr., 1904, ii, 335) the

composition of the volatile glucinum compounds described by Urbain and Lacombe (Abstr., 1902, i, 132) should be expressed by the formula  $\text{Gl}_2\text{OR}_6$ , in which glucinum is quadrivalent, and not by the formula  $\text{Gl}_4\text{OR}_6$ , in which this element is bivalent. The present author, however, regards these substances as salts of bivalent glucinum with anhydrides of ortho-fatty acids. It is assumed that acetic acid can act as an octo-basic acid by the elimination of 5 mols. of water from 6 mols. of ortho acid,  $6\text{CH}_3\cdot\text{C}(\text{OH})_3 = (\text{CH}_3\text{C})_6\text{O}_5(\text{OH})_8 + 5\text{H}_2\text{O}$ , and the glucinum salt is regarded as a normal salt of this acid.

P. H.

**$\zeta$ -Bromoheptoic Acid.** JULIUS VON BRAUN (*Ber.*, 1906, 39, 4362—4365).— $\zeta$ -Phenoxyheptoic acid,  $\text{OPh}\cdot\text{CH}_2\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$ , m. p. 56—57°, is obtained quantitatively by hydrolysing the nitrile, prepared from  $\zeta$ -phenoxyhexyl iodide; the silver salt is a white, crystalline powder decomposed only slowly by light. The acid and hydrobromic acid react at 80° to form ultimately  $\zeta$ -bromoheptoic acid,  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$ , m. p. 30—31°, b. p. 165—167°/12 mm., which distils almost unchanged between 280° and 300°, and by treatment with hot water yields a hydroxy-acid, which does not tend to form an eight-membered lactone ring (compare Baeyer and Villiger, Abstr., 1900, i, 328).

C. S.

**Action of Reagents for the Aldehydic Function on Ethyl Glyoxalate.** LOUIS J. SIMON and G. CHAVANNE (*Compt. rend.*, 1906, 143, 904—907. Compare Abstr., 1906, i, 636).—Ethyl glyoxylate condenses with phenylhydrazine, hydroxylamine, or semicarbazide in the normal manner of compounds containing the aldehyde grouping, and the following compounds have been prepared. (1) The phenylhydrazone,  $\text{NHPh}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , readily obtained by the action of phenylhydrazine hydrochloride on ethyl glyoxylate, forms pale yellow, triclinic crystals, m. p. 131°, can be distilled under reduced pressure at 170°, and is identical with the compound obtained by von Pechmann from diazobenzene acetate and ethyl sulphohydrazimethylenecarboxylate (Abstr., 1896, i, 678; compare also Reissert, Abstr., 1895, i, 460). The potassium salt,  $\text{N}_2\text{HPh}\cdot\text{CH}\cdot\text{CO}_2\text{K}\cdot\frac{1}{2}\text{C}_2\text{H}_5\cdot\text{OH}$ , is crystalline; the acid,  $\text{N}_2\text{HPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , has m. p. 141° when heated slowly or 163° on a mercury bath (Reissert, Abstr., 1895, i, 460). (2) The oxime,  $\text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , crystallises from ether and light petroleum in long, hard needles, m. p. 35°, b. p. 115°/15 mm. or 110—111°/12 mm., is identical with ethyl isonitrosoacetate, obtained by Bouveault and Wahl by the action of nitrosylsulphuric acid on ethyl acetate (Abstr., 1904, i, 546), and on hydrolysis with dilute potassium carbonate yields the acid  $\text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , which decomposes at 130—140° according to the rate of heating (Bouveault and Wahl, *loc. cit.*); the amide,  $(\text{NOH})\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ , forms colourless, transparent, rhombic plates, which decompose at 126° (compare Ratz, Abstr., 1904, i, 857). (3) The semicarbazone,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , has m. p. 228° (decomp.); the acid decomposes at 258° on a mercury bath (Bouveault and Wahl give 240°, Abstr., 1904, i, 547). The amide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ , forms a coarse, white mass decomposing at 217—218°. M. A. W.



**Ricinoleic Acid.** ADOLF GRÜN (*Ber.*, 1906, **39**, 4400—4408. Compare Goldsobel, *Abstr.*, 1895, i, 81; Walden, *ibid.*, i, 125; Behrend, *ibid.*, i, 647).—A study of the dihydroxystearic acids obtained from ricinoleic acid with a view to the elucidation of the relations existing between oleic, ricinoleic, and dihydroxystearic acids.

When ricinoleic acid is treated with sulphuric acid at  $-5^{\circ}$  and the sulphuric esters hydrolysed, the product obtained consists of 12.6% of ricinoleic acid, 6.4% of dihydroxystearic acid, and 81% of the anhydro-compound  $C_{17}H_{33}(OH)_2 \cdot CO \cdot O \cdot C_{17}H_{33}(OH) \cdot CO_2H$ , the latter being easily converted into the acid by alcoholic potash. Juillard's acid, m. p.  $67-69^{\circ}$  (*Abstr.*, 1895, i, 82), is a mixture, and by repeated recrystallisation is resolved into four acids, one, m. p.  $120^{\circ}$ , only occurring in small quantities; the other three are dihydroxystearic acids. *Dihydroxystearic acid*,  $C_{17}H_{33}(OH)_2 \cdot CO_2H$ , m. p.  $108^{\circ}$ , crystallises from alcohol in snow-white, crystalline aggregates, and is optically inactive. Between the other two acids there is a very close connexion as the *d*- $\theta\lambda$  *dihydroxystearic acid*,

$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot [CH_2]_2 \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H$ ,  
a white, crystalline powder, m. p.  $90^{\circ}$ ,  $[\alpha]_D + 6.45^{\circ}$  in alcohol, is converted into the *d*-*l*-acid, white, waxy, spherical, crystalline aggregates, m. p.  $69.5^{\circ}$ , optically inactive, in alcoholic solution spontaneously or on heating at  $130-140^{\circ}$ . The *diacetates* are bright yellow, mobile oils, that obtained from the *d*-acid giving  $a_D + 10'$  in 25% alcoholic solution. That the acid is an  $\alpha\delta$ -dihydroxy-derivative is shown by its conversion into a pyrrole derivative.

*$\lambda$ -Bromo- $\theta$  dihydroxystearic acid*,

$CH_3 \cdot [CH_2]_5 \cdot CHBr \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H$ ,  
prepared by the action of phosphorus pentabromide on ricinoleic acid (compare Kasansky, *Abstr.*, 1900, i, 426) and oxidation of the bromo-oleic acid so obtained by potassium permanganate, is a thick, pale yellow oil, which yields a solid benzoyl derivative. The bromine atom is firmly attached to the carbon, and attempts to reduce this compound to a dihydroxystearic acid failed. Reduction by zinc and hydrochloric acid of the iodo-derivative, obtained by digestion with calcium iodide at  $100^{\circ}$ , gave stearic acid. An attempt to reduce bromo-oleic acid was also unsuccessful.

W. R.

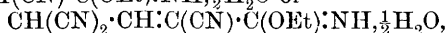
**Behaviour of Chloroform towards Methylene and Methenyl Groups.** ARTHUR KÖTZ and W. ZÖRNIG (*J. pr. Chem.*, 1906, [ii], **74**, 425—448. Compare Oppenheim and Pfaff, this *Journal*, 1874, **27**, 1161; 1875, **28**, 1261. Conrad and Guthzeit, *Abstr.*, 1883, 311. Claisen, *Abstr.*, 1897, i, 592. Errera, *Abstr.*, 1898, i, 298; 1901, i, 43; 1903, i, 265. Coutelle, *Abstr.*, 1906, i, 139).—Acetylacetone, diketohydrindene, and malononitrile react with sodium ethoxide and chloroform in a similar manner to ethyl acetoacetate or ethyl malonate, whereas chloroform and sodium ethoxide do not react with benzyl cyanide or, below  $100^{\circ}$ , with deoxybenzoin; at higher temperatures, the last substance is reduced to stilbene.

In compounds containing two or three halogen atoms attached to the same carbon atom, the first and second halogen atoms may be substituted successively by the action of ethyl sodioalkylmalonates. The

third halogen atom is exceedingly inactive, so that the halogen free compounds,  $\text{CH}[\text{CR}(\text{CO}_2\text{Et})_2]_3$ , cannot be formed by the action of chloroform on ethyl alkylmalonates, or of ethyl sodioalkylmalonates on ethyl chloromethylenebisalkylmalonates (compare Auwers and Keil, Abstr., 1903, i, 620). Only small amounts of the corresponding aldehydes have been obtained, and that with difficulty by the hydrolysis of the ethyl dichloromethylalkylmalonates.

The action of ethyl sodiomalonate on ethyl benzylidicarboxyglutaconate leads to the formation of only a small amount of ethyl benzylmalonate.

When treated with chloroform in absolute alcoholic solution, sodiomalononitrile yields *methenylbismalononitrilemonoimino-ethyl ether*,  $\text{C}(\text{CN})_2 \cdot \text{CH} \cdot \text{CH}(\text{CN}) \cdot \text{C}(\text{OEt}) \cdot \text{NH} \cdot \frac{1}{2} \text{H}_2\text{O}$  or



which is precipitated by light petroleum from its solution in benzene in small, yellow crystals, m. p.  $244^\circ$  (decomp.).

Acetylacetone reacts with sodium ethoxide and chloroform in absolute alcoholic solution in a sealed tube at  $130^\circ$ , forming 5-hydroxy-2:4-diacetyltoylene (Claisen, *loc. cit.*).

The action of sodium ethoxide and chloroform on diketohydrindene in absolute alcoholic solution leads to the formation of methenylbisdiketohydrindene (Errera, Abstr., 1903, i, 265).

*Ethyl iodomethylethylmalonate*,  $\text{CH}_2\text{I} \cdot \text{CEt}(\text{CO}_2\text{Et})_2$ , is formed by the action of an excess of methylene di-iodide on ethyl sodioethylmalonate in absolute ethereal solution; it is obtained as a colourless oil, b. p.  $137-138^\circ/12$  mm., which gradually becomes red.

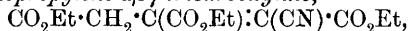
*Ethyl methylchloromethylmalonate*,  $\text{CHCl}_2 \cdot \text{CMe}(\text{CO}_2\text{Et})_2$ , and *ethyl chloromethylenebismethylmalonate*,  $\text{CHCl}[\text{CMe}(\text{CO}_2\text{Et})_2]_2$ , are formed together by the action of chloroform on ethyl sodiomethylmalonate and are separated by fractional distillation. The dichloro-ester is a transparent, white oil, b. p.  $129^\circ/12$  mm., which yields small amounts of silver chloride when heated with silver oxide and water in a sealed tube at  $100^\circ$ . The monochloro-ester forms a yellow oil, b. p.  $171-173^\circ/12$  mm.

In the same manner are formed *ethyl dichloromethylpropylmalonate*,  $\text{CHCl}_2 \cdot \text{CPr}(\text{CO}_2\text{Et})_2$ , b. p.  $156-158^\circ/16$  mm.; *ethyl chloromethylenebispropylmalonate*,  $\text{CHCl}[\text{CPr}(\text{CO}_2\text{Et})_2]_2$ , b. p.  $210-213^\circ/12$  mm.; *ethyl dichloromethylbenzylmalonate*,  $\text{CHCl}_2 \cdot \text{C}(\text{CO}_2\text{Et})_2 \cdot \text{CH}_2\text{Ph}$ , b. p.  $207-209^\circ/16$  mm., and *ethyl chloromethylenebisbenzylmalonate*,  $\text{CHCl}[\text{C}(\text{CO}_2\text{Et})_2 \cdot \text{CH}_2\text{Ph}]_2$ , b. p.  $263-265^\circ/14$  mm.

The action of chloroform and sodium ethoxide on ethyl chloromalonate in absolute alcoholic solution at  $120^\circ$  leads to the formation of ethyl ethanetetra-carboxylate.

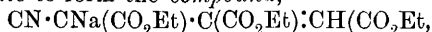
G. Y.

**Condensation of Ethyl Oxalacetate and Ethylcyanoacetate in the presence of Piperidine.** CH. SCHMITT (*Compt. rend.*, 1906, 143, 912—913. Compare Abstr., 1905, i, 508).—Ethyl oxalacetate condenses with ethyl cyanoacetate in the presence of piperidine to form *ethyl  $\alpha$ -cyanopropylene- $\alpha\beta\gamma$ -tricarboxylate*,



which crystallises from benzene in needles, m. p.  $75^\circ$ , has a neutral

reaction, and is isomeric with the acid compound obtained by Errera and Perciabosco by the action of dilute alkali on ethyl isoiminocarboxy-aconitate (Abstr., 1902, i, 116), which probably has the constitution  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}(\text{CO}_2\text{Et})$  (compare Rogerson and Thorpe, Trans., 1881, 39, 631). Ethyl oxalacetate reacts with ethyl sodiocyanoacetate to form the compound,



which yields aconitic acid when treated with hydrochloric acid, ethyl 2:6-dihydroxypyridine-4:5-dicarboxylate (ethyl dihydroxycinchomerone) when treated with cold concentrated sulphuric acid, and 2:6-dihydroxypyridine-4-carboxylic acid (citrazinic acid) on treatment with alcoholic potassium hydroxide. M. A. W.

**Tetrabromo-derivative of Methyl Ethyl Ketone.** PASTUREAU (*Compt. rend.*, 1906, 143, 967—969. Compare Abstr., 1905, i, 572).—*Methyl ethyl ketone peroxide*, formed by the action of hydrogen peroxide on the ketone in dilute acid solution, reacts with bromine in presence of water at the ordinary temperature, yielding oxygen and the tetrabromo-derivative of the ketone. The reaction is completed on the water-bath.

*Bromomethyl  $\beta\beta\beta$ -tribromoethyl ketone*,  $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CBr}_3$ , crystallises from boiling 95% alcohol in white octahedra, m. p. 50°, has an irritating odour, and is insoluble in water. When boiled with aqueous potassium carbonate in a reflux apparatus, it yields acetol and acetic and formic acids. The formation of acetol must result from the decomposition of immediately formed hydroxyacetoacetic acid,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . G. Y.

**Compounds of Ketones with Ammonia. Methyl Propyl Ketone Ammonia.** CARL THOMAE and HERMANN LEHR (*Arch. Pharm.*, 1906, 244, 664).—*Methyl propyl ketone ammonia*,  $\text{C}_{15}\text{H}_{30}\text{N}_2$  or  $\text{CMePr}(\text{N}:\text{CMePr})_2$ , was obtained as an oil by the method already employed in the preparation of analogous compounds (Abstr., 1905, i, 509); the yield was 22% of the theoretical. C. F. B.

**Physico-Chemical Investigations on Glycogen.** FILIPPO BOTTAZZI and G. D'ERRICO (*Pflüger's Archiv*, 1906, 115, 359—385).—The viscosity of glycogen solutions increases gradually with the concentration for dilute solutions, but as the solution becomes more concentrated the viscosity suddenly increases enormously with the concentration, thus pointing to some physical change in the nature of the solution. A curve is given showing the relationship between the viscosity and temperature for 10% and 20% solutions. No distinct breaks are noticeable.

The electrical conductivity of a solution of glycogen containing electrolytes first increases with the concentration, attains a maximum, then rapidly decreases, and, finally, slowly diminishes.

The melting point falls as the concentration increases, but the curve shows no characteristic breaks.

Saliva under suitable conditions reduces the viscosity of glycogen solutions, owing to its fermenting action on the carbohydrate. The

effect is the most pronounced at the beginning of the diastatic action and in concentrated solutions. If the saliva is first boiled and the diastatic ferment destroyed, no appreciable effect on the viscosity is noticeable. J. J. S.

**Novaine.** FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1906, **49**, 484. Compare this vol., i, 21).—When novaine is distilled with barium hydroxide the whole of the nitrogen is eliminated as trimethylamine. The residue contains a characteristic decomposition product which is probably crotonic acid. W. D. H.

**Hydrogenation by Catalysis of Hexamethylenetetramine.** GIUSEPPE GRASSI-CRISTALDI (*Gazzetta*, 1906, **36**, ii, 505—511) —Hexamethylenetetramine volatilises without decomposing, especially in a current of hydrogen, and sublimes on the cooler parts of the tube [S. DI FRANCO: the crystals formed are rhombic decahedra belonging to the regular system (compare Wohl, Abstr., 1886, 863)]. When a mixture of the base with reduced nickel is heated at 80° in a current of hydrogen, reduction takes place in the sense of the equation  $N(CH_2 \cdot N \cdot CH_2)_3 + 9H_2 = NMe_3 + 3NH_3 + 3CH_4$  T. H. P.

**Oxalylaminoacetic Acid: A Product of the Oxidation of Glycylglycine.** ADOLF KRAEMER (*Ber.*, 1906, **39**, 4385—4388. Compare Pollak, Abstr., 1905, i, 750).—Pollak's statement that oxalylaminoacetic acid is formed when a cold aqueous solution of glycylglycine is oxidised by calcium permanganate is confirmed, as the calcium salt prepared by Pollak's method is found to be identical with the salt obtained from Kerp and Unger's ethyl oxalylaminoacetate (Abstr., 1897, i, 269). The salt,  $C_4H_3O_5NCa \cdot 4H_2O$ , crystallises in white rhombic plates. The statement, however, that this acid is hydrolysed by hydrochloric acid into ammonia and acetic and oxalic acids is controverted, the products obtained being oxalic acid and glycine; the latter was isolated in the form of the hydrochloride of the ester; acetic acid could not be detected. W. R.

**Glutamine.** ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1906, **65**, 237—246).—Earlier results obtained with glutamine from sugar beet (Schulze and Bosshard, Abstr., 1885, 759) indicated that the substance has no appreciable rotatory power. Sellier (Abstr., 1904, i, 372) has recently examined a preparation which gave  $[\alpha]_D^{20} + 6 \cdot 15^\circ$ .

New results with seven preparations of glutamine, from mangolds, pumpkins, mustard, and brake-fern, varied from  $[\alpha]_D^{20} + 1 \cdot 9$  to  $+ 9 \cdot 5^\circ$ . The variations and the former negative result are attributed to the presence of varying amounts of racemic glutamine.

Solutions of glutamine can be distilled with magnesia at 40° without liberation of ammonia. When boiled with water alone, glutamine yields a considerable amount of ammonia; whilst by boiling in presence of magnesia nearly the whole of the nitrogen of the  $CO \cdot NH_2$  group is converted into ammonia in two hours. N. H. J. M.

**Electrolysis of Aqueous, Acetone, and Pyridine Solutions of Thiocyanates.** Part I. STEVENSON BINNING and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1906, **2**, 94—97).—On electrolysing a

20% solution of ammonia thiocyanate in water with a current density at the anode of ten amperes per square decimetre, a yellow colouring matter is obtained in 15–20% yield. In the experiments the cathode was rotated within a cylindrical anode, and it was found necessary to remove the colouring matter continuously from the surface of the anode by means of brush-like appendages attached to the cathode. The substance does not appear to be identical with canarine. It blackens when heated with pyridine. When alkaline solutions are electrolysed, the yellow substance is not formed.

Acetone solutions of ammonium thiocyanate also give rise to an orange-yellow substance when electrolysed. This substance dissolves in boiling solutions of alkali hydroxides, and is reprecipitated as a brown, flocculent substance on acidifying with sulphuric acid, hydrogen sulphide being evolved. It is not acted on by strong nitric acid at the ordinary temperature. On boiling with pyridine, a part of it dissolves and the remainder turns black.

Pyridine solutions of the thiocyanate remain clear during electrolysis, but an orange-yellow substance is precipitated when the solution is poured into ten times its volume of water. The substance dissolves in boiling alkali, is reprecipitated by sulphuric acid, and dissolves in nitric acid, from which it is reprecipitated on the addition of water. When a lead anode is used in the pyridine solution, the metal dissolves, and on pouring the solution into water light brown crystals of lead thiocyanate separate. The product is readily soluble in pyridine.

H. M. D.

**Cyanogen Bromide.** THOMAS EWAN (*J. Soc. Chem. Ind.*, 1906, **25**, 1130–1133).—In connexion with the use of cyanogen bromide as a reagent for the extraction of gold from refractory ores, the author has measured the velocity of the reactions  $\text{HBrO}_3 + 5\text{HBr} + 3\text{HCN} = 3\text{BrCN} + 3\text{HBr} + 3\text{H}_2\text{O}$ ,  $\text{HBrO}_3 + 2\text{HBr} + 3\text{HCN} = 3\text{BrCN} + 3\text{H}_2\text{O}$ ,  $\text{HBrO}_3 + 5\text{HBr} = 3\text{Br}_2 + 3\text{H}_2\text{O}$ . Solutions containing sodium bromate, bromide, and cyanide in quantities corresponding with these equations were heated at 25° and the reaction started by addition of a quantity of hydrochloric acid sufficient to neutralise the cyanide and liberate the bromic and hydrobromic acids. After measured intervals of time, the reaction was stopped by the addition of an excess of sodium hydroxide, which converts the cyanogen bromide into cyanate and bromide; the unchanged cyanide was then titrated with silver nitrate and potassium iodide as indicator, after which the solution was acidified, excess of potassium iodide added, and the iodine liberated by the unchanged bromic acid was titrated.

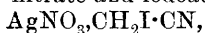
Assuming that the strong acids are completely dissociated and the hydrocyanic acid undissociated, it is found that the experimental data satisfy the velocity equation  $-dC_{\text{BrO}_3}/dt = k[C_{\text{H}^+}]^2[C_{\text{Br}^-}][C_{\text{BrO}_3}]$ , in which the bracketed symbols denote the concentration of the hydrogen, bromide, and bromate ions respectively. The values obtained for  $k$  in the three reactions are practically identical and warrant the conclusion that no secondary change of importance takes place. The interaction between bromic and hydrobromic acids determines therefore the rate of the reaction between bromate, bromide, and cyanide.

When sulphuric acid is used instead of hydrochloric acid, the rate of change is considerably smaller, but this can in all probability be accounted for by the smaller hydrogen dissociation.

Cyanogen bromide has no action on hydrocyanic acid, but reacts quickly with potassium cyanide according to the equation  $\text{CNBr} + \text{KCN} = \text{KBr} + \text{C}_2\text{N}_2$ . With alkali hydroxides, carbonates, and water, reaction takes place according to the equation  $\text{CNBr} + 2\text{OH}' = \text{Br}' + \text{CNO}' + \text{H}_2\text{O}$ . Quantitative measurements of the yield of cyanogen bromide under different conditions show that this approximates to the theoretical value the more closely the experimental conditions approach those indicated by the study of the reaction velocities. H. M. D.

**Preparation of Calcium Cyanamide.** FREDRIK CARLSON (*Chem. Zeit.*, 1906, 30, 1261).—The calcium chloride, used in Polzeniusz's method for the preparation of calcium cyanamide (D.R.-P. 1901, 163320), can with advantage be replaced by calcium fluoride; the product is not hygroscopic and can be kept without deterioration for a long time. C. S.

**Additive Compounds of Organic Haloids with Silver Nitrate.** ROLAND SCHOLL and WILHELM STEINKOPF (*Ber.*, 1906, 39, 4393—4400).—The compounds of nitriles with metallic salts greatly resemble hydrates. Although a solution of silver nitrate in acetonitrile yields only silver nitrate on evaporation, it has been found possible to isolate additive compounds from halogen derivatives of acetonitrile. The halogen atoms share in the formation of these compounds. A double compound of silver nitrate and iodoacetonitrile,



is obtained, together with nitric oxide and silver iodide, when a solution of silver nitrite in acetonitrile is added carefully to a mixture of iodoacetonitrile and acetonitrile at  $0^\circ$ , or in a pure state when the iodoacetonitrile is added drop by drop to a well-stirred aqueous silver nitrate solution. It forms almost colourless crystals, probably orthorhombic, m. p.  $121^\circ$ , and may be recrystallised from water at  $50^\circ$ , but is decomposed into its constituents by boiling water. When distilled it yields *cyanomethyl nitrate*,  $\text{CN} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}_2$ , a colourless oil, b. p.  $69-70^\circ/13$  mm. (slight decomp.), exploding when quickly heated. *Silver nitrate-bromoacetonitrile*,  $\text{AgNO}_3 \cdot \text{CH}_2\text{Br} \cdot \text{CN}$ , crystallises in small, almost colourless plates when the aqueous solution is quickly cooled. It sinters and decomposes at  $110^\circ$ . *Silver nitrate-methylene iodide*,  $\text{AgNO}_3 \cdot \text{CH}_2\text{I}_2$ , is a white, crystalline powder, m. p.  $80-81^\circ$ , and only slightly stable. Chloroacetonitrile does not yield an additive compound, and methyl iodide, ethyl iodide, iodoform, and ethyl iodoacetate give Fanto's silver iodide-nitrate (*Abstr.*, 1903, ii, 648).

The paper concludes with a discussion of the nature of these compounds from the standpoint of Werner's theory of supplementary valency (*Abstr.*, 1902, ii, 554) and their importance in the theory of the interaction of organic haloids and silver nitrate (compare Euler, *Abstr.*, 1906, i, 789; Burke and Donnan, *Trans.*, 1904, 85, 555).

W. R.

**New Method of Forming Organic Compounds of Phosphorus.** J. BERTHAUD (*Compt. rend.*, 1906, 143, 1166—1167).—By the action of white phosphorus (1 atom) on methyl or ethyl alcohol (2 mols.) in a sealed tube at 250° the chief product is the corresponding tetra-alkylphosphonium hydroxide to the extent of 20—30% of the phosphorus employed; the other products are phosphoric acid, the alkyl phosphinic acids, and hydrogen phosphide, together with a small quantity of the alkylphosphines in the case of methyl alcohol, but in the case of ethyl alcohol the quantity of ethylphosphine corresponds with 20% of the original phosphorus.

M. A. W.

**Chlorination, in Organic Chemistry, in presence of Thallous Chloride.** VICTOR THOMAS (*Cômt. rend.*, 1907, 144, 32—34. Compare Abstr., 1898, i, 640; 1899, i, 26, 676).—Thallous chloride acts similarly to ferric chloride in the chlorination of aromatic hydrocarbons and their haloid derivatives. Benzene gives a mixture of chlorobenzenes. Bromobenzene gives the series of chlorobromobenzenes  $C_6H_{[6-(n+1)]}BrCl_n$ , but no evidence was obtained of the displacement of bromine by chlorine. From *p*-dibromobenzene the same series of chlorobromobenzenes,  $C_6H_{[6-(n+1)]}BrCl_n$ , is obtained, one atom of bromine being displaced. In particular, the trichlorobromobenzene, m. p. 138°, is described. Iodobenzene invariably gives a complex mixture of chloriodobenzenes. Iodine is displaced from only a very small proportion of the iodobenzene, if at all. Among the products isolated are the three isomeric chloriodobenzenes and a *trichloriodobenzene*, m. p. 106—107°. The latter gives a mononitro-derivative, m. p. 57·5—58°, probably identical with that described by Istrati (*Bull. Soc. Sci. Bucarest*, 2, 8), and two polynitro-derivatives. (1) White or very light yellow needles, m. p. 177°, probably a dinitro-compound. (2) Golden-yellow lamellæ resembling lead iodide, very volatile, but melting when thrown on a surface previously heated to 279°, probably a trinitro-compound.

No intermediate additive products could be isolated. Thallous chloride is useless in the chlorination of acetic acid. E. H.

**1-Chloro-2:4:6-tri-iodobenzene.** W. V. GREEN (*Amer. Chem. J.*, 1906, 36, 600—604).—1-Chloro-2:4:6-tri-iodobenzene,  $C_6H_3ClI_3$ , prepared from 2:4:6-tri-iodoaniline by the diazo-reaction, crystallises from a mixture of alcohol and benzene in faintly pink, pyramidal-ended, slender prisms, m. p. 119—120°. When treated with sodium ethoxide it gives up some of its iodine, thus differing in behaviour from the analogous chlorotribromobenzene. Nitric acid converts it into 1-chloro-2:4:6-tri-iodo-3:5-dinitrobenzene, which crystallises from a mixture of benzene and light petroleum in yellowish-white needles, m. p. 266—269°.

T. H. P.

**The Sixth Di-iodonitrobenzene.** GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 577—579. Compare Abstr., 1906, i, 641).—1:2-Di-iodo-3-nitrobenzene, prepared by a

method similar to that used for the synthesis of 1:2-dibromo-3-nitrobenzene (*loc. cit.*), crystallises from alcohol in bundles of long needles, m. p.  $110\cdot2^{\circ}$ , is markedly greener than its isomerides and dissolves in ethyl acetate.

2:4-Di-iodo-6-nitroaniline crystallises from alcohol in slender, orange-yellow needles, m. p.  $152^{\circ}$ .

6-Iodo-2-nitroaniline crystallises from alcohol in orange-red needles or scales, m. p.  $122^{\circ}$ . T. H. P.

### The Sixth Tribromonitrobenzene and some of its Derivatives.

GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 580—588).—3:4:5-Tribromoacetanilide,  $C_6H_2Br_3\cdot NHAc$ , prepared by the action of bromine on 3:5-dibromoacetanilide in acetic acid solution, crystallises from ether in slender, white needles, m. p.  $255\text{—}256^{\circ}$ .

3:4:5-Tribromo-2-nitroacetanilide,  $NO_2\cdot C_6H_2Br_3\cdot NHAc$ , obtained by the action of sulphuric and nitric acids on 3:4:5-tribromoacetanilide, crystallises from alcohol or benzene in needles, and from ethyl acetate in mamillary masses of white prisms, m. p.  $229\text{—}230^{\circ}$ .

3:4:5-Tribromo-2-nitroaniline,  $NO_2\cdot C_6H_2Br_3\cdot NH_2$ , crystallises from alcohol in orange-yellow needles, and from ethyl acetate in tufts of shining, yellowish-red needles, m. p.  $134^{\circ}$ .

1:2:3-Tribromo-4-nitrobenzene,  $C_6H_2Br_3\cdot NO_2$ , prepared either by the action of ethyl nitrite on 3:4:5-tribromo-2-nitroaniline in alcoholic solution under pressure or by direct nitration of 1:2:3-tribromobenzene, crystallises from alcohol in faintly green, satiny needles, m. p.  $85\cdot4^{\circ}$ , and dissolves readily in benzene, ether, or ethyl acetate.

2:3-Dibromo-6-nitroaniline,  $NO_2\cdot C_6H_2Br_2\cdot NH_2$ , prepared by the action of alcoholic ammonia on 1:2:3-tribromo-4-nitrobenzene, crystallises from ethyl acetate in bundles of lanceolated, flattened, dichroic needles which appear red in reflected and yellow in transmitted light, m. p.  $149^{\circ}$ .

2:3:4-Tribromoaniline,  $C_6H_2Br_3\cdot NH_2$ , prepared by the reduction of 1:2:3-tribromo-4-nitrobenzene by means of stannous chloride and hydrochloric acid, is a feeble base crystallising from aqueous alcohol in white lamellæ, m. p.  $100\cdot6^{\circ}$ .

2:3:4-Tribromoacetanilide,  $C_6H_2Br_3\cdot NHAc$ , crystallises from alcohol in flattened, white needles, m. p.  $160^{\circ}$ .

Nitration of 1:2:3-tribromo-4-nitrobenzene with a mixture of concentrated sulphuric and nitric acids at  $130^{\circ}$  yields: (1) 1:2:3-tribromo-4:5-dinitrobenzene (compare Jackson and Fiske, *Abstr.*, 1902, i, 362); (2) 1:2:3-tribromo-4:6-dinitrobenzene,  $C_6H_2Br_3(NO_2)_2$ , which crystallises from alcohol in greenish-yellow, flat needles or prisms, m. p.  $150^{\circ}$ .

2:3-Dibromo-4:6-dinitroaniline,  $C_6H_2Br_2(NO_2)_2\cdot NH_2$ , obtained on treating 1:2:3-tribromo-4:6-dinitrobenzene with alcoholic ammonia, crystallises in sulphur-yellow needles, m. p.  $219^{\circ}$ . T. H. P.

**A New Method of Reductoin.** I. THEODOR WEYL (*Ber.*, 1906, 39, 4340—4343).—Hydrogen phosphide, obtained from water and red



phosphorus, acts as a reducing agent when nascent. Thus, when a mixture of nitrobenzene, red phosphorus, and water is heated at  $100^{\circ}$  under pressure for several hours, the nitrobenzene is reduced to aniline. In successive experiments the yield of aniline was 24.8, 31.7, 32.5, 64.0, 41.7, 86.2, and 55.5% respectively the duration of heating being 8, 8, 9, 12, 28, 35, and 42 hours. The phosphorus is partly converted into phosphorous and phosphoric acids.

When a mixture of nitrobenzene, red phosphorus, and water is heated at  $110-115^{\circ}$ , only very little aniline is formed; ammonia, however, is formed in considerable amount.

The reduction of nitrobenzene to aniline is represented by the equation:  $3C_6H_5 \cdot NO_2 + 4PH_3 = 3C_6H_5 \cdot NH_2 + 2H_3PO_3 + 2P$ .

A. McK.

**Reduction of Nitrobenzene by Aliphatic Alcohols in Light.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1906, 39, 4343—4344).—Aniline and paracetaldehyde do not yield quinaldine in the light, even after one year's exposure; moreover, the formation of quinoline bases in the reduction of nitrobenzene by aliphatic alcohols in light is prevented almost entirely by the absence of acids (compare *Abstr.*, 1906, i, 10).

C. S.

**Ammonium and Sodium Sulphides as Partial Reducing Agents for Aromatic Dinitro- and Polynitro-compounds.** KURT BRAND (*J. pr. Chem.*, 1906, [ii], 74, 449—472).—A systematic investigation of the reduction of aromatic polynitro-compounds by means of sodium sulphide has been undertaken, as accounts of the method occur chiefly in patents and are somewhat scattered in chemical literature. In the present paper, the work of previous authors whose statements are in many cases contradictory is reviewed, and the results of the investigation so far obtained are described.

The reduction of *m*-dinitrobenzene with ammonium hydrogen sulphide, dissolved in a mixture of alcohol and ethyl acetate at  $5^{\circ}$ , leads to the formation of *m*-nitrophenylhydroxylamine (*Abstr.*, 1906, i, 80), or with sodium sulphide in boiling alcoholic solution to the formation of di-*m*-nitroazoxybenzene and a small amount of *m*-nitroaniline, whilst on reduction with sodium sulphide in alcoholic solution in presence of ethyl acetate the chief product is *m*-nitroaniline, only small amounts of the azoxybenzene being formed (de Bruyn and Blanksma, *Abstr.*, 1901, i, 460; Blanksma, *ibid.*, 461). When boiled with 1 mol. of sodium disulphide in alcoholic solution, *m*-dinitrobenzene is almost completely reduced, the product consisting of *m*-nitroaniline in a yield of 87% and di-*m*-nitroazoxybenzene in a yield of 5.5% of the dinitrobenzene, but with  $\frac{1}{2}$  mol. of sodium disulphide 38% of the dinitro-compound is regained unchanged, *m*-nitroaniline being formed to the extent of 35% and di-*m*-nitroazoxybenzene to the extent of 47% of the dinitrobenzene (compare Blanksma, *loc. cit.*; Kunz, *Abstr.*, 1903, i, 813). In boiling alcoholic solution, *m*-dinitrobenzene is reduced almost quantitatively by sodium pentasulphide, forming *m*-nitroaniline, or by sodium hydrogen sulphide forming *m*-nitroaniline and traces of di-*m*-nitroazoxybenzene.

2:6-Dinitrotoluene is reduced by sodium hydrogen sulphide in

alcoholic-ethyl acetate solution, forming 6-nitro-2-aminotoluene, together with traces of 2:6-tolylenediamine; 2:4-dinitrotoluene is reduced similarly to 2-nitro-4-aminotoluene, together with smaller quantities of 4-nitro-2-aminotoluene, the total yield of nitroamines amounting to 80% of the theoretical.

The action of sodium hydrogen sulphide on 2:4-dinitroaniline leads to the formation of 4-nitro-*o*-phenylenediamine and traces of nitro-*p*-phenylenediamine, or on picric acid to the formation of picramic acid. G. Y.

**The Two Modifications of *o*-Nitrotoluene.** IWAN VON OSTROMISSENSKY (*Zeit. physikal. Chem.*, 1906, 57, 341—348).—When freshly-distilled *o*-nitrotoluene is rapidly cooled to  $-20^{\circ}$ , it solidifies sometimes to the labile  $\alpha$ -modification (m. p.  $-10.56^{\circ}$ ), sometimes to the stable  $\beta$ -modification (m. p.  $-4.14^{\circ}$ ). Superheating of the vapour during distillation favours the subsequent separation of the  $\beta$ -modification. Another method for preparing the latter is to cool the liquid substance to  $-50^{\circ}$  or  $-60^{\circ}$ ; the primary crystallisation from the cooled liquid consists of the  $\alpha$ -modification, but after a short time this changes spontaneously into the  $\beta$ -modification. At all temperatures not too close to the melting point of the  $\alpha$ -modification, the change  $\alpha \rightarrow \beta$  takes place, so that the two modifications are monotropic. It is probable, however, that the transition point is close to the melting point of the  $\alpha$ -form.

The freezing point depression constants are found to be: for the  $\alpha$ -form, 50.8; for the  $\beta$ -form, 71.8. The molecular weights of iodine and sulphur dissolved in the  $\beta$ -form are found by the freezing point method to correspond with  $I_5$  and  $S_{10} - S_{11}$  respectively.

Allied substances existing in two modifications (the m. p.'s. of which are  $\Delta^{\circ}$  apart) are *o*-chlorotoluene ( $\Delta = 5.8^{\circ}$ ), *o*-toluidine ( $\Delta = 5^{\circ}$ ), *o*-chlorophenol ( $\Delta = 7^{\circ}$ ), *o*-bromotoluene ( $\Delta = 5.1^{\circ}$ ). The two modifications of *o*-chlorotoluene are enantiotropic; at  $-50^{\circ}$  the change  $\alpha \rightarrow \beta$  takes place, at  $-17^{\circ}$  the change  $\beta \rightarrow \alpha$ ; the transition temperature lies therefore between  $-17^{\circ}$  and  $-50^{\circ}$ . J. C. P.

**Nitration of Aniline and of certain of its Derivatives** J. BISHOP TINGLE and F. C. BLANCK (*Amer. Chem. J.*, 1906, 36, 605—610).—Attempts were made to nitrate aniline (or aniline nitrate) directly by the action of 99% nitric acid free from nitrous acid, but although carbamide was added to decompose any nitrous acid formed and the reactions were carried out in platinum vessels immersed in a freezing mixture, it was found to be impossible to keep the temperature sufficiently low, tarry or carbonaceous products being always formed.

Nitric acids of 50.71—75.33% concentrations give with aniline a pink solid, stable at  $0^{\circ}$ , the colour being instantly discharged by the addition of a little water or aniline. Slight excess of acid increased or restored the colour, and, if the added acid were sufficiently concentrated, the pink colour darkened until it became black, the whole mass gradually charring and sometimes incandescing. With nitric acids of

concentrations up to 75.33%, any charring produced is due to attack of the aniline nitrate and not of the nitrate. The readiness of nitration of aniline by means of nitric and sulphuric acid hence cannot be due to "protection" of the amino-group by the sulphuric acid, as this group is equally well "protected" in aniline nitrate.

Experiments were also made on the action on anilines substituted in the amino-group of 80% nitric acid (D 1.46) in presence of acetic, oxalic, trichloroacetic, or 92% sulphuric acid (D 1.83). The results show that the position assumed by the entrant nitro-group is definitely influenced both by the acid present with the nitric acid and by the amino-substituent.

T. H. P.

**Preparation of Simple Aromatic Cyanamides.** PAUL PIERRON (*Bull. Soc. chim.*, 1906, [iii], 35, 1197—1204).—The method of preparation described by Cloez and Cannizzaro (*Compt. rend.*, 1851, 32, 62) gives good results in the case of naphthalene derivatives, whilst a modification of that proposed by Hofmann (*Ber.*, 1869, 2, 600, and 1870, 3, 264) furnishes better results in the case of benzene derivatives, especially when the desulphuration of the thiocarbamides is accomplished by the use of cupric sulphate in place of litharge.

*m*-Tolylcyanamide, prepared from *m*-tolylthiocarbamide by the modification of Hofmann's method referred to, is a viscous, nearly colourless liquid, which in contact with water forms a hydrate (m. p. 27°) (compare Heller and Bauer, *Abstr.*, 1902, i, 444), and in contact with hydrochloric acid furnishes *m*-tolylcarbamide (m. p. 142°).

$\alpha$ -Naphthylcyanamide and the isomeric  $\beta$ -compound were prepared by Cloez and Cannizzaro's method, cyanogen bromide being employed instead of cyanogen chloride. *m*-Ethoxyphenylcyanamide was also prepared by this method, alcohol being employed as a solvent for the *m*-ethoxyaniline in place of ether. It crystallises in colourless needles, m. p. 57°, and is readily hydrolysed by acids to the corresponding carbamide, which crystallises in colourless, flattened needles, m. p. 112°. *m*-Ethoxyphenylcarbamide is also readily obtained by the action of potassium cyanate on *m*-aminophenetole hydrochloride.

*o*-Bromophenylcyanamide, similarly obtained, crystallises in brilliant, slender, colourless needles, m. p. 94°, and by boiling its solution in alcohol with hydrochloric acid is transformed into the corresponding carbamide, which crystallises in colourless, flattened needles, m. p. 202°, and by repeated evaporation with hydrochloric acid furnishes ammonia, *o*-bromoaniline, and carbon dioxide. *m*-Bromophenylcyanamide, similarly obtained from *m*-bromoaniline, crystallises from benzene in brilliant, colourless lamellæ, m. p. 84°, is readily soluble in alcohol and less so in ether, and with acids yields *m*-bromophenylcarbamide (compare Folin, *Abstr.*, 1897, i, 470). *p*-Bromophenylcyanamide, prepared from *p*-bromoaniline, crystallises in colourless, long, slender, prismatic needles, m. p. 112°, is very soluble in alcohol, fairly so in ether, less so in chloroform, and slightly so in water; it is readily soluble in alkalis and insoluble in dilute acids.

Hofmann's method is not applicable to the preparation of the bromophenylcyanamides, owing to the difficulty of preparing the necessary thiocarbamides.

T. A. H.

**Influence of Certain Substituting Groups on the Oxidation of Tertiary Amines to Amine Oxides.** EUGEN BAMBERGER and LEO RUDOLF (*Ber.*, 1906, **39**, 4285—4293. Compare Abstr., 1902, i, 364; Bamberger and Tschirner, Abstr., 1899, i, 347).—The amount of amine oxides, formed by the oxidation of tertiary aromatic bases by means of Caro's acid, varies with the alkyl groups attached to the nitrogen atom and with the absence or presence and position of methyl groups in the benzene nucleus. In comparative experiments, 10 grams each of dimethylaniline, dimethyl-*p*-toluidine, dimethyl-*o*-toluidine, diethylaniline, *vm*-dimethylxylylidine, and dimethylmesidine yielded 11.1, 10.9, 7.16, 6.89, 0, and 0 grams respectively of the corresponding amine oxides; in a second series of experiments in more dilute solution, of 10 grams each of dimethylaniline, dimethyl-*o*-toluidine, dimethyl-*p*-toluidine, diethylaniline, diethyl-*o*-toluidine, and diethyl-*p*-toluidine, 0.0, 6.35, 0.3, 6.43, 8.84, and 6.18 respectively, remained unoxidised; whilst in a third series of 10 grams each of diethyl-*o*-toluidine and diethyl-*p*-toluidine, 8.7 and 5.8 grams respectively, remained unchanged. The oxidation takes place more easily with dimethyl- than with diethyl-aniline, is hindered by the presence of an *o*-methyl group, and is prevented by the presence of two *o*-methyl groups.

The action of methyl sulphate on mesidine leads to the formation of dimethyl- and methyl-mesidines, which are separated by conversion of the latter into its *acetyl* derivative,  $C_6H_2Me_3 \cdot NMeAc$ ; this crystallises in glistening prisms, m. p. 51—51.5°, b. p. 150—150.5°/13 mm. Dimethylmesidine is colourless, b. p. 213.3—213.5°/716 mm.,  $D_4^{20.5}$  0.905 (Hofmann, *Ber.*, 1872, **5**, 718; b. p. 213—214°,  $D$  0.9076), but after treatment with Caro's acid is slightly yellow,  $D_4^{21.2}$  0.9076.

*vm*-Dimethylxylylidine, prepared together with *vm*-methylxylylidine by the action of methyl sulphate on *vm*-xylylidine, is colourless, b. p. 192.5—192.8°/716 mm. or 76.8—77.2°/11 mm.,  $D_4^{20.5}$  0.912 (b. p. 196°,  $D$  0.9296; Hofmann, *loc. cit.*, 712; b. p. 195—196°: Friedländer, Abstr., 1899, i, 350), but after treatment with Caro's acid is yellow,  $D_4^{21.2}$  0.914. Contrary to Friedländer's statement (*loc. loc.*), the base does not react with nitrous acid. G. Y.

**Asymmetric Nitrogen XXVI. Optically Active Phenylbenzylmethylethyl Ammonium Bases.** EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1906, **39**, 4437—4442. Compare Abstr., 1906, i, 161, 162).—The values  $[M]_D + 17.3$  for the active cation  $NMeEtPh \cdot C_6H_5$ , obtained by Wedekind (*Ber.*, 1907, **37**, 2727), and  $[M]_D + 19.3$ , obtained by H. O. Jones (*Trans.*, 1904, **85**, 225), appear too low in view of the values  $[M]_D + 285$  for the active cation  $NMePrPh \cdot C_6H_5$  and  $[M]_D - 279$  for the corresponding *isobutyl* base (compare Abstr., 1905, 878).

*Phenylbenzylmethylethylammonium bromide* forms prisms, m. p. 158—159°; it was not found possible to resolve it by crystallisation of the *d*-bromocamphorsulphonate. By continued fractional crystallisation of a large quantity of the *d*-camphorsulphonate, a fraction  $[M]_D + 116.1^\circ$  was obtained equivalent to  $[M]_D + 64.4^\circ$  for the cation  $NMeEtPh \cdot C_6H_5$ .

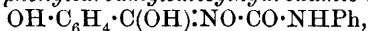
The ammonium iodide prepared from this fraction had  $[\alpha]_D + 41.4^\circ$  in alcohol, and did not alter when kept; in chloroform,  $[\alpha]_D + 56.5^\circ$ , autoracemisation quickly set in.  
E. F. A.

**Preparation of *s*-Hexanitrodi-*m*-xylylamine.** JAN J. BLANKSMA (*Rec. trav. chim.*, 1906, 25, 373—375).—5-Bromo-2:4:6-trinitro-*m*-xylene, which forms colourless crystals, m. p.  $224^\circ$ , is obtained by nitrating 5-bromo-*m*-xylene; when heated with *m*-xylidine in alcoholic solution it yields 2:4:6-trinitro-di-1:3:5-xylylamine, which on nitration is converted into *s*-hexanitrodi-1:3:5-xylylamine, m. p.  $222^\circ$ . This substance separates from chloroform in glistening crystals which contain 1 molecule of the solvent.  
P. H.

**Hydroxamic Acids.** RAYMOND MARQUIS (*Compt. rend.*, 1906, 143, 1163—1165. Compare Abstr., 1905, i, 524).—Thiele and Pickard (Abstr., 1900, i, 29) explain the formation of symmetrical disubstituted carbamides from the alkali salts of the dihydroxamic acids (Lossen, Abstr., 1894, i, 415) on the assumption that the acid undergoes the Beckmann rearrangement, with the formation of a carbimide, which is converted into the carbamide by the action of water. The author has examined the behaviour of hydroxamic acid towards reagents which induce the Beckmann rearrangement and finds that in certain cases the reaction is normal. Thus, benzhydroxamic acid yields phenylcarbamide when treated with thionyl chloride in the presence of boiling benzene, and salicylhydroxamic acid when similarly treated yields oxycarbanil (Ransom, Abstr., 1898, i, 415), the acetyl derivative of which has m. p.  $91^\circ$  [Kalekchhoff gives  $95^\circ$  (Abstr., 1883, 734) and Bender gives  $97-98^\circ$  (Abstr., 1887, 37)].

Phenyl-*p*-tolylcarbamide, obtained by the condensation of phenylcarbamide and *p*-toluidine, m. p.  $218^\circ$ , then solidifies and melts sharply at  $221^\circ$  [Paal and Valvolxem (Abstr., 1894, i, 621) give  $212^\circ$  and Dixon (Trans., 1901, 79, 103) gives  $215^\circ$ ].

*Phenylcarbamybenzhydroxamic acid*,  $\text{OH}\cdot\text{CPh}\cdot\text{NO}\cdot\text{CO}\cdot\text{NHPh}$ , obtained by the condensation of phenylcarbamide and benzhydroxamic acid in pyridine solution, crystallises from alcohol in small needles, m. p.  $209-210^\circ$ ; *phenylcarbamylsalicylhydroxamic acid*,



crystallises from benzene and alcohol in flat, pearly needles, m. p.  $181^\circ$ , which rapidly redden in the light.  
M. A. W.

**Preparation of Aromatic Thiocarbamides by the Hydrogen Peroxide Method.** JULIUS VON BRAUN and ERICH BESCHKE (*Ber.*, 1906, 39, 4369—4378. Compare Abstr., 1900, i, 644; 1902, i, 271).—Continuing the work on the mechanism of the reaction between primary aromatic amines and carbon disulphide in the presence of hydrogen peroxide, the authors have applied the method in the following cases.

*m*- and *p*-Toluidine, *p*-cumidine, 1:3:4-xylidine, and *p*-aminobenzyl cyanide react within a few minutes. *Dicumylthiocarbamide* has m. p.  $149^\circ$ ; *ω*-dicyanoditolylthiocarbamide, m. p.  $191^\circ$ , is insoluble in alcohol.

*o*- and *p*-Chloroanilines react after two days, whereas the meta-isomeride undergoes a rapid conversion into the carbamide. *m*-Bromoaniline readily yields the carbamide, m. p.  $128^{\circ}$ , whilst *p*-bromoaniline and *p*-iodoaniline require many hours.

*p*-Anisidine and *p*-phenetidine react as readily as aniline itself, *o*-anisidine only very slowly.

Methyl anthranilate and ethyl *p*-aminobenzoate yield the corresponding carbamides after many days, but they have not yet been examined completely. C. S.

**Decomposition of Dinitrophenyl Thiocyanate.** OSCAR HINSBERG (*Ber.*, 1906, 39, 4331—4332).—According to Austen and Smith (*Abstr.*, 1886, 693), dinitrophenyl thiocyanate, obtained by the action of potassium thiocyanate on 4-bromo-1:3-dinitrobenzene, forms dinitrophenyl mercaptan, m. p.  $195^{\circ}$ , when warmed with concentrated sulphuric acid. According to the author, this observation is not correct, since the product of the action in question is not uniform, but a mixture of 2:4-dinitrophenyl mercaptan, m. p.  $131^{\circ}$ , and 2':4'-tetranitrodiphenyl disulphide.

The observation of Austen and Smith that, when dinitrophenyl thiocyanate is warmed with a mixture of concentrated sulphuric acid and fuming nitric acid, a tetranitrodiphenyl sulphide, m. p.  $245^{\circ}$ , is produced is also erroneous. A. McK.

**Use of Compounds of Bases with Sulphurous Acid as Photographic Developers.** AUGUSTE LUMIERE, LOUIS LUMIERE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 1204—1207).—Compounds of this type with *p*-aminophenol, *p*-methylaminophenol, and *p*-phenylenediamine have been obtained (1) by the action of sulphur dioxide on the free bases suspended in warm water, (2) by cooling warm solutions of the bases in "liquid commercial sodium bisulphite" (40%), or (3) by heating *p*-methylaminophenol sulphate with a solution of anhydrous sodium sulphite to which one-fourth of its volume of sodium hydrogen sulphite had been added.

The product,  $10\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{H}_2\text{SO}_3$ , obtained with *p*-aminophenol occurs in white crystals having a faint odour of sulphur dioxide and does not become brown on exposure to air.

The compound,  $6\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}\cdot\text{H}_2\text{SO}_3$ , yielded by *p*-methylaminophenol, occurs in small white crystals, is stable in air, has no odour of sulphur dioxide, and has m. p.  $87^{\circ}$ , evolving sulphur dioxide.

The compound,  $9\text{C}_6\text{H}_4(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_3$ , obtained from *p*-phenylenediamine, forms small white crystals having a feeble odour of sulphur dioxide, is stable in air, and has m. p.  $137^{\circ}$ , evolving sulphur dioxide.

These three substances are comparable as developers with the three bases from which they are derived, and the solubility in water of the *p*-methylaminophenol product enables it to be used as a developer by the addition of sodium sulphite. T. A. H.

**Action of Bromine and Chlorine on Phenols. Substitution Products,  $\psi$ -Bromides, and  $\psi$ -Chlorides. XX. Action of Bromine on *o*-Cresol.** THEODOR ZINCKE and AUGUST VON HEDENSTRÖM (*Annalen*, 1905, 350, 269—287. Compare *Abstr.*, 1906, i, 739).—*o*-Cresol reacts

readily with the calculated quantities of bromine alone or in presence of iron in chloroform or carbon tetrachloride solution, forming mono-, di-, tri-, and tetra-bromo-derivatives.

The *acetyl* derivative of 5-bromo-*o*-cresol (Claus and Jackson, Abstr., 1889, 128) is an oil. The *acetyl* derivative of 3:5-dibromo-*o*-cresol (*loc. cit.*) crystallises in glistening needles, m. p. 62°.

3:4:5-(or 3:3:5:6-)*Tribromo-o-cresol*,  $C_6HMeBr_3 \cdot OH$ , crystallises from light petroleum in long, colourless needles, m. p. 79°; the *acetyl* derivative crystallises in glistening needles, m. p. 72—73°.

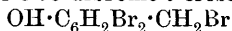
*Tetrabromo-o-cresol*,  $C_6MeBr_4 \cdot OH$ , crystallises in glistening needles, m. p. 205°; the *acetyl* derivative forms glistening needles, m. p. 154°.

The action of sodium nitrite on these bromo-*o*-cresols in glacial acetic acid solution leads to the formation of bromonitro-derivatives. 5-Bromo- and 3:5-dibromo-*o*-cresols yield 5-bromo-3-nitro-*o*-cresol (Wroblewski, this Journal, 1874, 27, 52).

4:5-*Dibromo-3-nitro-o-cresol*,  $C_7H_5O_3NBr_2$ , formed from 3:4:5-tribromo-*o*-cresol, crystallises in yellow needles, m. p. 141° (decomp.).

4:5:6-*Tribromo-3-nitro-o-cresol*,  $NO_2 \cdot C_6MeBr_3 \cdot OH$ , formed from tetrabromo-*o*-cresol, crystallises in yellow, monoclinic prisms, m. p. 156° (decomp.).

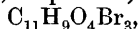
The action of bromine on 5-bromo- or 3:5-dibromo-*o*-cresol at 170° leads to the formation of 3:5-dibromo-*o*-cresol  $\psi$ -bromide,



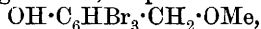
or  $C_6H_3OBr_2 \cdot CH_2Br$  (Auwers and Büttner Abstr., 1899, i, 36).

3:4:5-*Tribromo-o-cresol*  $\psi$ -bromide,  $C_7H_4OBr_4$ , formed by heating the tribromo-cresol with bromine in a sealed tube in the water bath, crystallises in monoclinic needles or prisms, m. p. 134°, reacts only very slowly with alkali hydroxides, and when shaken in ethereal solution with dilute alkali hydroxides forms a white, amorphous, polymeric *methyl-enequinone*. Reduction of the  $\psi$ -bromide with zinc and hydrogen bromide in glacial acetic acid solution leads to the formation of 3:4:5-tribromo-*o*-cresol. The *acetyl* derivative,  $OAc \cdot C_6HBr_3 \cdot CH_2Br$ , forms glistening needles, m. p. 137°.

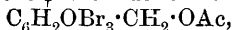
3:4:5-*Tribromo-2-hydroxybenzyl alcohol*,  $OH \cdot C_6HBr_3 \cdot CH_2 \cdot OH$ , prepared by boiling the  $\psi$ -bromide with aqueous acetone, crystallises in stellate aggregates of needles, m. p. 141°; the *diacetyl* derivative,



crystallises in glistening needles, m. p. 92°. The *methyl ether*,



prepared by boiling the  $\psi$ -bromide with methyl alcohol, crystallises in glistening needles, m. p. 81—82°; the *acetyl* derivative forms white needles, m. p. 90—91°. When boiled for a few minutes with acetic acid and sodium acetate, the  $\psi$ -bromide forms the *acetyl* derivative,



which crystallises in glistening needles, m. p. 130—131°, on hydrolysis yields tribromohydroxybenzyl alcohol, and forms the *diacetyl* derivative of this when heated with sodium acetate and acetic anhydride.

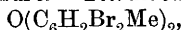
*Tetrabromo-o-cresol*  $\psi$ -bromide,  $C_6HOBr_4 \cdot CH_2Br$ , or  $OH \cdot C_6Br_4 \cdot CH_2Br$ , formed by heating the tetrabromocresol with bromine in a sealed tube at 100°, crystallises in colourless needles, m. p. 156°, yields a white, amorphous *product* when shaken with ether and a dilute alkali hydr-

oxide, and if shaken with benzene and a dilute alkali hydroxide forms the amorphous substance and a yellow solution which on evaporation deposits a yellow *residue*, probably the *o*-methylenequinone. The *acetyl* derivative,  $\text{OAc}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2\text{Br}$ , formed by boiling the  $\psi$ -bromide with acetic anhydride, crystallises in small, hard needles, m. p.  $156^\circ$ . *Tetrabromo-o-hydroxybenzyl alcohol*,  $\text{C}_7\text{H}_7\text{O}_2\text{Br}_4$ , crystallises in small needles, m. p.  $158^\circ$  (decomp.); the *diacetyl* derivative,  $\text{C}_{11}\text{H}_8\text{O}_4\text{Br}_4$ , crystallises in glistening needles, m. p.  $138-139^\circ$ . The *methyl ether*,  $\text{C}_8\text{H}_6\text{O}_2\text{Br}_4$ , forms white needles, m. p.  $94-95^\circ$ ; the *acetyl* derivative forms glistening needles, m. p.  $98-99^\circ$ .

The *acetyl* derivative,  $\text{C}_6\text{HOBr}_4\cdot\text{CH}_2\cdot\text{OAc}$ , prepared by boiling the  $\psi$ -bromide with glacial acetic acid and sodium acetate, forms white needles, m. p.  $133^\circ$ , on hydrolysis yields tetrabromo-*o*-hydroxybenzyl alcohol, and the diacetate of this when boiled with acetic anhydride and sodium acetate. G. Y.

***m*-Tolyl Ether and Derivatives.** ALFRED N. COOK (*Amer. Chem. J.*, 1906, 36, 543—551. Compare Gladstone and Tribe, *Trans.*, 1882, 41, 11).—*Aluminium m-tolyl oxide*, prepared by the action of commercial aluminium on *m*-cresol, is a brittle, grey to black, translucent solid, having a vitreous lustre and a conchoidal fracture. When distilled in a vacuum, it yields a small quantity of *m*-cresol and a large proportion of a substance, b. p.  $240^\circ/30$  mm., but under ordinary pressure it gives *m*-cresol, *m*-tolyl ether, a solid, b. p. about  $300^\circ$  (uncorr.), and a red liquid, b. p. about  $360^\circ$ .

*m*-Tolyl ether has b. p.  $290.5-291.5^\circ$  and  $D_{21} 1.0323$  and its viscosity is  $1.333$  at  $15.5^\circ$ ,  $1.194$  at  $30^\circ$ ,  $1.166$  at  $40^\circ$ , and  $1.139$  at  $50^\circ$ ; its viscosity is hence 9.4% greater than that of phenyl ether ( $1.095$ ) at  $30^\circ$ , in spite of its lower specific gravity. It is volatile in a current of steam. Chromic acid in glacial acetic acid oxidises it to a white powder insoluble in alkalis. *Dibromo-m-tolyl ether*,  $\text{O}(\text{C}_6\text{H}_3\text{Br}_2\text{Me})_2$ , is a white, crystalline substance, m. p.  $48^\circ$ , b. p.  $250^\circ/15$  mm. and  $340-350^\circ$  (uncorr.) at ordinary pressure. *Tetrabromo-m-tolyl ether*,



is a pale yellow, sticky, viscous substance crystallising in nodular aggregates, b. p.  $260-270^\circ/35$  mm. *Dinitro-m-tolyl ether*,



separates from alcohol in yellow crystals, m. p.  $112-113^\circ$ . *Diamino-m-tolyl ether hydrochloride*,  $\text{O}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2\cdot\text{HCl})_2$ , was prepared and also the free base. T. H. P.

**Nitration of Meta-Substituted Phenols.** JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 278—280).—The nuclear hydrogen atoms in *m*-nitrophenols, containing a hydroxyl, methyl, methoxy-, or ethoxy-group, or chlorine or bromine in position 5, are readily substituted by three atoms of bromine by treatment with bromine water, or by three nitro-groups by nitration by nitric acid ( $D 1.52$ ) and sulphuric acid. The tetranitro-compounds separate from a mixture of these acids in colourless crystals, turn yellow in the presence of water, have a bitter taste, and an acid reaction, and are



explosive. If the phenolic hydrogen atom is replaced by methyl, only two nitro-groups can be introduced.

By boiling water, *tetranitro-m-cresol*, m. p.  $175^{\circ}$ , is converted into trinitro-oreinol, whilst *tetranitroresorcinol*, m. p.  $152^{\circ}$ , *chlorotetranitrophenol*, m. p.  $147^{\circ}$ , or *bromotetranitrophenol*, m. p.  $157^{\circ}$ , yield trinitro-phloroglucinol.

*5-Nitroresorcinol* has m. p.  $158^{\circ}$ , and the *ethyl ether*, m. p.  $80^{\circ}$ ; the *tetranitro-methyl* and *ethyl ethers* have respectively m. p.  $115^{\circ}$  and  $110^{\circ}$ ; *3-chloro-5-nitrophenol*, m. p.  $147^{\circ}$ , and the *bromo-compound*, m. p.  $145^{\circ}$ . C. S.

**Synthesis of  $\alpha\delta$ -Halogen Ethers and of  $\alpha\delta$ -Dihalogen Derivatives of Butane.** JULIUS VON BRAUN and ERICH BESCHKE (*Ber.*, 1906, **39**, 4357—4362).— $\alpha\delta$ -Dichloro- or -dibromo-butane can be obtained in 10% yield by reducing succinonitrile with sodium and alcohol, benzoylating the product, and treating the resulting mixture with phosphorus pentachloride or pentabromide.

Benzo- $\delta$ -phenoxybutylamide (compare this vol., i, 80) and phosphorus pentachloride in molecular quantities react to form ultimately  *$\alpha$ -chloro- $\delta$ -phenoxybutane*,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$ , which is a colourless, refractive, pleasant-smelling liquid, b. p.  $147^{\circ}/12$  mm., and reacts with sodium phenoxide to form Grignard's  $\alpha\delta$ -diphenoxybutane (*Abstr.*, 1904, i, 494).

$\alpha\delta$ -Dichlorobutane,  $\text{C}_4\text{H}_8\text{Cl}_2$ , b. p.  $53$ — $58^{\circ}/12$  mm., is obtained from the preceding chlorinated ether and concentrated hydrochloric acid above  $130^{\circ}$ .

*$\alpha$ -Iodo- $\delta$ -phenoxybutane*,  $\text{CH}_2\text{I}\cdot[\text{CH}_2]_2\cdot\text{CH}_2\cdot\text{OPh}$ , obtained from the chlorinated ether and sodium iodide in alcoholic solution, forms white leaflets, m. p.  $43$ — $44^{\circ}$ , b. p.  $155$ — $160^{\circ}/15$  mm., and is changed quantitatively by hydriodic acid at  $100^{\circ}$  into  $\alpha\delta$ -di-iodobutane.

$\alpha\delta$ -Dibromobutane cannot be obtained from phosphorus pentabromide and benzo- $\delta$ -phenoxybutylamide, but is prepared readily from  $\alpha\delta$ -diphenoxybutane and hydrobromic acid at  $130$ — $140^{\circ}$ . C. S.

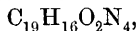
**Constitution and Colour of Nitrophenols.** HUGO KAUFFMANN (*Ber.*, 1906, **39**, 4237—4242. Compare *Abstr.*, 1900, i, 480; 1901, i, 318; 1906, i, 577; Kauffmann and Franck, *Abstr.*, 1906, i, 841).—A reply to Hantzsch (*Abstr.*, 1906, i, 353, 833; Ley and Hantzsch, *ibid.*, 790). Nitroquinol dimethyl ether is a very stable substance, and its yellow colour cannot be attributed to the presence of nitroquinol. Its solution in light petroleum is colourless, but deposits yellow crystals. Free nitroquinol dissolves in light petroleum to a yellow solution. G. Y.

**Nitroquinol Dimethyl Ether.** HUGO KAUFFMANN and IMANUEL FRITZ (*Ber.*, 1906, **39**, 4243—4248. Compare Kauffmann, *Abstr.*, 1906, i, 577; preceding abstract; Hantzsch, *Abstr.*, 1906, i, 353, 833).—When prepared by nitration of quinol dimethyl ether, nitroquinol dimethyl ether contains traces of a hydrolytic product, probably the monomethyl ether, which is removed completely on recrystallisation from alcohol. The pure dimethyl ether is yellow, and is unchanged on

addition of an alkali hydroxide, whereas 0.007 gram of the hydrolytic product dissolved in 1 litre of water gives a distinct change of colour. The solubility of the dimethyl ether in water is diminished by the addition of sodium carbonate. It yields only traces of hydrolytic products when treated at the laboratory temperature with concentrated, or boiled with dilute, sulphuric acid; a substance crystallising in orange-red needles, m. p. 79—80°, is formed on boiling with aqueous or alcoholic alkali hydroxides. The dimethyl ether is hydrolysed only slowly by aluminium chloride in boiling light petroleum or benzene solution, and is decomposed in boiling toluene solution. G. Y.

### Methylene and Other Derivatives of *m*-Dihydroxybenzenes.

A. LUTHER (*Arch. Pharm.*, 1906, **244**, 561—568).—Methylenediresorcinol,  $\text{CH}_2[\text{C}_6\text{H}_3(\text{OH})_2]_2$ , is broken down by prolonged boiling with zinc dust and aqueous sodium hydroxide; the formation (in about 20% yield) of cresorcinol,  $\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$  [ $\text{Me} : (\text{OH})_2 = 1 : 2 : 4$ ], and resorcinol was ascertained by first treating the product with sodium nitrite and nitrous oxide, then oxidising with nitric acid of D 1.3, and, finally, crystallising from water, when dinitroresorcinol, m. p. 142°, and dinitrocresorcinol, m. p. 90°, crystallised in succession. Cresorcinol forms a *mono*- and a *di*-benzoyl derivative, m. p. 115—116° and 83°, and a *diacetyl* derivative, b. p. 293—295°; with bromine in chloroform solutions it yields *dibromocresorcinol*,  $\text{C}_7\text{H}_4\text{O}_2\text{Br}_2$ , m. p. 86—87°, with bromine and water, *tetrabromocresorcinol*,  $\text{C}_7\text{H}_4\text{O}_2\text{Br}_4$ , m. p. 99—100°, and in chloroform solution with gaseous chlorine, *tetrachlorocresorcinol*,  $\text{C}_7\text{H}_4\text{O}_2\text{Cl}_4$ , m. p. 69—70°, which yields *dichlorocresorcinol*,  $\text{C}_7\text{H}_6\text{O}_2\text{Cl}_2$ , m. p. 78—79°, when reduced with stannous chloride and hydrochloric acid; with diazoaminobenzene in alcoholic solution it condenses to the scarlet cresorcinolbisazobenzene,



m. p. 211—212°; and with formaldehyde it yields methylenediresorcinol, m. p. 195—200°.

The last substance,  $\text{CH}_2[\text{C}_6\text{H}_2\text{Me}(\text{OH})_2]_2$ , is broken down by reduction with zinc dust and aqueous sodium hydroxide to xylorcinol,  $\text{C}_6\text{H}_2\text{Me}_2(\text{OH})_2$  [ $\text{Me}_2 : (\text{OH})_2 = 1 : 3 : 4 : 6$ ], and cresorcinol, which can be separated by fractional crystallisation from hot benzene. Xylorcinol, which can crystallise with  $1\text{H}_2\text{O}$ , forms a *dibenzoyl* derivative, m. p. 155°; with bromine in chloroform solution it yields *bromoxylorcinol*,  $\text{C}_8\text{H}_9\text{O}_2\text{Br}$ , m. p. 119—120°; with diazoaminobenzene it does not condense; with formaldehyde and dilute sulphuric acid it yields *methylenedixylorcinol*,  $\text{C}_{17}\text{H}_{20}\text{O}_4$ , m. p. 251°, which crystallises with  $1\text{H}_2\text{O}$ .

The last substance is not attacked by zinc dust and aqueous sodium hydroxide. The same is true of *methylenedis-4:6-dihydroxy-1:2:3-trimethylbenzene*,  $\text{C}_{19}\text{H}_{24}\text{O}_4$ , m. p. 228°, which was obtained from 4:6-dihydroxy-1:2:3-trimethylbenzene (Simon, *Abstr.*, 1904, i, 406) and formaldehyde in the presence of dilute sulphuric acid.

C. F. B.

**Action of Organo-Magnesium Haloids on Acetylenic Aldehydes and Ketones. Acetylenic Alcohols.** MAURICE BRACHIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 1163—1179).—Phenylpropionaldehyde,

obtained by condensing the sodium derivative of phenylacetylene with ethyl formate (compare Moureu and Delange, Abstr., 1901, i, 581), reacts with magnesium methyl iodide in presence of ether, forming the *additive* compound  $\text{CPh:C}\cdot\text{CHMe}\cdot\text{OMgI}\cdot\text{Et}_2\text{O}$ , a yellowish-white, deliquescent powder, which when suspended in ether and the mixture poured into water containing acetic acid, decomposes, forming phenylacetylenemethylcarbinol,  $\text{CPh:C}\cdot\text{CHMe}\cdot\text{OH}$  (compare Moureu and Desmots, Abstr., 1902, i, 289), which has b. p.  $132\text{--}134^\circ/16\text{ mm.}$ ,  $D_0^\circ 1\cdot0449$ ,  $D_4^{12\cdot6} 1\cdot0363$ ,  $n_D^{12\cdot6} 1\cdot57305$ , and reacts with mercuric chloride in alcohol, yielding the *product*  $\text{CPh:C}\cdot\text{CHMe}\cdot\text{OHgCl}$ , which crystallises in faintly yellow, prismatic needles, has m. p.  $111^\circ$ , and on hydrolysis with dilute sulphuric acid regenerates the parent alcohol.

Phenylpropionaldehyde reacts with magnesium ethyl bromide, forming  *$\alpha$ -phenyl- $\Delta^{\alpha}$ -pentinene- $\gamma$ -ol*,  $\text{CPh:C}\cdot\text{CHEt}\cdot\text{OH}$ , a faintly yellow oil having b. p.  $141\text{--}143^\circ/15\text{ mm.}$ ,  $D_0^\circ 1\cdot0298$ ,  $D_4^{13} 1\cdot0138$ , and  $n_D^{13} 1\cdot5633$ . With magnesium propyl iodide, phenylpropionaldehyde yields  *$\alpha$ -phenyl- $\Delta^{\alpha}$ -hexinene- $\gamma$ -ol*,  $\text{CPh:C}\cdot\text{CHPr}\cdot\text{OH}$ , an amber-coloured oil, which has b. p.  $149\text{--}152^\circ/17\text{ mm.}$ ,  $D_0^\circ 1\cdot0180$ , and decomposes when kept.  *$\alpha$ -Phenyl- $\epsilon$ -methyl- $\Delta^{\alpha}$ -hexinene- $\gamma$ -ol*,  $\text{CPh:C}\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{CHMe}_2$ , similarly obtained by means of magnesium *isobutyl* iodide, is a slightly coloured oil, has b. p.  $149\text{--}151^\circ/16\text{ mm.}$  and  $D_0^\circ 1\cdot0148$ . With phenyl magnesium bromide,  *$\alpha$ -diphenylpropinyl alcohol*,  $\text{CPh:C}\cdot\text{CHPh}\cdot\text{OH}$ , is obtained; it is a colourless oil, has b. p.  $208\cdot5\text{--}209\cdot5^\circ(\text{corr.})/15\text{ mm.}$ ,  $D_0^\circ 1\cdot1127$ ,  $D_4^{17\cdot05} 1\cdot0964$ , and  $n_D^{17\cdot05} 1\cdot6173$  (compare Moureu and Desmots, *loc. cit.*). The *additive* product,  $\text{CPh:C}\cdot\text{CHPh}\cdot\text{OMgBr}\cdot\text{Et}_2\text{O}$ , initially formed in the foregoing reaction, is crystalline.

No acetylenic alcohols are formed when amylpropionaldehyde reacts with organo-magnesium haloids.

Propionylphenylacetylene,  $\text{CPh:C}\cdot\text{COEt}$  (compare Moureu and Brachin, Abstr., 1904, i, 95), reacts with magnesium methyl iodide in presence of ether, forming a crystalline *product*, which on decomposition by water yields the *tert.-alcohol*,  $\text{CPh:C}\cdot\text{CMeEt}\cdot\text{OH}$ , and this on distillation furnishes *phenylbutenylacetylene*,  $\text{CPh:C}\cdot\text{CEt}\cdot\text{CH}_2$  or  $\text{CPh:C}\cdot\text{CMe}\cdot\text{CHMe}$ . This is a colourless liquid with a geraniol-like odour, has b. p.  $113\text{--}115^\circ/15\text{ mm.}$ ,  $D_0^\circ 0\cdot9452$ ,  $D_4^{13} 0\cdot93$ , and  $n_D^{13} 1\cdot5828$ .

Butyrylphenylacetylene,  $\text{CPh:C}\cdot\text{COPr}$  (*loc. cit.*), reacts with magnesium ethyl bromide, forming *phenylacetylene-ethylpropylcarbinol*,  $\text{CPh:C}\cdot\text{CEtPr}\cdot\text{OH}$ , which has b. p.  $155\text{--}157^\circ/16\text{ mm.}$  and  $D_0^\circ 0\cdot9885$ .

T. A. H.

**Stigmasterol**, a new Phytosterol from the Calabar Bean. ADOLF WINDAUS and A. HAUTH (*Ber.*, 1906, 39, 4378—4384).—Phytosterol (m. p. 130), prepared according to Hesse's directions (Abstr., 1878, 850), is shown not to be a single substance, as successive extractions by solvents result in the m. p. of the residue being gradually raised. The bromine additive product obtained from the acetate is easily resolved into two different bromides by fractional crystallisation from glacial acetic acid, alcohol, acetone, or ether. By careful treatment with zinc dust and acetic acid, the unsaturated acetates are recovered and the alcohols obtained by hydrolysis with

alcoholic potash. They have a constant m. p. and behave as chemical entities; 80% of the mixture consists of phytosterol, identical with the phytosterol obtained from germinating wheat and with sitosterol (Burián, Abstr., 1898, i, 72; Ritter, Abstr., 1902, i, 446). The remainder consists of an alcohol, *stigmasterol*,  $C_{30}H_{48}O, H_2O$  or  $C_{30}H_{50}O, H_2O$ , with m. p.  $170^\circ$ ,  $[\alpha]_D^{21} - 45.01^\circ$  in chloroform, and  $[\alpha]_D^{24} - 44.67^\circ$  in ethyl ether; it is isomorphous with phytosterol, forms mixed crystals with it, and gives the same colour reactions. The crude phytosterol obtained from rape-seed oil is also a mixture, one constituent of which contains one double linking, whilst the other has two double linkings; these substances are very similar in properties to stigmasterol.

*Stigmasterol acetate tetrabromide*,  $C_{32}H_{50}O_2Br_4$  (or  $C_{32}H_{52}O_2Br_4$ ), is prepared by acetylating the crude phytosterol and then treating the ethereal solution of the dry acetate with a solution of bromine in acetic acid; the tetrabromide separates in small crystals, whilst the phytosterol acetate dibromide remains in solution. When recrystallised from a mixture of chloroform and alcohol it forms four- or six-sided plates, m. p.  $211-212^\circ$ . *Stigmasterol acetate* crystallises from alcohol in rectangular plates, m. p.  $141^\circ$ ; a cryoscopic determination agrees with the formula  $C_{32}H_{50}O_2$ . The *propionate* crystallises from alcohol in prisms, m. p.  $122^\circ$ ; the *propionate tetrabromide*, m. p.  $202^\circ$ , is similar to the corresponding derivative of the acetate. The *benzoate*, m. p.  $160^\circ$ , crystallises from a mixture of chloroform and alcohol in rectangular plates, the *chloride*,  $C_{30}H_{47}Cl$  or  $C_{30}H_{49}Cl$ , from alcohol in prisms, m. p.  $95^\circ$ , and the *chloride tetrabromide* melts and decomposes at  $180^\circ$ .  
W. R.

**Transposition of Hydrobenzoin; Study of Alkylhydrobenzoin and some Trisubstituted Aromatic Glycols.** MARC TIFFENEAU and DORLENCOURT (*Compt. rend.*, 1906, 143, 1242—1244).—Aromatic trisubstituted glycols of the types  $OH \cdot CHPh \cdot CRPh \cdot OH$  and  $OH \cdot CHPh \cdot CRR \cdot OH$  yield the aldehydes  $CHO \cdot CPh_2R$  and  $CHO \cdot CPhR_2$  respectively, when treated with sulphuric acid and not the ketones as previously stated (Abstr., 1906, i, 724, 965). These trisubstituted (tertiary) aromatic aldehydes do not combine with alkali hydrogen sulphites or give a colour reaction with Schiff's reagent, but they are oxidised by silver oxide to form the corresponding acid,  $CPh_2R \cdot CO_2H$  or  $CPhR_2 \cdot CO_2H$ .

*aa-Diphenylpropaldehyde*, obtained by the action of sulphuric acid on methylhydrobenzoin, does not crystallise, b. p.  $187-191^\circ/22$  mm.,  $174-178^\circ/12$  mm., or  $301-304^\circ/760$  mm.,  $D_4^{20} 1.087$ ; the *oxime*, m. p.  $123^\circ$ , yields a *nitrile*, b. p.  $310-313^\circ$ ; the *semicarbazone* has m. p.  $122^\circ$ .

*aa-Diphenylpropionic acid*, m. p.  $173^\circ$  (Thörmer and Zincke, Abstr., 1879, 322), is obtained when the aldehyde is oxidised by means of silver oxide; and the *oxide*,  $C_{32}H_{34}O$ , m. p.  $121-122^\circ$ , is prepared by the action of magnesium phenyl bromide.

*aa-Diphenylbutaldehyde*, obtained from ethylhydrobenzoin, has b. p.  $312-316^\circ$ , yields an *oxime*, m. p.  $128-129^\circ$ , and a *semicarbazone*, m. p.

167°, and is oxidised to *aa*-diphenylbutyric acid, m. p. 170—171° (Klingemann, Abstr., 1893, i, 590).

*a*-Phenyl- $\beta$ -methylpropane- $\alpha\beta$ -diol,  $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{OH}$ , m. p. 56°, obtained by the action of magnesium methyl iodide on methyl phenylglycolate, is converted by the action of sulphuric acid into *a*-phenyl-*a*-methylpropaldehyde, b. p. 105—110°/14 mm., which yields *a*-phenyl-*a*-methylpropionic acid on oxidation, and forms a *semicarbazone*, m. p. 176°.

*a*-Phenyl- $\beta$ -ethylbutane- $\alpha\beta$ -diol, m. p. 89°, b. p. 163—165°/20 mm. or 275—280°/760 mm., is partially converted by the action of sulphuric acid into *a*-phenyl-*a*-ethylbutaldehyde, b. p. 135—140°/26 mm. or 235—238°/760 mm.,  $D_4^{20}$  0.978, which forms a *semicarbazone*, m. p. 178—179°. M. A. W.

**Application of the Grignard Reaction to Ethyl Aspartate.** CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, 39, 4344—4346. Compare Abstr., 1905, i, 436; 1906, i, 236, 583).—The reaction between ethyl ethyl-*i*-aspartate and excess of magnesium phenyl bromide in ether at 0°, leads to the formation of *r*- $\beta$ -amino- $\alpha\delta\delta$ -tetraphenylbutane- $\alpha\delta$ -diol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$ , m. p. 149—150°, which separates from dilute alcohol in white leaflets and forms sparingly soluble salts; the *hydrochloride* has m. p. 235°, and the *nitrate*, 168°.

C. S.

**The Six Isomeric Dinitrobenzoic Acids.** ARNOLD F. HOLLEMAN and H. A. SIRKS (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 280—286).—When *m*-nitrotoluene is nitrated by nitric and sulphuric acids at 50°, 3:4-dinitrotoluene is obtained together with smaller quantities of 2:3-dinitrotoluene and of 3:6-dinitrotoluene; the three isomerides are separated by fractional distillation in a vacuum and freezing the distillate. The corrected solidifying points of the dinitrotoluenes of the benzoic esters and of their ethyl esters are tabulated; also  $D_4^{25}$  for the toluenes and the esters.

The dissociation constants and the velocity of esterification of the dinitrobenzoic acids have been measured with results in accordance with expectation; the dissociation constants cannot be calculated correctly from those of the monosubstituted acids by Ostwald's rule. For a detailed criticism of the results the original paper must be consulted.

C. S.

**Action of Nitrous Acid on *p*-Dimethylamino- and *p*-Diethylamino-benzoic Acids.** OSKAR BAUDISCH (*Ber.*, 1906, 39, 4293—4300).—The author has reinvestigated the action of nitrous acid on *p*-dimethylaminobenzoic acid, and, contrary to the statement of Bischoff (Abstr., 1889, 511), found it to lead to the formation of *p*-nitrodimethylaniline, *p*-nitrosomethylaminobenzoic acid, and *m*-nitro-*p*-dimethylaminobenzoic acid.

*p*-Nitrosomethylaminobenzoic acid,  $\text{NO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , crystallises from toluene or alcohol in glistening, straw-coloured needles, m. p. 217°, gives Liebermann's reaction, and when boiled with concentrated hydrochloric acid yields *p*-methylaminobenzoic acid, which is formed

also by the action of methyl sulphate on *p*-aminobenzoic acid (Johnston, *Proc.*, 1905, 21, 156).

3-Nitro-4-dimethylaminobenzoic acid crystallises from toluene or chloroform in glistening, golden-yellow needles, m. p. 222—223°, does not give Liebermann's reaction, gives a red coloration changing through violet and bluish-green to dark red when reduced with zinc and hydrochloric acid and treated with ferric chloride, and forms a *hydrochloride* which is readily decomposed by water (compare Noelting and Demant, *Abstr.*, 1904, i, 424).

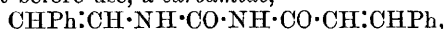
The action of sodium nitrite on *p*-diethylaminobenzoic acid in hydrochloric acid solution leads to the formation of 4-nitrosoethylaminobenzoic acid, 4-nitronitrosoethylalanine, 3-nitro-4-ethylaminobenzoic acid, 3-nitro-4-diethylaminobenzoic acid, and 4-nitrodiethylalanine in amounts varying with the quantity of sodium nitrite and the concentration of the hydrochloric acid employed. The original must be consulted for the method of separating the products.

4-Nitrosoethylaminobenzoic acid,  $\text{NO} \cdot \text{NEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , crystallises from alcohol in glistening, straw-coloured needles, m. p. 193—194°, and gives Liebermann's reaction.

3-Nitro-4-ethylaminobenzoic acid,  $\text{NHEt} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{H}$ , crystallises from light petroleum in glistening, golden-yellow needles, m. p. 239—240, forms a colourless *sulphate* which is readily decomposed by water, and when reduced with zinc and hydrochloric acid and treated with ferric chloride gives a dark red coloration, or with sodium nitrite a dark red, flocculent precipitate.

3-Nitro-4-diethylaminobenzoic acid,  $\text{NEt}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{H}$ , crystallises from light petroleum in glistening, reddish-yellow needles, m. p. 117°, and gives a dark red coloration when reduced with zinc and hydrochloric acid and treated with ferric chloride. G. Y.

**Action of Potassium Hypochlorite on Cinnamamide.** R. A. WEERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 303—304).—When an alcoholic solution of cinnamamide (2 mols.) is treated with potassium hypochlorite (1 mol.), in which the free alkali has been neutralised just before use, a *carbamide*,



is obtained, which separates from glacial acetic acid in needles, m. p. 225—226°. C. S.

**Hydroxytoluic Acids. I. 4-Hydroxy-*o*-toluic Acid.** THEODOR ZINCKE and H. FISCHER (*Annalen*, 1906, 350, 247—268. Compare Jacobson, *Abstr.*, 1881, 599; Kalle & Co., D.R.-P. 81484, 91201; Einhorn, *Abstr.*, 1900, i, 439).—The behaviour of 4-hydroxy-*o*-toluic acid towards bromine has been investigated from the point of view of its character as a derivative of *p*-cresol.

The action of bromine on 4-hydroxy-*o*-toluic acid with or without glacial acetic acid as solvent, at the laboratory temperature, and finally at 60—65°, leads to the formation of 3:5-dibromo-4-hydroxy-*o*-toluic acid,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{MeBr}_2 \cdot \text{CO}_2\text{H}$ , which crystallises from benzene in slender needles, from acetic acid in stout needles, m. p. 141°, and forms a white, crystalline *silver* salt. The *acetyl* derivative crystallises in slender

needles, m. p. 125°; the *methyl ester* forms long white needles, m. p. 108—109°.

A monobromo-4-hydroxy-*o*-toluic acid cannot be obtained, a part of the acid remaining unchanged when insufficient bromine for the formation of the dibromo-derivative is employed.

3:5:6-Tribromo-4-hydroxy-*o*-toluic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}_3\cdot\text{CO}_2\text{H}$ , prepared by heating 4-hydroxy-*o*-toluic acid or its dibromo-derivative with bromine on the water-bath, crystallises from hot benzene or water in glistening needles, m. p. 193—194°, decomposes slowly on prolonged boiling with aqueous sodium carbonate, forms a *silver* salt which blackens on exposure to air, and is converted by concentrated nitric acid into a *bromodinitro-acid*, crystallising in long needles, and commencing to decompose at 200°. The *acetyl* derivative of the tribromo-acid crystallises in short, monoclinic prisms, m. p. 176°.

3:5:6-Tribromo-4-hydroxy-*o*-toluic acid  $\psi$ -bromide (3:5:6- $\omega$ -tetrabromo-4-hydroxy-*o*-toluic acid),  $\text{CO}\left\langle\begin{array}{c} \text{CBr} \\ \text{CBr}\cdot\text{C}(\text{CO}_2\text{H}) \end{array}\right\rangle\text{CH}\cdot\text{CH}_2\text{Br}$  or  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Br}$ , formed by heating the tribromo-acid with an excess of bromine in a sealed tube at 120—125°, crystallises in long, white needles, m. p. 168°, and when treated with acetic anhydride and concentrated sulphuric acid, yields an *acetyl* derivative,  $\text{OAc}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Br}$ ; this crystallises in stout, glistening needles, m. p. 198—199°, and is converted by aqueous sodium carbonate into *tribromo-4-hydroxyphthalide*.

When treated with methyl alcohol and concentrated sulphuric acid, the tetrabromo-acid yields 3:5:6-tribromo-4-hydroxy- $\omega$ -methoxy-*o*-toluic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{OMe}$ , which crystallises from benzene in stout, colourless needles, m. p. 145—146°, or from dilute acetic acid in glistening prisms containing  $\text{H}_2\text{O}$ , m. p. 114—115°; it dissolves unchanged in aqueous sodium carbonate, and is converted by acetic anhydride and sulphuric acid into the *acetyl* derivative of the phthalide.

The action of boiling acetic anhydride and sodium acetate on the tetrabromo-acid leads to the formation of the phthalide and a sandy, sparingly soluble *substance*, m. p. above 260°, which is formed also on heating the tribromomethoxy-acid above its melting point.

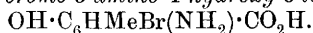
Tetrabromo-4-hydroxy-*o*-toluic acid *perbromide*,  $(\text{C}_6\text{H}_4\text{O}_3\text{Br}_4)_2\text{Br}_2$ , prepared by heating the tetrabromo-acid with an excess of bromine at 135—140° or with bromine in carbon tetrachloride solution, forms glistening, red needles, is moderately stable at the laboratory temperature, is decolorised by acetone, sodium hydrogen sulphite, or sodium hydroxide, and yields the tetrabromo-acid when heated, when dissolved in ether, or when boiled with benzene.

3:5:6-Tribromo-4-hydroxyphthalide,  $\text{OH}\cdot\text{C}_6\text{H}_3\left\langle\begin{array}{c} \text{CH}^2 \\ \text{CO} \end{array}\right\rangle\text{O}$ , prepared by the action of 10% sodium carbonate solution on the tetrabromo-acid or by boiling the acid with aqueous acetone, crystallises in glistening needles, m. p. 207°, remains unchanged when heated with hydrogen bromide or with aniline, and forms a *sodium* salt crystallising in long, white needles. The *acetyl* derivative crystallising in glistening needles, m. p. 222—223°.

*Tribromo-4-hydroxyphthalideanil*,  $\text{OH} \cdot \text{C}_6\text{Br}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} > \text{NPh}$ , formed by the action of aniline on tetrabromo-4-hydroxy-*o*-toluic acid, crystallises in glistening needles, m. p.  $220^\circ$ ; the *acetyl* derivative,  $\text{C}_{16}\text{H}_{10}\text{O}_3\text{NBr}_3$ , forms broad, glistening needles, m. p.  $225$ — $226^\circ$ .

The nitro-4-hydroxy-*o*-toluic acids formed by nitration of 4-hydroxy-*o*-toluic acid (Einhorn, *loc. cit.*) are separated by boiling with methyl-alcoholic hydrogen chloride, when 3-nitro-4-hydroxy-*o*-toluic acid, m. p.  $197^\circ$ , remains unchanged, whilst 5-nitro-4-hydroxy-*o*-toluic acid, m. p.  $160^\circ$ , is converted into its *methyl* ester,  $\text{C}_9\text{H}_9\text{O}_5\text{N}$ , crystallising in yellow leaflets, m. p.  $99^\circ$ . 3-Nitro-4-acetoxy-*o*-toluic acid, forms long, broad, almost colourless leaflets, m. p.  $139$ — $140^\circ$ .

5-Bromo-3-nitro-4-hydroxy-*o*-toluic acid,  $\text{OH} \cdot \text{C}_6\text{HMeBr}(\text{NO}_2) \cdot \text{CO}_2\text{H}$ , formed by the action of nitric acid or sodium nitrite on 3:5-dibromo-4-hydroxy-*o*-toluic acid or by the nitration of 3-nitro-4-hydroxy-*o*-toluic acid, crystallises in stout, yellow needles, m. p.  $208^\circ$ , forms characteristic *ammonium*, *sodium*, *barium*, and *silver* salts, and is reduced by tin and hydrogen chloride in methyl alcoholic solution, forming 5-bromo-3-amino-*p*-cresol, or by zinc dust in neutral solution, or by alkali sulphides, forming 5-bromo-3-amino-4-hydroxy-*o*-toluic acid,



This crystallises in colourless needles, m. p.  $179$ — $180^\circ$ , becomes brown on exposure to air in alkaline solution, and yields a sparingly soluble *diazo*-derivative. The *diacetyl* derivative,  $\text{C}_{12}\text{H}_{11}\text{O}_5\text{NBr}$ , crystallises in long needles, m. p.  $189$ — $190^\circ$ . G. Y.

**Tyrosamines.** ARMAND GAUTIER (*Bull. Soc. chim.*, 1906, [iii], 35, 1195—1197).—Water extracts from codfish livers, which have been allowed to ferment spontaneously, a mixture of amylamine and like substances with three *bases* represented by the formulae  $\text{C}_7\text{H}_9\text{ON}$ ,  $\text{C}_8\text{H}_{11}\text{ON}$ , and  $\text{C}_9\text{H}_{13}\text{ON}$ , which form colourless needles or lamellæ, and when heated at  $220^\circ$  sublime slightly and decompose. They are bitter, possess a slight, non-ammoniacal odour, are alkaline to test-paper, and give all the characteristic colour reactions of tyrosine. It is suggested that these bases are derived from tyrosine and its next two lower homologues by the loss of a molecule of carbon dioxide. The most abundant of the three bases is that having the formula  $\text{C}_8\text{H}_{11}\text{ON}$ , which on the above assumption is *p*-hydroxyphenylethylamine. It is soluble in 95 parts of water at  $15^\circ$ , crystallises in the cold, but blackens by oxidation on exposure to air. Its salts are neutral and bitter, the *hydrochloride* and *sulphate* form hygroscopic spangles or needles, and the *platinichloride* is yellow and readily soluble. All three tyrosamines are but slightly toxic. Similar products have been obtained by Leger (*Abstr.*, 1906, i, 204, 761) and by Brieger. T. A. H.

**Isomerism of Ethylcoumaric and Ethylcoumarinic Acids.** ARTHUR MICHAEL and ARTHUR B. LAMB (*Amer. Chem. J.*, 1906, 36, 552—580).—The question whether coumaric and coumarinic acids are spacial or structural isomerides has not been conclusively decided, but spacial modifications of the hydroxycinnamic acids are undoubtedly



capable of existence. Cinnamic acid is changed into *allocinnamic acid* by converting it into phenylpropionic acid, adding hydrogen bromide to this, and reducing the bromocinnamic acid thus obtained. A similar series of operations with ethylcoumaric acid is found to yield ethylcoumarinic acid, an observation which argues strongly that the relation between these acids is similar to that existing between the stereoisomeric cinnamic acids.

In the reduction of  $\beta$ -bromo-*o*-ethoxy*allocinnamic acid* no indications are given of the formation of an acid corresponding with *isocinnamic acid*.

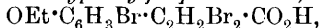
The method given by Ebert (Abstr., 1883, 471) for the preparation of ethylcoumarinic acid from coumarin, an absolute alcoholic solution of sodium ethoxide and ethyl iodide, gives the isomeric ethylcoumaric acid; if, however, the absolute alcohol is replaced by 96% alcohol, a good yield of ethylcoumarinic acid is obtained. Ebert's conclusion (*loc. cit.*) that the addition of bromine to ethylcoumaric and to ethylcoumarinic acid yields the same dibromide is confirmed.

Using the method given by Claus (*Annalen*, 1892, 269, 2) for the preparation of ethoxyphenylpropionic acid, the authors were unable to obtain an acid free from traces of halogen, which could only be removed by conversion of the acid into the calcium salt, followed by digestion with 50–60% alcohol and reconversion into the acid. The acid obtained in this way has m. p. 115.5–116°; Ebert gave 114°.

The action of hydrobromic acid on ethoxyphenylpropionic acid yields: (1) ethylbromocoumaric acid, m. p. 120°, with the bromine atom in the  $\beta$ -position to the carboxyl group; (2) a small proportion of an acid,  $C_{10}H_{11}O_3$ , crystallising from a mixture of acetone and light petroleum in white needles, m. p. 211–212.5°.

The reduction of  $\beta$ -bromo*allocinnamic acid* in alcoholic solution by means of zinc dust yields mainly *allocinnamic acid*, together with cinnamic acid and an acid with a very low melting point. When reduced in this way, bromo- $\beta$ -ethylcoumaric acid is converted almost entirely into ethylcoumarinic acid, the proportion of ethylcoumaric acid yielded being small; ethylmellilic acid could not be detected among the products of the reduction and cannot be formed in other than very minute quantities.

*a* $\beta$ -Dibromo- $\beta$ -bromoethoxyphenylpropionic acid,

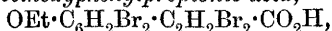


prepared by the action of bromine (4 atoms) on ethylcoumarinic acid in chloroform solution, separates from toluene in colourless, rectangular crystals, and from a mixture of acetone and light petroleum in short, slightly rhombic needles, m. p. 182–183° (decomp.).

The action of bromine (4 atoms) on ethylcoumaric acid yields a gummy residue which, when dissolved in alcohol and treated with sodium hydroxide and the solution acidified, gives *bromo-*o*-ethoxyphenylpropionic acid*,  $OEt \cdot C_6H_3Br \cdot C \cdot CO_2H$ , crystallising in needles, m. p. 134–136°. The gummy residue hence consists principally of a tribromo-derivative of ethylcoumaric acid or of bromo-*o*-ethoxyphenyldibromopropionic acid. This evidence of the dissimilarity of the corresponding products derived from ethylcoumarinic and ethylcoumaric acids requires confirmation, since Perkin found that the two

methyl acids gave the same bromo-*o*-methoxyphenyldibromopropionic acid.

The action of bromine vapour in excess on ethylcoumaric acid yields  $\alpha\beta$ -dibromo- $\beta$ -dibromoethoxyphenylpropionic acid,

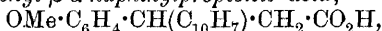


which crystallises from toluene or light petroleum in thin, rhombic plates, m. p. 183—184°. Ethylcoumarinic acid probably yields the same acid, but the product could not be purified.

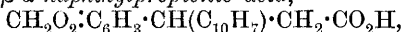
When treated with a solution of chlorine in carbon tetrachloride, ethylcoumarinic acid yields the compound,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_2\text{H}_2\text{Cl} \cdot \text{CO}_2\text{H}$ , which separates from light petroleum in crystals, m. p. 130—131°.

Ethylcoumarinic acid is not acted on by alcoholic solution of sodium ethoxide, but heating with dilute mineral acid converts it into ethylcoumaric acid (compare Perkin, *Trans.*, 1877, **31**, 388), as also does treatment with iodine in carbon disulphide solution. T. H. P.

**Replacement of the Hydroxyl of some Carbinols by the Group  $-\text{CH}_2 \cdot \text{CO}_2\text{H}$ .** ROBERT FOSSE (*Compt. rend.*, 1906, **143**, 914—916).— $\beta\beta$ -Disubstituted propionic acids are readily obtained by the condensation of malonic acid and secondary aromatic carbinols which contain the group  $-\text{OMe}$ ,  $:\text{O}_2:\text{CH}_2$  or  $-\text{NMe}_2$ , according to the equation  $:\text{CH} \cdot \text{OH} + \text{CH}_2(\text{CO}_2\text{H})_2 = \text{H}_2\text{O} + \text{CO}_2 + :\text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , and the following acids were thus prepared: (1)  $\beta$ -phenyl- $\beta$ -*p*-methoxyphenylpropionic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 121·5—122·5°; (2)  $\beta$ -*p*-methoxyphenyl- $\beta$ - $\alpha$ -naphthylpropionic acid,



and its *p*-toluidide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_{10}\text{H}_7) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , melts at 176—177°; (3)  $\beta$ -phenyl- $\beta$ -3:4-dioxymethylenephenylpropionic acid,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 155—156°; (4)  $\beta$ -3:4-dioxymethylenephenyl- $\beta$ - $\alpha$ -naphthylpropionic acid,



m. p. 205°; (5)  $\beta$ -3:4-dioxymethylenephenyl- $\beta$ -*p*-tolylpropionic acid,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{C}_7\text{H}_7) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 161°; (6)  $\beta$ -phenyl- $\beta$ -*p*-dimethylaminophenylpropionic acid,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 184·5°; (7)  $\beta$ -*p*-dimethylaminophenyl- $\beta$ - $\alpha$ -naphthylpropionic acid,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_{10}\text{H}_7) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 183°, the silver, lead, and calcium salts have been prepared; (8)  $\beta\beta$ -di-*p*-dimethylaminophenylpropionic acid,  $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 222—230°, the potassium, sodium, calcium, lead, barium, and silver salts have been prepared. Most of the acids described form white, amorphous silver salts. M. A. W.

**Nitration of Phthalic Acid and of isoPhthalic Acid.** ARNOLD F. HOLLEMAN and J. HUISINGA (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 286—292).—5-Nitroisophthalic acid, obtained by nitrating isophthalic acid, crystallises with  $1\text{H}_2\text{O}$ , and has m. p. 255—256°.

4-Nitroisophthalic acid is obtained by oxidising the corresponding xylene, prepared by nitrating xylene at 0° with nitric acid of D 1·48, with an alkaline solution of potassium permanganate. It has m. p. 245°.

2-Nitroisophthalic acid, obtained by oxidising the corresponding nitroxylenes, crystallises in needles, m. p. 300°.

The quantitative nitration of phthalic acid requires three weeks at 30°, and yields 49·5% of  $\alpha$ - and 50·5% of  $\beta$ -nitrophthalic acids. Under similar conditions, isophthalic acid yields 96·9% of the 5-nitro- and 3·1% of the 4-nitroisophthalic acids, the proportions being ascertained by solubility determinations. C. S.

**Santonin.** EDGAR WEDEKIND (*Arch. Pharm.*, 1906, 244, 623—639).—The oxonium salts of santonin (compare Abstr., 1905, i, 211) with ferrocyanic and ferricyanic acids,  $C_{15}H_{18}O_3 \cdot H_4Fe(CN)_6$  and  $C_{15}H_{18}O_3 \cdot H_3Fe(CN)_6$  respectively, were analysed; the cobalticyanide, which is distinctly crystalline, was not analysed.

A sodium santoninsulphonate,  $C_{15}H_{17}O_3 \cdot SO_3Na$ ,  $[\alpha]_D^{20} - 10 \cdot 25^\circ$ , was obtained by heating chlorosantonin (Abstr., 1905, i, 212, 529) with aqueous sodium sulphite for several hours at 140—150°; the purest sample prepared contained 96·5%. The substance is not a vermifuge.

With hydroxylamine, santonin yields a product, m. p. 92—96°, which contains N 9·3%, corresponding approximately with two atoms of nitrogen in the molecule. The substance is not a dioxime, however, for when it is heated with dilute mineral acids it yields, not santonin, but a resinous product which contains nitrogen.

Concentrated hydrochloric acid, either at the ordinary temperature or at 60°, converts santonin acid partially into desmotroposantonin.

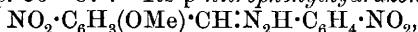
The paper contains a short statement of the modern views of the constitution of santonin and of some of its derivatives. C. F. B.

**Action of Light on Oximes.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 721—728. Compare Ciamician and Silber, Abstr., 1904, i, 161).—The author confirms Go'dschmidt's observation (Abstr., 1904, i, 250) that the oxime, m. p. 121—122°, obtained directly from *m*-nitrobenzaldehyde is the *anti*-oxime, which, when transformed by the Beckmann method, yields the *syn*-oxime, m. p. 118—119°.

The oximes of *m*-nitroanisaldehyde and *p*-chlorobenzaldoxime behave normally towards light and are transformed into the corresponding *syn*-oximes. *anti*-Benzaldoxime and *anti*-piperonaldoxime, however, remain unchanged, so that the presence of a negative group in the molecule of the aldehyde appears necessary for the passage from the *anti*- to the *syn*-oxime.

*syn*-Benzaldoxime is converted almost entirely into the *anti*-oxime on exposure to light, but with *syn*-*m*-nitrobenzaldoxime, 53% remains unchanged after six months.

*m*-Nitroanisaldehyde, prepared by Würner's method (Abstr., 1896, i, 225), has m. p. 86—87°. Its *p*-nitrophenylhydrazone,



separates from a mixture of alcohol and acetone in yellow crystals, m. p. 244°. The *oxime*,  $NO_2 \cdot C_6H_3(OMe) \cdot CH:NOH$ , is deposited from alcohol in silky, white, acicular crystals, m. p. 170°. The *syn*-oxime, prepared by Beckmann's method, crystallises from benzene in faintly yellow needles, m. p. 168—170°. The *benzyl* derivative of the *anti*-

oxime,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH}:\text{NO} \cdot \text{CH}_2\text{Ph}$ , separates from alcohol in shining, white needles, m. p.  $124^\circ$ , and the corresponding *syn-derivative* crystallises from alcohol in slender, yellow needles, m. p.  $195^\circ$ .

*anti-p*-Chlorobenzaldoxime, has m. p.  $110^\circ$ , and the *syn*-compound, m. p.  $146^\circ$  (compare Erdmann and Schwechten, Abstr., 1891, 448).

T. H. P.

**Methyl *p*-Tolyl Ketone.** CARL THOMAE and HERMANN LEHR (*Arch. Pharm.*, 1906, 244, 651—652).—Some details are given of the preparation of this ketone from acetyl chloride, toluene, and aluminium chloride, and carbon disulphide (?) (Claus and Riedel, Abstr., 1886, 642).

C. F. B.

**Compounds of Ketones with Ammonia.** CARL THOMAE (*Arch. Pharm.*, 1906, 244, 641—642. Compare Abstr., 1905, i, 509, also 684, 718).—A paper introductory to those with which the following two abstracts deal. Ketone ammonias are hydrolysed readily to ketones and ammonia by dilute aqueous acids. Alcoholic picric acid removes  $\text{NH}_3$ , forming *monoazo-ketone ammonias*; when these are distilled they lose 1 mol. of a hydrocarbon, aliphatic or aromatic, yielding trialkyl derivatives of pyridine, which sometimes can be obtained directly from the ketones by heating these strongly with alcoholic ammonia in closed vessels. The yields obtained from the ketones are small, amounting to but a few per cents. of the theoretical ones.

C. F. B.

**Compounds of Ketones with Ammonia. Action of Ammonia on Acetophenone.** CARL THOMAE (*Arch. Pharm.*, 1906, 244, 643—651).—The crude product of the action of ammonia on acetophenone at the ordinary temperature, after spontaneous evaporation of the ammonia and of most of the alcohol, was diluted with ether, mixed with coarsely powdered ice, and shaken with a slight excess of dilute (1 : 9) hydrochloric acid; from the ethereal solution, which contains much unaltered acetophenone, acetophenone ammonia hydrochloride separates. This was suspended in much alcohol, and the mixture was shaken with solid potassium hydroxide until the reaction was faintly alkaline; the liquid was filtered and the alcohol allowed to evaporate at the ordinary temperature; the residue was stirred with a little alcohol, and the crystals drained, and recrystallised from alcohol; the yield was small.

Thus obtained, *acetophenone ammonia*,  $\text{CMePh}(\text{N}:\text{CMePh})_2$  or  $\text{C}_{24}\text{H}_{24}\text{N}_2$  (molecular weight determined ebullioscopically in benzene), has m. p.  $115^\circ$ ; it reacts like a tertiary base with benzenesulphonyl chloride. It is not decomposed rapidly by water, but if a few drops of hydrochloric acid are added, hydrolysis to acetophenone and ammonia begins at once; in consequence the hydrochloride was not obtained in the pure state, nor could a platinichloride be prepared.

With picric acid in alcoholic solution, acetophenone ammonia yields yellow *monoazo-acetophenone ammonia picrate*,  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , elimination of  $\text{NH}_3$  taking place; this melts at  $210.5^\circ$ . The corresponding hydrochloride is present in the aqueous portion of the aqueous-

ethereal mixture from which the acetophenone ammonia hydrochloride separated. The base is formed in larger yield when an alcoholic solution of acetophenone is saturated with ammonia in the cold and then heated at 150—180° for twenty-seven hours in sealed glass tubes (under these circumstances no acetophenone ammonia is formed); it was only obtained in an oily or pasty condition.

When crude monoazo-acetophenone ammonia is distilled, it yields triphenylpyridine (acetophenine),  $C_{23}H_{17}N$ , with elimination of  $CH_4$ .

From the ethereal portion of the aqueous-ethereal mixture already mentioned (which contains much unchanged acetophenone), a crystalline substance of another type, containing no nitrogen, was obtained by distillation; it is undergoing investigation. C. F. B.

**Compounds of Ketones with Ammonia. Action of Ammonia on Methyl *p*-Tolyl Ketone.** CARL THOMAE and HERMANN LEHR (*Arch. Pharm.*, 1906, 244, 653—664).—The method of manipulation and the products obtained were of a similar character to those in the case of acetophenone (compare preceding abstract).

*Methyl p-tolyl ketone ammonia*,  $C_6H_4Me \cdot CMe(N \cdot CMe \cdot C_6H_4Me)_2$  or  $C_{27}H_{30}N_2$  (molecular weight determined ebullioscopically in benzene), has m. p. 111°; the *platinichloride*,  $C_{27}H_{30}N_2 \cdot H_2PtCl_6$ , has m. p. 203—204°.

*Monoazo-methyl p-tolyl ketone ammonia picrate*,  $C_{27}H_{27}N \cdot C_6H_3O_7N_3$ , has m. p. 211°. The base is not formed in appreciable quantity when the ketone is heated strongly with alcoholic ammonia.

In these circumstances, *methyl ditolylpyridine*,  $C_{20}H_{19}N$  (molecular weight determined ebullioscopically in benzene), is formed, corresponding with elimination of  $NH_3$  and  $C_6H_5Me$  from the ketone ammonia; it has m. p. 97.5°; the *picrate*,  $C_{20}H_{19}N \cdot C_6H_3O_7N_3$ , m. p. 211°, is hydrolysed by water, as also is the chloride. A small quantity of a substance of m. p. 176° was also obtained; possibly this was tritolylpyridine, resulting from elimination of  $NH_3$  and  $CH_4$  from the ketone ammonia.

A crystalline product free from nitrogen was obtained, as in the case of acetophenone. C. F. B.

**Reaction Between Unsaturated Compounds and Organo-Magnesium Compounds. X. Reactions with  $\alpha$ -Methylcinnamic Acid.** ELMER P. KOHLER (*Amer. Chem. J.*, 1906, 36, 529—538. Compare Abstr., 1906, i, 753).—The author has studied the interactions between  $\alpha$ -methylcinnamic acid and organo-magnesium compounds in order to determine the influence exerted on the action by a "positive" group in the  $\alpha$ -position of unsaturated esters. The results obtained with benzylidenepropiophenone are exactly analogous with those yielded by benzylideneacetophenone (Abstr., 1904, i, 595).

The results given in the present paper show that Blaise and Courtot's interpretation of the course of the reaction between Grignard's reagent and methylacrylic acid (Abstr., 1905, i, 257) as a direct union of the reagent to the double linking between carbon atoms is erroneous. The formation of a certain amount of saturated ketone in the action between the methylacrylic acid and magnesium

methyl iodide is due to  $\alpha\delta$ -addition, thus: (1)  $\text{CH}_2\text{:CMe}\cdot\text{CO}_2\text{Et} + \text{MgMeI} = \text{CH}_2\text{:CMe}\cdot\text{COMe} + \text{MgI}\cdot\text{OEt}$ ; (2)  $\text{CH}_2\text{:CMe}\cdot\text{COMe} + \text{MgMeI} = \text{CMeEt}\cdot\text{CMe}\cdot\text{O}\cdot\text{MgI}$  and this  $+ \text{H}_2\text{O} = \text{CMeEt}\cdot\text{CMe}\cdot\text{OH} = \text{CHMeEt}\cdot\text{COMe}$ .

The first action between methyl  $\alpha$ -methylcinnamate and an organo-magnesium derivative invariably consists in the replacement of methoxyl by a hydrocarbon residue, an unsaturated ketone being formed. When an excess of the reagent is present, the unsaturated ketone reacts immediately with a second molecule, forming either the magnesium derivative of a tertiary alcohol by addition to carbonyl or the derivative of an unsaturated alcohol by  $\alpha\delta$ -addition. When the magnesium derivative is carefully decomposed with iced acid, the resulting ethereal solution, on heating, gives only an unsaturated ketone, but when it is evaporated at a low temperature in a stream of moist air or oxygen, a peroxide is formed. This behaviour is peculiar to unsaturated alcohols obtained by  $\alpha\delta$ -addition to ketones with a hydrocarbon residue in the  $\alpha$ -position.

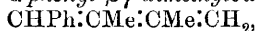
$\alpha\gamma$ -Triphenyl- $\beta$ -methylpropenyl benzoate,  $\text{OBz}\cdot\text{CPh}\cdot\text{CMe}\cdot\text{CHPh}_2$ , prepared by the action of benzoyl chloride on the intermediate magnesium derivative obtained in the interaction of magnesium phenyl bromide and methyl  $\alpha$ -methylcinnamate, crystallises from a mixture of chloroform and alcohol in needles, m. p.  $122^\circ$ .

$\alpha$ -Bromo- $\beta\beta$ -diphenyl- $\alpha$ -methylpropiofenone,  $\text{CHPh}_2\cdot\text{CBrMe}\cdot\text{COPh}$ , prepared by the action of bromine on the magnesium derivative of triphenylmethylpropenol, crystallises from a mixture of ether and light petroleum in large, lustrous plates, m. p.  $93^\circ$ .

$\alpha\gamma$ -Triphenyl- $\beta$ -methylpropenol peroxide,  $\text{CHPh}_2\cdot\text{CMe}\cdot\text{O}$   
 $\text{OH}\cdot\text{CPh}\cdot\text{O}$ , crystal-

lises from a mixture of ether and light petroleum in colourless needles, m. p.  $127^\circ$ , has the normal molecular weight in boiling ethyl ether, and, when pure, is stable at the ordinary temperature. When heated on a steam-bath or melted, it explodes, giving benzoic acid, *s*-tetraphenylethane, and a small proportion of diphenylmethane, the first two of these products being also obtained on warming the peroxide with concentrated alcoholic potassium hydroxide. If, however, the peroxide is added slowly to cooled, dilute, alcoholic potassium hydroxide, it yields the intermediate  $\alpha$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -methylpropiofenone,  $\text{CHPh}_2\cdot\text{CMe}(\text{OH})\cdot\text{COPh}$ , which crystallises from a mixture of acetone and alcohol in colourless plates, m. p.  $188^\circ$ , has the normal molecular weight in boiling ether, and is also obtained when dilute potassium hydroxide solution is gradually added to a cooled solution of  $\alpha$ -bromo- $\beta\beta$ -diphenyl- $\alpha$ -methylpropiofenone.

Methyl  $\alpha$ -methylcinnamate reacts with 2 mols. of magnesium methyl iodide, even when the latter is slowly added to excess of the ester, the product being  $\alpha$ -phenyl- $\beta\gamma$ -dimethylbutadiene,



b. p.  $165^\circ/30$  mm.

T. H. P.

**Intramolecular Atomic Transpositions. IV. Aromatic Oximes.** P. J. MONTAGNE (*Rec. trav. chim.*, 1906, 25, 376—378. Compare Abstr., 1905, i, 445).—The fact that 4:4'-dichlorobenzo-

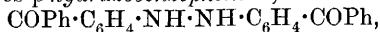
phenone after undergoing the Beckmann transformation yields on hydrolysis *p*-chlorobenzoic acid and *p*-chloroaniline shows that the rearrangement does not involve any change in the point of attachment of the ketonic carbon atom to the aromatic nucleus. P. H.

**Intramolecular Atomic Transpositions. V. Conversion of 4:4':4'':4'''-Tetrachlorobenzopinacolin into *s*-4:4':4'':4'''-Tetraphenylethane.** P. J. MONTAGNE (*Rec. trav. chim.*, 1906, 25, 379—410. Compare Abstr., 1905, i, 58, 445, 524).—The theory put forward by Klinger and Lonnes (Abstr., 1896, i, 691, 692) to explain the transformation of  $\beta$ -benzopinacolin into *s*-tetraphenylethane, first described by Thörner and Zincke (Abstr., 1878, 425), necessitates a change in the carbon atom by which the aromatic nucleus is attached. The results obtained in the present communication refute this theory, since there is no alteration in the positions of the chlorine atoms when 4:4':4'':4'''-tetrachlorobenzopinacolin is converted into 4:4':4'':4'''-tetrachlorotetraphenylethane. In the interaction of 4:4'-dichlorobenzophenone with *p*-chlorobenzoyl chloride in the presence of aluminium chloride (Abstr., 1902, i, 472) the yield, which in bright daylight is 75—80%, may be increased to 90% or more in the presence of direct sunlight; in addition to 4:4'-dichlorobenzophenone some 2:4'-dichlorobenzophenone is formed, thus disproving Beilstein's rule that only para-substituted derivatives are formed during a Friedel and Craft condensation. 4:4'-Dichlorodiphenylmethane, obtained by reducing 4:4'-dichlorodiphenylmethane with hydriodic acid and amorphous phosphorus, crystallises from light petroleum in large, flattened, monoclinic crystals [ $a:b:c = 1.8365:1.16586$ ;  $\beta = 88^\circ 45'$ ], m. p.  $55^\circ$ . 4:4':4'':4'''-Tetrachlorobenzopinacone (Abstr., 1905, i, 445) can in the absence of sunlight be prepared by reducing dichlorobenzophenone with zinc and sulphuric acid. The reduction of 4:4':4'':4'''-tetrachlorobenzopinacolin with hydriodic acid and amorphous phosphorus yields in addition to 4:4':4'':4'''-tetrachlorotetraphenylethane a substance of the molecular formula  $C_{26}H_{18}Cl_4$ , which crystallises from light petroleum in slender needles, m. p.  $215.5^\circ$ , or from benzene in triclinic prisms,  $C_{26}H_{18}Cl_4 \cdot 2C_6H_6$  [ $a:b:c = 1.0792:1.09831$ ;  $\alpha = 131^\circ 54'$ ;  $\beta = 118^\circ 50\frac{2}{3}'$ ;  $\gamma = 74^\circ 41\frac{1}{2}'$ ]. A quantitative yield of diphenylcarbinol was obtained by adding successively 25 grams of benzophenone and 30 grams of zinc powder to a boiling solution of 25 grams of potassium hydroxide in 200 c.c. of pure alcohol. P. H.

**Intramolecular Atomic Transpositions. VI. Conversion of  $\alpha$ -4:4':4'':4'''-Tetrachlorobenzopinacolin into the  $\beta$ -Variety.** P. J. MONTAGNE (*Rec. trav. chim.*, 1906, 25, 411—414. Compare Abstr., 1905, i, 58, 445—524).—On reducing 4:4'-dichlorobenzophenone by means of zinc dust and acetic acid in presence of dilute sulphuric acid for eight days, only a very small quantity of 4:4'-dichlorodiphenylcarbinol is obtained, the main product of the reaction being 4:4'-dichlorodiphenylmethane and  $\alpha$ -4:4':4'':4'''-tetrachlorobenzopinacolin  $O < \begin{smallmatrix} C(C_6H_4Cl)_2 \\ | \\ C(C_6H_4Cl)_2 \end{smallmatrix}$ . The latter crystallises from light petrol-

eum in small needles, m. p.  $235^{\circ}$  (decomp.). On oxidation with chromic acid it yields 4:4'-dichlorobenzophenone, and when heated with acetyl chloride at  $100^{\circ}$  it is converted into  $\beta$ -4:4':4'':4'''-tetrachlorobenzopinacolin,  $C(C_6H_4Cl)_3 \cdot CO \cdot C_6H_4Cl$ ; boiling alcoholic potassium hydroxide breaks it up into *p*-chlorobenzoic acid and 4:4':4''-trichlorotriphenylmethane, showing that during the migration of the group  $C_6H_4Cl$ -, necessitated by the change from the  $\alpha$ - to the  $\beta$ -variety, the relative position of the chloride atom has not been altered, and accordingly that the aromatic nucleus must be attached by the same carbon atom both before and after the transposition. P. H.

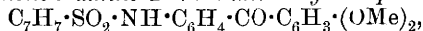
**The Alkaline Reduction of *p*- and *m*-Nitrobenzophenones.** PAUL CARRÉ (*Compt. rend.*, 1907, 144, 34—35).—The *m*- and *p*-nitrobenzophenones were prepared by the condensation of the corresponding nitrobenzoyl chlorides with benzene in the presence of aluminium chloride. *m*-Nitrobenzophenonephenylhydrazone crystallises in yellow needles, m. p.  $116^{\circ}$ ; the corresponding *p*-nitro-compound forms small, reddish-orange crystals, m. p.  $142^{\circ}$ . *p*-Nitrobenzophenone, when boiled with zinc and alcoholic soda, gives first a mixture of azo- and azoxybenzophenone which cannot be separated. By continued reduction, the ketonic group is attacked. Reduction of this mixture with ammonium hydrosulphide gives *p*-hydrazobenzophenone,



which crystallises with  $H_2O$  in white needles, m. p.  $130^{\circ}$ ; the anhydrous substance has m. p.  $162^{\circ}$ . On oxidation with mercuric oxide it gives *p*-azobenzophenone,  $N_2(C_6H_4 \cdot COPh)_2$ , which forms red lamellæ, m. p.  $219^{\circ}$ . The phenylhydrazone forms small, bright red crystals, m. p.  $130^{\circ}$ . *m*-Nitrobenzophenone gives by similar reduction *m*-azoxybenzophenone (Elbs and Wogrinz, *Abstr.*, 1903, i, 635). Ammonium hydrosulphide reduces this to an oily compound which cannot be purified and is oxidised by mercuric oxide to *m*-azobenzophenone (Elbs and Wogrinz, *loc. cit.*). Continued reduction of the *m*-azoxybenzophenone results in the attack of the ketonic group and the breaking up of the molecule. The results are analogous to those observed in the reduction of *m*- and *p*-nitrobenzyl alcohols (*Abstr.*, 1905, i, 889). E. H.

***o*-Aminobenzophenone Derivatives.** FRITZ ULLMANN and WALTER DENZLER (*Ber.*, 1906, 39, 4332—4339. Compare *Abstr.*, 1903, i, 176).—The authors have prepared a series of *o*-aminomethoxybenzophenones by condensing arylsulphoneanthranilic chlorides with the methyl ethers of the three dihydroxy-benzenes, pyrogallol, and the two naphthols respectively. The behaviour of the resulting *o*-aminoketones on diazotisation is also described.

*p*-Toluenesulphone-2-amino-2'-:5'-dimethoxybenzophenone,



obtained by the addition of quinol dimethyl ether and aluminium chloride to *p*-toluenesulphoneanthranilic chloride, crystallises in colourless leaflets, m. p.  $156^{\circ}$ . When warmed with a mixture of equal parts of concentrated sulphuric acid and glacial acetic acid, it forms 2-amino-2':5'-dimethoxybenzophenone,  $C_{15}H_{15}O_3N$ , which separates from a mixture of ether and light petroleum in amber-coloured crystals, m. p.  $98^{\circ}$ . When the latter compound is diazotised and the resulting

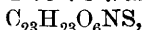


solution heated, 2-methoxyxanthone, m. p.  $131^{\circ}$ , is obtained, which is converted into 2-hydroxyxanthone when warmed with aluminium chloride.

*p-Toluenesulphone-2-amino-2':4'-dimethoxybenzophenone*, obtained from resorcinol in similar manner, separates from a mixture of benzene and light petroleum in glistening needles, m. p.  $139^{\circ}$ . On saponification it forms 2-amino-2':4'-dimethoxybenzophenone, which crystallises in yellow, stellate needles, m. p.  $128^{\circ}$ . When diazotised, as in the preceding case, it forms 3-methoxyxanthone, which is readily converted into 3-hydroxyxanthone.

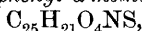
*p-Toluenesulphone-2-amino-3':4'-dimethoxybenzophenone*, obtained from veratrol, has m. p.  $125^{\circ}$  and resembles its isomerides. It forms 2-amino-3':4'-dimethoxybenzophenone, which separates from a mixture of benzene and light petroleum in yellow needles, m. p.  $74^{\circ}$ , and, when diazotised, forms a mixture of dimethoxyfluorenone,  $C_{15}H_{12}O_3$ , m. p.  $164^{\circ}$ , and 2-hydroxy-3'-4'-dimethoxybenzophenone.

*p-Toluenesulphone-2-amino-2':3':4'-trimethoxybenzophenone*,



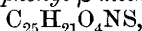
obtained by the condensation of pyrogallol trimethyl ether with *p*-toluenesulphoneanthranilic chloride, separates from alcohol in colourless, glistening scales, m. p.  $190^{\circ}$ . When the product obtained on saponification is diazotised, it forms 3:4-dimethoxyxanthone,  $C_{15}H_{12}O_4$ , which separates from a mixture of benzene and light petroleum in yellow needles, m. p.  $155^{\circ}$ , and gives a green fluorescence with concentrated sulphuric acid.

*p-Toluenesulphone-2-aminophenyl  $\alpha$ -methoxynaphthyl ketone*,



obtained by the condensation of *p*-toluenesulphoneanthranilic chloride with  $\alpha$ -naphthyl methyl ether, separates from alcohol in colourless leaflets, m. p.  $192^{\circ}$ . When saponified, it forms 2-aminophenyl  $\alpha$ -methoxynaphthyl ketone,  $C_{18}H_{15}O_2N$ , which separates from dilute alcohol in yellow, glistening crystals, m. p.  $147^{\circ}$ , and on diazotisation forms  $\alpha$ -methoxynaphthylfluorenone,  $C_{18}H_{13}O_2$ , which crystallises from alcohol in orange-red needles, m. p.  $183^{\circ}$ , and forms a yellowish-green solution with concentrated sulphuric acid. 2-Hydroxyphenyl  $\alpha$ -methoxynaphthyl ketone,  $C_{18}H_{14}O_3$ , crystallises from dilute alcohol in yellow leaflets, m. p.  $124^{\circ}$ .

*p-Toluenesulphone-2-aminophenyl  $\beta$ -methoxynaphthyl ketone*,



obtained from  $\beta$ -naphthyl methyl ether, separates from alcohol in glistening crystals, m. p.  $181^{\circ}$ . When heated with concentrated sulphuric acid in the usual manner it undergoes sulphonation as well as saponification, forming 2-aminophenyl  $\beta$ -methoxynaphthyl ketone-sulphonic acid,  $C_{18}H_{15}O_5NS$ , which separates in yellow crystals. When diazotised, the latter yields a product the solution of which in sulphuric acid is yellow and exhibits a green fluorescence, and is accordingly a xanthone derivative.

1:2-Phenonaphthacridone,  $C_{17}H_{11}ON$ , obtained by heating *p*-toluenesulphone-2-aminophenyl  $\beta$ -methoxynaphthyl ketone with hydrochloric acid at  $150$ — $180^{\circ}$ , separates from pyridine in brownish-yellow needles, m. p.  $383^{\circ}$ . Its alcoholic solution exhibits a blue fluorescence; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence.

A. McK.

**Triquinoyl.** FRANZ HENLE (*Annalen*, 1906, 350, 330—343. Compare Nietzki and Benckiser, *Abstr.*, 1885, 779, 1127; Nietzki and Schmidt, *Abstr.*, 1888, 690, 943).—Triquinoyl is readily soluble in moderately concentrated solutions of sodium, potassium, ammonium, calcium, barium, or magnesium chloride, potassium iodide, or potassium or sodium nitrate at the ordinary temperature, but is only sparingly so in alkali sulphates, and is insoluble in mercuric chloride solutions. It may be purified by solution in hot aqueous sodium chloride, from which on cooling more than 60% separates, m. p. 98°, or after recrystallisation from dilute nitric acid, m. p. 100° (decomp.). These solutions of triquinoyl decompose slowly at the laboratory temperature, more quickly when heated, evolving carbon dioxide and forming rhodizonic acid. The solution in aqueous barium chloride yields a red barium salt,  $\begin{matrix} \text{C(OH)}_2 \cdot \text{C(OH)}_2 \cdot \text{C} \cdot \text{O} \cdot \text{BaCl} \\ | \\ \text{C(OH)}_2 \cdot \text{C(OH)}_2 \cdot \text{C} \cdot \text{O} \cdot \text{BaCl} \end{matrix}$  together with a volume of carbon dioxide corresponding with the equation  $7\text{C}_6\text{O}_6 + 6\text{H}_2\text{O} = 6\text{C}_6\text{H}_2\text{O}_6 + 6\text{CO}_2$ ; the red salt is only slowly decomposed by boiling water, forming barium rhodizonate and chloride. The formation of this salt serves for the characterisation of triquinoyl.

The action of baryta on triquinoyl in aqueous solution leads to the formation, according to the conditions, of four salts: a red salt,  $\text{C}_6\text{O}_6, 3\text{H}_2\text{O}, 3\text{baOH}$ , and three white salts:  $\text{C}_6\text{O}_6, 4\text{H}_2\text{O}, 5\text{baOH}$ ;  $\text{C}_6\text{O}_6, 4\text{H}_2\text{O}, 4\text{baOH}$ , and  $\text{C}_6\text{O}_6, 3\text{H}_2\text{O}, 4\text{baOH}$  respectively. The results obtained on titration of triquinoyl with baryta agree with the compositions of the salts  $\text{C}_6\text{O}_6, 4\text{H}_2\text{O}, 5\text{baOH}$  and  $\text{C}_6\text{O}_6, 4\text{H}_2\text{O}, 4\text{baOH}$ . When treated with hydrochloric or sulphuric acid, the red salt yields carbon dioxide and rhodizonic acid, whilst the white salts form carbon dioxide and a syrup which reduces silver nitrate and Fehling's solutions in the cold.

Triquinoyl is soluble in acetic anhydride in presence of traces of concentrated sulphuric acid, in ether when shaken with phosphorus pentoxide, or in methyl alcohol in presence of traces of hydrogen chloride. On evaporation in a vacuum at 20°, the methyl alcoholic solution yields crystalline triquinoyl, but if first shaken with anhydrous sodium sulphate, a yellow syrup, which readily decomposes, evolving carbon dioxide, and forms crystalline triquinoyl only on addition of water. The action of sodium acetate on the methyl alcoholic solution leads to the formation of sodium rhodizonate; the action of anhydrous ammonia on the ethereal or methyl alcoholic solution leads to that of a blackish-red substance, which is converted by water into ammonium rhodizonate.

Anhydrous triquinoyl,  $\text{C}_6\text{O}_6$ , which must be present in the ethereal and methyl alcoholic solutions, is formed also together with silver bromide when silver rhodizonate is treated with bromine in ethereal solution.

G. Y.

**Buchu camphor.** IWAN L. KONDAKOFF (*Chem. Zeit.*, 1906, 30, 1090—1091 and 1100—1101).—Polemical. The author maintains that the results published by Semmler and McKenzie (*Abstr.*, 1906, i, 373) are in the main a repetition of his own (*Abstr.*, 1905, i, 798).

The paper contains a historical summary of the work which has been done on this subject. P. H.

**Components of Ethereal Oils. I. Resolution of the Bicyclic Triocean System in Sabinene and Tanacetone. II. A New Series of Terpenes (*cyclopentadienes*).** FRIEDRICH W. SEMMLER (*Ber.*, 1906, 39, 4414—4428).—From tanacetone both *cyclohexane* and *cyclopentane* derivatives can be obtained, whereas in the case of bicyclic hydrocarbons only the conversion into terpinenes or limonenes, both *cyclohexane* derivatives, is known. It has hitherto not been possible to break the three-membered ring in the bicyclic triocean system of sabinene and obtain a *cyclopentane* derivative.

By the action of formic acid on sabinene, a product is obtained which is separated into two fractions on distillation. The one, a *formate*,  $C_{11}H_{18}O_2$ , b. p. 102—106°/10 mm.,  $n_D +14.15'$  (100 mm.),  $n_D 1.4745$ ,  $D^{20}_D 0.975$ , yields on hydrolysis an *alcohol*,  $C_{10}H_{18}O$ , b. p. 93—96°/11 mm.,  $n_D 1.48033$ ,  $D^{20}_D 0.926$ , which forms a dihydrochloride, m. p. 51—52°, identical with that formed on acting on sabinene with acetic acid and hydrogen chloride, and probably identical with terpinene dihydrochloride. On oxidation with permanganate, the alcohol forms a glycerol,  $C_{10}H_{18}O_3$ , b. p. 175—177°/10 mm., which crystallises from chloroform and is perhaps identical with the glycerol obtained by Biltz (*Abstr.*, 1899, i, 535) from origanol (*p*-methylisopropyl*cyclohexenol*). The formate on distillation with quinoline forms a terpene,  $C_{10}H_{16}$ , b. p. 174—177°,  $n_D 1.479$ ,  $D^{20}_D 0.839$ . The alcohol,  $C_{10}H_{18}O$ , is thus a mixture of dimethylisopropyl*cyclopentenol* and origanol.

The second product of the action of formic acid on sabinene is a terpene,  $C_{10}H_{16}$ , b. p. 50—54°/10 mm., 169—173°/760 mm.,  $n_D 1.47$ ,  $D^{20}_D 0.829$ —0.831,  $n_D +13$ —14° (10 mm. tube), M.R. 45.71, which constants point to its being a *cyclopentadiene*. E. F. A.

**Sandarac.** ALEXANDER TSCHIRCH and MAX WOLFF (*Arch. Pharm.*, 1906, 244, 684—712. Compare Tschirch and Balzer, *Abstr.*, 1896, i, 493; Henry, *Trans.*, 1901, 1144).—The resin examined had  $D 1.071$ , acid number 141, and saponification number 166. Some of it was submitted to dry distillation: among the products, acetic acid was detected, but not butyric acid or acetic acid; attempts to isolate retene were unsuccessful.

From an ethereal solution of the resin, 1% aqueous ammonium carbonate extracted amorphous *sandaracic acid*,  $C_{25}H_{34}O_3$ , in 2.3% yield; m. p. 186—188° (decomp.), has acid number 163 (corresponding with monobasicity), and saponification number 175, and does not contain methoxyl.

With 1% aqueous sodium carbonate, acids were then extracted in 87% yield. The bulk of these consisted of an amorphous acid of which the lead salt is insoluble in alcohol, *sandaracinolic acid*,  $C_{24}H_{36}O_3$ ; this decomposes at 265—275°, has acid number 160 (corresponding with monobasicity), and saponification number 169, does not contain methoxyl, and forms with acetic anhydride a product that yields acetic acid when hydrolysed. Mixed with this acid is a small quantity of

another, *sandaracopimaric acid*,  $C_{30}H_{50}O_2$ ; this is crystalline, has m. p.  $170^\circ$ , acid number 187 (corresponding with monobasicity), saponification number 194, and iodine number 140 (addition of 3I requires 126); it forms an amorphous *silver* salt containing Ag 26.7%; it does not contain methoxyl or form an acetyl derivative. From the later portions of sodium carbonate solution used in the extraction, when they were allowed to remain, a crystalline *sodium* salt separated in yield equal to 0.7% of the resin; this melted at  $83\text{--}85^\circ$ , dissolved in benzene as well as in water, and contained Na 7.7%; the corresponding *silver* salt contained Ag 22.4%; the *acid* decomposed at  $146\text{--}148^\circ$ , contained C 71—76%, H 9.4%, and seemed to undergo slowly a transformation of which the *bitter principle*, which also occurs in the resin itself, is a product.

From the remaining ethereal solution, aqueous potassium hydroxide, even of 50% strength, did not extract anything. The ether was distilled off, and the residue steam-distilled, when an *essential oil*, of b. p.  $152\text{--}159^\circ$ , distilled over in 1.3% yield, while amorphous *sandaracoresen*,  $C_{22}H_{36}O_2$ , of m. p.  $57^\circ$ , remained in 3.3% yield; the resin appears to undergo spontaneously a slow transformation of which acid and essential oil are products.

The acids obtained are optically inactive, even before the treatment with alkali.

C. F. B.

**Molecular Weight of Elaterin.** ARMAND BERG (*Compt. rend.*, 1906, 143, 1161—1163. Compare Abstr., 1898, ii, 447; 1906, i, 596).—Chiefly polemical against Pollak (Abstr., 1906, i, 973). Further evidence in favour of the formula  $C_{28}H_{38}O_7$  for elaterin is afforded by the results of the analyses of the *sodium*, *cadmium*, and *copper* salts of elateric acid.

M. A. W.

**Reduction of the Furan Nucleus.** MAURICE PADOA and U. PONTI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 610—615. Compare Abstr., 1906, i, 530).—When mixed with hydrogen and passed over reduced nickel heated at about  $190^\circ$ , furfuraldehyde vapour yields mainly furfuryl alcohol, together with small proportions of more highly hydrogenated compounds. To obtain larger quantities of the latter, furfuryl alcohol itself was reduced in the above manner, the products then obtained being 2-methylfuran, 2-methyltetrahydrofuran,  $\alpha$ -methyl-*n*-butyl alcohol, and methyl propyl ketone.

When passed over reduced nickel heated at about  $270^\circ$ , furfuraldehyde vapour is decomposed into carbonic oxide and furan.

T. H. P.

**Ethyl Pyromucylacetate [Furfuroylacetate].** HENRY A. TORREY and JOAQUIN E. ZANETTI (*Amer. Chem. J.*, 1906, 36, 539—543).—Ethyl furfuroylacetate, prepared by Sandelin's method (Abstr., 1900, i, 305), is a pale yellow, heavy oil, b. p.  $143\text{--}145^\circ/10$  mm. Its *oxime*,  $C_4OH_3 \cdot C(NO_2) \cdot CH_2 \cdot CO_2Et$ , crystallises from aqueous alcohol in long, silky needles, m. p.  $131\text{--}132^\circ$ . Its *semicarbazone*,  $C_4OH_3 \cdot C(N_2H \cdot CO \cdot NH_2) \cdot CH_2 \cdot CO_2Et$ , crystallises from alcohol in flat, rhombic plates, m. p.  $142\text{--}144^\circ$ .

*Acetyl-1-phenyl-3-furylpyrazolone*,  $C_{13}H_9O_2N_2Ac$ , crystallises from light petroleum in flat, faintly yellow prisms, m. p. 69—72°. *Benzoyl-1-phenyl-3-furylpyrazolone*,  $C_{18}H_9O_2N_2Bz$ , crystallises from aqueous alcohol in white needles, m. p. 113—114°, and dissolves in alcohol or ether. *Nitroso-1-phenyl-3-furylpyrazolone*,  $C_{13}H_9O_2N_2NO$ , separates from aqueous alcohol as a bright red, amorphous, hygroscopic precipitate, softens at about 170°, and decomposes at 183—184°. T. H. P.

**The Pyran Series. II. Condensation of Ethyl Oxalacetate with Cyclic Aldehydes.** H. GAULT (*Bull. Soc. chim.*, 1906, [iii], 35, 1264—1275. Compare Abstr., 1904, i, 762; 1906, i, 300).—This series of ketoarylparaconic esters has been obtained by condensing ethyl oxalacetate with cyclic aldehydes: (1) by Wislicenus' method (Abstr., 1893, i, 146 and 714), condensation by means of hydrogen chloride, or (2) by condensation in presence of diethylamine, the diethylamine derivative being first obtained in the latter case. All the esters give red colorations with ferric chloride and are soluble in aqueous solutions of alkali carbonates, from which they are reprecipitated unchanged on the addition of acids.

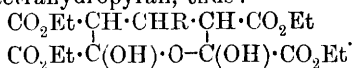
Ethyl ketophenylparaconate,  $CO \begin{array}{c} \diagup CO \cdot CH \cdot CO_2Et \\ \diagdown O - CHPh \end{array}$ , m. p. 104—105° (compare Wislicenus, *loc. cit.*), furnishes a *diethylamine* derivative,  $CO \begin{array}{c} \diagup C(O \cdot NH_2Et_2) : C \cdot CO_2Et \\ \diagdown O - CHPh \end{array}$ , which is formed when benzaldehyde is

condensed with ethyl oxalacetate in presence of diethylamine, and separates from alcohol in colourless crystals, m. p. about 160° (decomp.). *Ethyl ketoanisylparaconate*,  $CO \begin{array}{c} \diagup CO \cdot CH \cdot CO_2Et \\ \diagdown O - CH \cdot C_6H_4 \cdot OMe \end{array}$ , similarly obtained from anisaldehyde, separates from benzene or dilute alcohol in crystals, m. p. 96°. The *diethylamine* derivative forms colourless crystals, m. p. about 160° (decomp.). *Ethyl keto-o-nitrophenylparaconate*, similarly prepared from *o*-nitrobenzaldehyde, separates from alcohol in colourless crystals, m. p. 115°. The *diethylamine* derivative forms small, faintly yellow crystals, m. p. about 165° (decomp.). *Ethyl keto-m-nitrophenylparaconate* separates from benzene or alcohol in crystals, m. p. 96°, and yields a *diethylamine* derivative which is faintly yellow, m. p. about 165° (decomp.). *Ethyl keto-p-hydroxyphenylparaconate*, m. p. 184°, crystallises from alcohol; the *diethylamine* derivative separates from dilute alcohol in crystals and melts and decomposes about 165°.

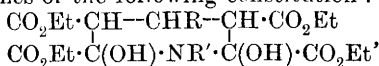
When ethyl oxalacetate is condensed with salicylaldehyde in presence of hydrogen chloride there is formed *ethyl salicylideneoxalacetate hydrochloride*,  $CO_2Et \cdot CO \cdot C(CO_2Et) : CH \cdot C_6H_4 \cdot OH, HCl$ , m. p. 98°, which crystallises from light petroleum; it readily loses  $HCl$  when warmed alone or when treated in the cold with potassium carbonate or potassium hydrogen carbonate, yielding the free *ester* which is obtained directly when the condensation is effected in presence of piperidine or diethylamine. The ester separates from dilute alcohol in crystals, m. p. 91°; its alcoholic solution is not coloured by ferric chloride.

T. A. H.

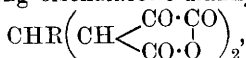
**The Pyran Series. III. Condensation of Ethyl Oxalacetate with Aliphatic Aldehydes.** H. GAULT (*Bull. Soc. chim.*, 1907, [iv], 1, 21—32).—Aliphatic aldehydes condense with ethyl oxalacetate in presence of piperidine to form the corresponding ethyl alkylidene-bisoxalacetates,  $\text{CHR}[\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CO}_2\text{Et}]_2$ . These are crystalline solids and combine with a molecule of water to form hydrates which are derivatives of tetrahydropyran, thus:



Alcoholic solutions of these hydrates give a red coloration with ferric chloride on warming, and furnish monophenylhydrazones and monosemicarbazones of the following constitution:



where  $\text{R}^1$  may be  $-\text{NHPh}$  or  $\text{NH}\cdot\text{CO}\cdot\text{CH}_2$ , and are hydrolysed by dilute acids, forming  $\alpha$ -diketonic acids, and by cold sulphuric acid, forming the corresponding bisoxalacetic dianhydrides,

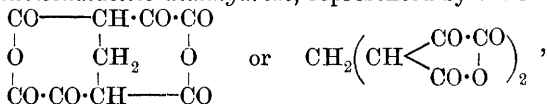


which in contact with water are transformed into the corresponding unstable di- $\beta$ -ketonic acids; these readily lose carbon dioxide and form  $\alpha$ -diketopimelic acids (compare Abstr., 1904, i, 762; 1906, i, 300).

Ethyl methylenebisoxalacetate, obtained from formaldehyde by the general method (*loc. cit.*), furnishes a *hydrate*, m. p. about  $112^\circ$ , which crystallises from dilute alcohol and is slightly soluble in cold, but readily so in hot alcohol. The *hydrosulphide*, obtained by treating a solution of the ether in alcohol with hydrogen sulphide, crystallises from ether on addition of light petroleum in small needles, m. p.  $118^\circ$ , and is regarded as having a constitution analogous to that of the hydrate. Both the hydrate and hydrosulphide regenerate ethyl methylenebisoxalacetate when heated at  $110^\circ$ . The *monophenylhydrazone*, m. p.  $143^\circ$ , obtained by the action of phenylhydrazine on the hydrate dissolved in alcohol, crystallises from dilute alcohol and is coloured red by ferric chloride on warming. The anhydrous ether furnishes a *diphenylhydrazone*, m. p.  $211^\circ$ , which separates from acetone in woolly crystals. The *monosemicarbazone* yielded by the hydrated ether crystallises from boiling water; m. p.  $167^\circ$  (decomp.).

*Methylenebisoxalacetotetra-amide*, m. p. about  $170^\circ$  (decomp.), is produced when either the ether or its hydrate, dissolved in alcohol, is treated with dry ammonia; it is coloured red by ferric chloride. *Methylenebisoxalacetotetrazenylamidedibenzylimide*, obtained by condensing benzylamine with the anhydrous ether, crystallises from boiling acetone and has m. p.  $216\text{---}217^\circ$ .

*Methylenebisoxalacetic dianhydride*, represented by the formula



of which the second is preferred, is produced on treating ethyl methylenebisoxalacetate with sulphuric acid. It is very unstable, and

in contact with a minute quantity of water at  $0^{\circ}$  forms a crystalline *monohydrate*, which when allowed to dry in the air loses carbon dioxide, but when dried over sulphuric acid under reduced pressure regenerates the dianhydride. The latter with excess of water dissolves and passes into the unstable diketonic tetracarboxylic acid, which decomposes rapidly, giving rise to diketopimelic acid (Abstr., 1905, i, 763). The dianhydride on treatment with aniline yields a dianilide, which also decomposes readily, forming the dianilide of diketopimelic acid. The latter acid is also produced directly by boiling the dianhydride with dilute acids.

T. A. H.

**Constituents of the Leaves of *Carpinus Betulus*. Ellagic Acid and Tannic Acids.** KARL ALPERS (*Arch. Pharm.*, 1906, 244, 575—601).—The author sums up the results of his investigation as follows. The leaves of the hornbeam (*Carpinus Betulus*, L.) contain a glucoside from which ellagic acid is eliminated very readily, even in the extraction of the leaves with 40% alcohol. Neither glucosides nor aldehyde could be detected. Methyl alcohol and acetone, as well as ethyl alcohol, dissolve ellagic acid to an appreciable, although slight, extent; in all other of the usual solvents, ellagic acid is practically insoluble. Ellagic acid chars at  $450-480^{\circ}$  without first melting. The shape of its crystals varies; under the microscope it appears to consist of short, rhombic prisms and long, prismatic needles. The constitution of ellagic acid probably is best expressed by Graebe's formula (Abstr., 1903, i, 262); the water that air-dried ellagic acid loses at  $100^{\circ}$  possibly is anhydride water and not water of crystallisation; in that case the air-dried acid might be regarded as hexahydroxydiphenyldicarboxylic acid, and the acid after drying at  $100^{\circ}$  as the dilactone of this as represented by Graebe's formula.

The tannin of hornbeam leaves has much similarity with ellagitanic acid (Löwe, *Zeit. anal. Chem.*, 1875, 14, 35); it yields gallic acid when hydrolysed. No glucosidic character could be detected in the tannin; in this respect it differs from the tannin of myrobalans, of algarobilla, and of divi-divi pods.

C. F. B.

**Behaviour of Alkaloid Salts and of other Organic Substances with Regard to Solvents. Reducing Action of Alkaloids.** A. SIMMER (*Arch. Pharm.*, 1906, 244, 672—684).—Aqueous solutions of salt of the alkaloids, containing 0.4% of the base, were percolated with solvents; so also were solutions containing the same percentage of alkaloid with excess of acid. The stronger the base the less of it passed into the organic solvent: chloroform dissolved out hardly appreciable amounts of nicotine and atropine; more veratrine, strychnine, brucine, codeine, cocaine, and morphine; and still more narcotine, papaverine, colchichine, caffeine, and anti-pyrine. In the presence of excess of acid, the amount of the stronger alkaloids extracted was much diminished; if the salt itself is soluble in chloroform, the amount of it extracted increases up to a certain point with the excess of free acid, if this be hydrochloric, hydrobromic, or nitric; if it be sulphuric, phosphoric, citric, or tartaric, of which the alkaloid salts are insoluble in chloroform, none of the alkaloid is

dissolved out, provided in the case of the last two acids that the excess of them is considerable.

Similar experiments were made with the sodium derivatives of picrotoxin, santonin, coussain, cantharidin, and salicylic acid, with and without excess of sodium hydroxide. In the absence of the latter all but cantharidin passed into the chloroform in appreciable quantity; in the presence of sodium hydroxide only coussain and picrotoxin, and of these but traces.

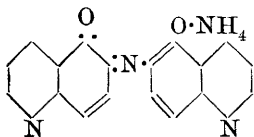
Experiments were also made with benzene and ether, in both of which alkaloids and alkaloid salts are less soluble than in chloroform, with carbon tetrachloride, and in the case of morphine, with amyl and isobutyl alcohols.

Many of the numerical results are tabulated.

When an alkaloid mixed with chloroform and water was percolated with chloroform for eight hours, in the cases of brucine, veratrine, strychnine, atropine, and cocaine, the chloroform was found to contain chloride equivalent to an amount of the alkaloid decreasing in the order named from 1.7% to 0.2% of the whole; in other cases there was no such action. Formation of formic acid could not be detected. The action of certain alkaloids and their salts in *N*/200 alcoholic or aqueous solution on various oxidising agents was studied, namely, silver nitrate, gold chloride, mercuric chloride, ferric salts, acid permanganate solution, &c. Morphine is particularly active as a reducing agent, atropine and cocaine were the only ones that did not reduce permanganate appreciably. The salts did not reduce silver nitrate or mercuric chloride; with gold chloride this difference between the alkaloids and their salts was not manifested to the same extent. C. F. B.

**The Thalleioquinine Reaction.** HERMANN FÜHNER (*Arch. Pharm.*, 1906, 244, 602—622).—An attempt to throw light on the nature of the thalleioquinine reaction. As the reaction is given not only by quinine but also by cupreine, it would seem that the reaction must be attributed to the *p*-hydroxyquinoline group. In the first phase, the action of chlorine water converts this into a dichloroquinone, in the second phase this is converted by ammonia into a quinonimine colouring matter. The constitution of the chlorine substitution products obtained from *p*-quinanisoole and quinine, where the contained phenol group is methylated, is a matter for further research.

5:5-Dichloro-6-ketoquinoline,  $C_9H_5ONCl_2$  (Abstr., 1905, i, 828), yields 5-chloro-6-hydroxyquinoline,  $C_9H_6ONCl$ , when it is boiled with dilute alcohol; when it is heated with aniline in alcoholic solution at 50° it yields 5-chloro-6-hydroxy-8-anilinequinoline,  $C_{15}H_{11}ON_2Cl$ , m. p. 127—128°, which forms both yellow and dark brown crystals; when a solution of it in dilute alcohol is mixed at once with an excess of ammonia, it yields dark blue, amorphous, colloidal thalleioquinoline,  $C_{18}H_{14}O_2N_4$ , probably having the annexed constitution, analogous with that of thalleioquinine. It is essential that an excess of ammonia be added at once; when ammonia is added gradually, the precipitate obtained is brown.





The urine of a dog to which quinoline had been administered was found to be coloured green by ammonia after it had been boiled with hydrochloric acid. The presence of 5:6-quinolinequinone was detected; and it was found by a special experiment that this substance, like the dichloroketoquinoline, reacts with ammonia to form thalleioquinoline.  
C. F. B.

**Constitution of Hordenine.** EUGÈNE LÉGER (*Compt. rend.*, 1906, 143, 916—918).—The author has shown already that hordenine has the formula  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$  (Abstr., 1906, i, 204, 761), and in the present paper it is shown that the hydroxyl group is in the para-position, because when the acetyl derivative of hordenine is oxidised by potassium permanganate, *p*-acetoxybenzoic acid is formed. Hordenine is therefore *p*-hydroxyphenylethyldimethylamine.

M. A. W.

**A Fifth Methylmorphimethine,** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, 39, 4412—4414).—The fifth or  $\epsilon$ -methylmorphimethine is obtained as a laevorotatory oil by the action of boiling sodium hydroxide on  $\psi$ -codeine methiodide; the hydrochloride crystallises in large, glistening cubes, m. p.  $150^\circ$  (decomp.), the methiodide in needles, m. p.  $195$ — $200^\circ$ , whilst acetyl- $\epsilon$ -methylmorphimethine methiodide forms sparingly soluble needles, m. p.  $205$ — $210^\circ$ .

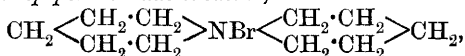
E. F. A.

**Conversion of Chlorocodide into  $\psi$ -Codeine.** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, 39, 4409—4411).—By acting on chlorocodide with water at  $140$ — $150^\circ$ , Göhlich (Abstr., 1893, i, 675) showed that codeine was formed. On adding, however, acetic acid to an emulsion of chlorocodide and warm water, the substance obtained is identical with Merck's  $\psi$ -codeine (Abstr., 1891, 1121). The hydriodide, m. p.  $260$ — $265^\circ$ , crystallises in glistening plates; the methiodide, m. p.  $270^\circ$ , also forms large, glistening plates. The hydriodide of acetyl- $\psi$ -codeine separates in opaque, anhydrous crystals decomposing at  $285^\circ$ .

E. F. A.

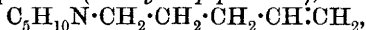
**Cyclic Imines. III.** JULIUS VON BRAUN, CARL MÜLLER, and ERICH BESCHKE (*Ber.*, 1906, 39, 4347—4357. Compare Abstr., 1905, i, 826; this vol., i, 28).—1-Alkylpiperidines are obtained in good yield from  $\alpha\epsilon$ -dibromopentane (1 mol.) and primary amines (3 mols.) (compare Abstr., 1904, i, 841).

*Pentamethylenepiperidinium bromide,*



which the author terms *dipiperidinium bromide*, obtained from  $\alpha\epsilon$ -dibromopentane and piperidine in nearly quantitative yield in chloroform solution, forms a snow-white, crystalline mass. The *platinichloride*,  $\text{C}_{10}\text{H}_{20}\text{NPtCl}_6$ , darkens at  $225^\circ$ , m. p.  $245^\circ$  (decomp.).

$\epsilon$ -Piperidino- $\Delta^a$ -pentene (1-amylenepiperidine),



b. p.  $201$ — $202^\circ$ , obtained by the action of moist silver oxide on the preceding bromide, is a colourless liquid with a basic odour; the

*platinichloride* has m. p. 99—101°; the *picrate*, 93—94°, and the *methiodide*, 159°. By treatment with concentrated hydrobromic acid at 0° it yields 1- $\delta$ -*bromoamylpiperidine*,  $C_5H_{10}N \cdot C_5H_{10}Br$ , the *picrate* of which has m. p. 122°. The free base is very unstable, changing readily into Scholtz and Friemehl's pentamethylene-2-methylpyrrolidinium bromide (Abstr., 1899, i, 541).

Pentamethylenepiperidinium bromide reacts extremely slowly with concentrated ammonia at 225°, forming a triacid base,  $C_{20}H_{41}N_3$ , b. p. 185—187°/22 mm., of which the *hydrochloride*, the *platinichloride*, m. p. 229° (decomp.), and the *aurichloride*, m. p. 170—171°, are described. C. S.

### Action of Grignard's Reagent on certain Indolenines.

GIUSEPPE PLANCHER and C. RAVENNA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 555—561).—When 2:3:3-trimethylindolenine or 2:3:3:5-tetramethylindolenine is treated with Grignard's reagent, it is transformed into the corresponding dimolecular polymeride, the compound behaving as if it had the tautomeric methyleneindoline formula  $C_6H_4 \begin{smallmatrix} \text{CRR} \\ \text{NH} \end{smallmatrix} \text{C:CH}_2$ . As the pure indolenines undergo polymerisation of themselves, Grignard's reagent here plays the part of a catalyst.

Under the action of magnesium phenyl bromide or magnesium methyl iodide, 2:3:3-trimethylindolenine yields the *polymeride*  $(C_{11}H_9N)_2$ , which separates from alcohol in pale yellow crystals, m. p. 132°, and is reconverted into the unimolecular base if heated above its melting point; with nitrous acid in acetic acid solution it gives the oxime of 2:3:3-trimethylindolenine; if the polymeride is dissolved in very dilute hydrochloric acid and the solution immediately rendered alkaline, it is reprecipitated in a flocculent condition, but generally the liquid base is attained.

Magnesium methyl iodide also acts on 2:3:3:5-tetramethylindolenine, converting it into the *polymeride*  $(C_{12}H_{15}N)_2$ , which separates from alcohol or light petroleum in pale yellow crystals, m. p. 111—112°, and is less readily polymerised than the polymeric 2:3:3-trimethyl derivative.

The interaction of magnesium phenyl bromide and 2-methyl-3:3:5-dimethylindolenine also yields a solid base.

The action of magnesium phenyl bromide on acetophenoneanilide gives a compound,  $CPh_2Me \cdot NHPh$  (?), m. p. 94—96°. T. H. P.

**New Method of Preparation of 1-Methylindole.** ORESTE CARRASCO and MAURICE PADOA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 729—731. Compare Abstr., 1906, i, 695).—On passing dimethyl-*o*-toluidine, drop by drop, through a tube containing reduced nickel heated at 300—330°, part of the base yields 1-methylindole and part undergoes demethylation, giving rise to methyl-*o*-toluidine, *o*-toluidine, and probably methane. By mixing the dimethyl-*o*-toluidine with hydrogen before passing it over the heated nickel, the yield of 1-methylindole is raised from 6 to 24%; the yield of indole

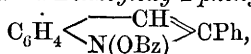
from methyl-*o*-toluidine (*loc. cit.*) is raised in the same way from 6 to 8%.

Under the above conditions, ethyl-*o*-toluidine yields a small proportion of a product of an indolic character, probably 2-methylindole.

T. H. P.

**Action of Chloroform and Potassium Hydroxide on Scatole [3-Methylindole].** ALEXANDER ELLINGER and CLAUDE FLAMAND (*Ber.*, 1906, **39**, 4388—4390. Compare *Abstr.*, 1906, i, 696).—3-Chloro-4-methylquinoline is formed by the action of chloroform and potassium hydroxide on 3-methylindole in alcoholic solution (Magnanini, *Abstr.*, 1887, 1113). The constitution of the chloro-methylquinoline was determined by heating the base with formaldehyde in a closed tube at 100°, and oxidising the resulting methylol compound with nitric acid, D 1·4, 3-chloroquinoline-4-carboxylic acid,  $C_6H_4 \begin{smallmatrix} < C(CO_2H) : CCl \\ & | \\ N = CH \end{smallmatrix}$ , was obtained, m. p. 262—263° (decomp.). The position of the chlorine atom was established by heating the acid 2—5° above its temperature of decomposition when 3-chloroquinoline was formed. The combined action of chloroform and alkali, therefore, consists in the introduction of the CCl residue between positions 2 and 3 in the indole nucleus. The m. p. of 3-chloroquinoline aurichloride is 183°, not 173° as previously stated (*loc. cit.*).  
W. R.

**1-Hydroxy-2-phenylindole.** ANGELO ANGELI and FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 761—767. Compare *Abstr.*, 1904, i, 526).—1-Benzoyloxy-2-phenylindole,



separates from alcohol in white crystals, m. p. 100°.

3-Nitroso-1-hydroxy-2-phenylindole,  $C_6H_4 \begin{smallmatrix} < C(NO) \\ & | \\ NO \end{smallmatrix} > CPh$  (*loc. cit.*), yields (1) an *acetyl* derivative,  $C_{16}H_{12}O_3N_2$ , crystallising from alcohol in yellow needles, m. p. 140°; (2) a *benzoyl* derivative,  $C_{21}H_{14}O_3N_2$ , crystallising from alcohol in slender, rose-coloured needles, m. p. 163° (decomp.); (3) an *ethyl* derivative,  $C_{16}H_{14}O_2N_2$ , which separates from light petroleum in orange-coloured crystals, m. p. 96°. Reduction of 3-nitroso-1-hydroxy-2-phenylindole by means of alcohol, hydroxylamine, or hydrazine yields ordinary nitrosophenylindole, whilst zinc, in presence of either acetic acid or ammonium chloride, converts it into 3-amino-2-phenylindole.

Oxidation of 3-nitroso-1-hydroxy-2-phenylindole with chromic acid gives a substance  $C_6H_4 \begin{smallmatrix} < CO \\ & | \\ NO \end{smallmatrix} > CPh$  (*loc. cit.*), which crystallises from alcohol in shining, red plates, m. p. 186° and has all the properties of a ketone; reduction of this substance by means of hydroxylamine yields nitrosophenylindole, whilst zinc and acetic acid convert it into a compound,  $C_{14}H_{11}ON$ , which crystallises from benzene in green needles, m. p. 225°, and is probably 3-hydroxy-2-phenylindole.

T. H. P.

**3-Pyrazolones.** II. AUGUST MICHAELIS (*Annalen*, 1906, 350, 288—329. Compare Abstr., 1905, i, 377).—The 5-pyrazolones yield reddish-yellow *isonitroso*-derivatives, whilst the action of sodium nitrite on 3-pyrazolones leads to the formation of green nitroso-compounds; on oxidation, both series yield strongly acid nitropyrazolones. On reduction, the *isonitroso*-5-pyrazolones form unstable aminopyrazolones (Knorr, Abstr., 1887, 678), whereas the 4-amino-3-pyrazolones, obtained from the nitroso-3-pyrazolones, are stable. The 4-amino-3-pyrazolones are highly reactive substances, which in their chemical behaviour closely resemble the primary aromatic amines.

In the present paper a large number of derivatives of 4-amino-1-phenyl-5-methyl-3-pyrazolone and of the corresponding 1-*p*-tolyl-compound are described, as are also a number of 4-alkyl-3-pyrazolones. Whilst in some reactions 5-pyrazolones behave as carbonyl compounds, 3-pyrazolones always react in the hydroxylic form.

*Nitroso- and Amino-derivatives of 3-Pyrazolones.*—[With PAUL KOTELMANN.]—4-Nitroso-1-phenyl-5-methyl-3-pyrazolone (Abstr., 1905, i, 244) forms a *hydrochloride*,  $C_{10}H_9ON_2 \cdot NO \cdot HCl$ , which crystallises in slender, yellow needles, m. p.  $206^\circ$ , and is not decomposed when heated with water or alcohol.

4-Nitro-1-phenyl-5-methyl-3-pyrazolone,  $NPh \begin{smallmatrix} NH-CO \\ | \\ CMe \cdot C \cdot NO_2 \end{smallmatrix}$ , prepared by the action of concentrated nitric acid on the nitroso-compound in glacial acetic acid solution, forms yellow crystals, m. p.  $222^\circ$ , and dissolves in dilute alkali hydroxides, forming a yellow solution; it is obtained also as a by-product in the preparation of the nitroso-compound.

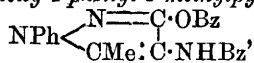
4-Amino-1-phenyl-5-methyl-3-pyrazolone,  $NPh \begin{smallmatrix} NH-CO \\ | \\ NMe \cdot C \cdot NH_2 \end{smallmatrix}$ , prepared by reducing the 4-nitroso-compound with zinc and acetic acid, crystallises in glistening, white leaflets, m. p.  $182^\circ$ , becomes red when exposed to air while moist, but is stable when dry, reduces Fehling's solution at the laboratory temperature, or ammoniacal silver nitrate when heated, and gives a red to reddish-brown coloration with bleaching powder solution. The *hydrochloride*,  $C_{10}H_{11}ON_3 \cdot HCl$ , forms white leaflets, m. p.  $222^\circ$ ; the *picrate*,  $C_{10}H_{11}ON_3 \cdot C_6H_2(NO_2)_3 \cdot OH$ , forms brownish-yellow needles, m. p.  $195^\circ$  (decomp.). The amine forms *condensation products* with the following aldehydes and ketones:  $R = C_8N_2 \cdot HOPhMe$ .

With benzaldehyde,  $R \cdot N : CHPh$ : small, yellow crystals, m. p.  $248^\circ$ ; anisaldehyde,  $R \cdot N : CH \cdot C_6H_4 \cdot OMe$ : slightly blue leaflets, m. p.  $245^\circ$ ; cinnamaldehyde,  $R \cdot N : CH \cdot C_2H_2Ph$ : yellow leaflets, m. p.  $232^\circ$ ; acetophenone,  $CPhMe(NHR)_2$ : slender, yellow needles, m. p.  $296^\circ$ , becoming brown; benzophenone,  $CPh_2(NHR)_2$ : yellow leaflets, m. p.  $301^\circ$ , becoming brown; pyruvic acid,  $CO_2H \cdot CMe(NHR)_2$ : glistening, white leaflets, m. p.  $299^\circ$ , becoming brown.

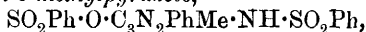
4-Acetylamino-1-phenyl-5-methyl-3-pyrazolone,  $NPh \begin{smallmatrix} NH-CO \\ | \\ CMe \cdot C \cdot NHAc \end{smallmatrix}$ , crystallises in slender, white needles, m. p.  $233^\circ$ . The 4-formylamino-

compound,  $C_{10}H_9ON_2 \cdot NH \cdot COH$ , crystallises in white needles, m. p.  $197^\circ$ .

4-Benzoylamino-3-benzoxyl-1-phenyl-5-methylpyrazole,



forms colourless crystals, m. p.  $176^\circ$ . 4-Benzenesulphonylamino-3-sulphonoxyl-1-phenyl-5-methylpyrazole,

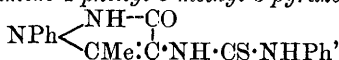


forms large, transparent crystals, m. p.  $171^\circ$ .

4-Thionylamino-1-phenyl-5-methyl-3-pyrazolone,  $NPh \begin{array}{l} \text{NH}-\text{CO} \\ \text{CMe} : \text{C} \cdot \text{N} : \text{SO} \end{array}$

crystallises in yellow leaflets, m. p.  $125^\circ$ , and is decomposed when heated with aqueous alkali hydroxides.

4-Phenylthiocarbamido-1-phenyl-5-methyl-3-pyrazolone,



separates from alcohol in small crystals, m. p.  $221^\circ$ , is soluble in aqueous alkali hydroxides, and is decomposed by hot mineral acids, forming phenylthiocarbimide and the 4-aminopyrazolone. Bis-1-phenyl-5-methyl-3-pyrazolonyl-4-thiocarbamide,  $CS \left( \text{NH} \cdot \text{C} \begin{array}{l} \text{CO}-\text{NH} \\ \text{CMe} : \text{NPh} \end{array} \right)_2$ , forms

small, white crystals, m. p.  $265^\circ$ , becoming brown.

The diazo-chloride,  $NPh \begin{array}{l} \text{NH}-\text{CO} \\ \text{CMe} : \text{C} \cdot \text{N}_2\text{Cl} \end{array}$ , formed by diazotisation of

the 4-aminopyrazolone, crystallises in colourless needles, decomposes at  $120^\circ$ , gradually becomes red on the surface, and gives reactions similar to those of diazobenzene chloride. It couples with  $\beta$ -naphthol in alkaline solution, forming 4- $\beta$ -naphtholazo-1-phenyl-5-methyl-3-

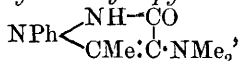
pyrazolone,  $NPh \begin{array}{l} \text{NH}-\text{CO} \\ \text{CMe} : \text{C} \cdot \text{N}_2 \cdot C_{10}H_6 \cdot OH \end{array}$ , which crystallises in small, yellowish-red leaflets, m. p.  $215^\circ$ . The diazo-chloride forms with resorcinol a dark brownish-red precipitate, soluble in an excess of alkali hydroxides, with salicylic acid an orange-red precipitate, and with aniline or dimethylaniline a dark red solution yielding a dark red to reddish-brown precipitate on addition of sodium acetate.

4-Azo-1-phenyl-5-methyl-3-pyrazolone,  $N_2(C_3N_2HOPhMe)_2$ , formed by the action of the 4-amino-3-pyrazolone on its diazo-chloride, separates as a yellowish-red, crystalline powder, m. p.  $160^\circ$ ; the hydrochloride,  $C_{20}H_{18}O_2N_6 \cdot 2HCl$ , crystallises in red leaflets, m. p.  $126^\circ$ .

4-Iodo-1-phenyl-5-methyl-3-pyrazolone,  $NPh \begin{array}{l} \text{NH}-\text{CO} \\ \text{CMe} : \text{C} \cdot \text{I} \end{array}$ , prepared by

boiling the 4-diazo-chloride with aqueous potassium iodide, forms small, yellow crystals, m. p.  $207^\circ$ .

4-Dimethylamino-1-phenyl-5-methyl-3-pyrazolone,



formed with development of heat by the action of methyl iodide, methyl alcohol, and potassium hydroxide on the hydrochloride of the

4-amino-3-pyrazolone, crystallises in matted, slender, white needles, m. p. 188°, is soluble in dilute acids or alkali hydroxides, and when heated on the water-bath with methyl iodide yields *dimethylamino-3-antipyryne* (4-dimethylamino-1-phenyl-2:5-dimethyl-3-pyrazolone; 3-pyramidone),  $O \left\langle \begin{array}{c} C \cdot C(NMe_2) \\ | \\ NMe - NPh \end{array} \right\rangle CMe$ , which is also obtained by the action

of methyl sulphate on the 4-amino-3-pyrazolone. It crystallises in slightly yellow needles, m. p. 74°. When heated with methyl iodide under pressure at 100°, it forms the *methiodide*,  $C_8H_7N_2OPhMe_2 \cdot NMe_3I$ , which crystallises in white leaflets, m. p. 126°, and when boiled with silver chloride in aqueous solution yields the *methochloride*; this when heated loses methyl chloride and forms dimethylamino-3-antipyryne.

The *methiodide* of 4-dimethylamino-1-phenyl-5-methyl-3-pyrazolone,  $NPh \left\langle \begin{array}{c} NH-CO \\ | \\ CMe : C \cdot NMe_3I \end{array} \right\rangle$ , formed by boiling the amino-base with methyl iodide and methyl alcohol, crystallises in white leaflets, m. p. 216°.

4-Nitroso-1-p-tolyl-5-methyl-3-pyrazolone,  $C_7H_7 \cdot N \left\langle \begin{array}{c} NH-CO \\ | \\ CMe : N \cdot NO \end{array} \right\rangle$ , prepared by the action of sodium nitrite on the 3-pyrazolone in glacial acetic acid solution, forms small, green crystals, m. p. 167°; the *hydrochloride*,  $C_{11}H_{11}O_2N_3 \cdot HCl$ , crystallises in slender, yellow needles, m. p. 235°.

4-Nitro-1-p-tolyl-5-methyl-3-pyrazolone,  $C_{11}H_{11}ON_2 \cdot NO_2$ , crystallises from alcohol in slender, white needles, m. p. 190°.

4-Amino-1-p-tolyl-5-methyl-3-pyrazolone,  $C_{11}H_{11}ON_2 \cdot NH_2$ , m. p. 249°, crystallises from chloroform and has a red lustre; the *hydrochloride*,  $C_{11}H_{13}ON_3 \cdot HCl$ , forms slightly red crystals, m. p. 291°. Condensation products of the amine with the following aldehydes and ketones are described;  $R = C_{11}H_{11}ON_2$ .

With benzaldehyde,  $CHPh \cdot NR$ , small, colourless crystals, m. p. 233°; anisaldehyde,  $OMe \cdot C_6H_4 \cdot CH \cdot NR$ , m. p. 235°; cinnamaldehyde,  $CHPh \cdot CH \cdot CH \cdot NR$ , yellow prisms, m. p. 217°; acetophenone,  $CPhMe(NHR)_2$ , small, glistening leaflets, m. p. 302°; benzophenone,  $CPh_2(NHR)_2$ , white leaflets, m. p. 305° (decomp.); pyruvic acid,  $CO_2H \cdot CMe(NHR)_2$ , white crystals, decomposing at 303°.

4-Acetylamino-1-p-tolyl-5-methyl-3-pyrazolone,  $C_{11}H_{11}ON_2 \cdot NHAc$ , crystallises in slender needles, m. p. 244°. The *dibenzoyl* derivative,  $OBz \cdot C_{11}H_{10}N_2 \cdot NHBz$ , forms slender, colourless needles, m. p. 193°. The *dibenzenesulphonyl* derivative forms colourless crystals, m. p. 159°.

4-Phenylthiocarbamido-1-p-tolyl-5-methyl-3-pyrazolone,

$C_{11}H_{11}ON_2 \cdot NH \cdot CS \cdot NPh$ ,  
m. p. 220°, crystallises from alcohol.

4-Diazo-1-p-tolyl-5-methyl-3-pyrazolone chloride,  $C_{11}H_{11}ON_2 \cdot N_2Cl$ , does not decompose when its aqueous solution is evaporated on the water-bath; it couples with  $\beta$ -naphthol forming a dark red, crystalline *azo-dye*,  $C_{21}H_{18}O_2N_4$ , m. p. 228°. The diazo-chloride also couples with dimethylaniline, salicylic acid, and resorcinol, forming dark red dyes.

4-Benzeneazo-1-phenyl- and 4-Benzeneazo-1-p-tolyl-5-methylpyrazole.—[With PAUL KOTELMANN.]—4-Benzeneazo-1-phenyl-5-methylpyrazole

cannot be obtained by reduction of 3-chloro-4-benzeneazo-1-phenyl-5-methylpyrazole, but is formed when 4-benzeneazo-1-phenyl-5-methyl-3-pyrazolone is heated with phosphorus pentasulphide at 220—230°; the *hydrochloride*,  $C_{16}H_{14}N_4 \cdot HCl$ , forms dark red needles, m. p. 138°, and gradually decomposes at the laboratory temperature.

4-Benzeneazo-1-*p*-tolyl-5-methylpyrazole,  $C_{11}H_{11}N_2 \cdot N_2Ph$ , formed by heating 4-benzeneazo-1-*p*-tolyl-5-methyl-3-pyrazolone with phosphorus pentasulphide at 220—230°, separates from light petroleum in yellowish-red crystals, m. p. 102°; the *hydrochloride*,  $C_{17}H_{16}N_4 \cdot HCl$ , forms yellowish-red needles, m. p. 156°, and readily decomposes.

4-Alkyl-3-pyrazolone.—[With ALEXANDER DREWS.]—1-Phenyl-4:5-dimethyl-3-pyrazolone,  $NPh \begin{smallmatrix} \text{NH}-\text{CO} \\ | \\ \text{CMe}:\text{CMe} \end{smallmatrix}$ , is prepared by the action of phosphorus trichloride on a mixture of acetylphenylhydrazine and ethyl methylacetoacetate; it forms small, white needles, m. p. 254°. The *benzenesulphonyl* derivative,  $NPh \begin{smallmatrix} \text{N}=\text{C}:\text{O} \cdot \text{SO}_2Ph \\ | \\ \text{CMe}:\text{CMe} \end{smallmatrix}$ , crystallises in colourless needles, m. p. 97°.

3-Chloro-1-phenyl-4:5-dimethylpyrazole,  $NPh \begin{smallmatrix} \text{N}=\text{CCl} \\ | \\ \text{CMe}:\text{CMe} \end{smallmatrix}$ , prepared by the action of phosphorus oxychloride on the pyrazolone at 210° under pressure, is obtained as a white, crystalline mass, m. p. 34°, b. p. 181°/15 mm., is slightly volatile in a current of steam, and when heated with methyl iodide in a sealed tube at 100°, yields 3-iodo-1-phenyl-4:5-dimethylpyrazolium methiodide,  $NPh \begin{smallmatrix} \text{NMeI}:\text{Cl} \\ | \\ \text{CMe}=\text{CMe} \end{smallmatrix}$ , which crystallises in slightly yellow needles, m. p. 217°.

Methyl-3-antipyrine,  $\text{CMe} \begin{smallmatrix} \text{NPh} \cdot \text{NMe} \\ | \\ \text{CMe} \cdot \text{C} \end{smallmatrix} \text{O}$ , prepared by heating the pyrazolone with an excess of methyl iodide in a sealed tube at 100°, crystallises in white leaflets, m. p. 97°, and gives a red coloration with ferric chloride. The *hydriodide*,  $NPh \begin{smallmatrix} \text{NMeI}:\text{C} \cdot \text{OH} \\ | \\ \text{CMe}=\text{CMe} \end{smallmatrix}$ , forms white needles, m. p. 176°, and on recrystallisation from water yields the crystalline salt,  $\text{NPh} \cdot \text{NMeI} \begin{smallmatrix} \text{C} \cdot \text{O} \cdot \text{NMe} \\ | \\ \text{CMe}=\text{CMe} \end{smallmatrix} \begin{smallmatrix} \text{NPh}-\text{CMe} \\ | \\ \text{C}(\text{OH}) \cdot \text{CMe} \end{smallmatrix}$ , m. p. 75°. The *picrate*,  $C_{12}H_{15}ON_2 \cdot O \cdot C_6H_2(NO_2)_3$ , forms yellow needles, m. p. 103°. The *chloride*,  $C_{12}H_{14}N_2Cl_2$ , m. p. 94°, is very hygroscopic.

Methyl-3-thiopyrine,  $\text{CMe} \begin{smallmatrix} \text{NPh} \cdot \text{NMe} \\ | \\ \text{CMe} \cdot \text{C} \end{smallmatrix} \text{S}$ , formed by the action of potassium hydrogen sulphide on the iodopyrazole hydriodide in aqueous solution or from the antipyrine chloride by Michaelis and Besson's method (Abstr., 1904, i, 780), separates from water in white crystals, m. p. 103°, and gives a yellow precipitate with sulphurous acid in concentrated solution; the *methiodide*,  $C_{13}H_{17}N_2SI$ , forms white crystals, m. p. 175°.

3-Thiomethyl-1-phenyl-4:5-dimethylpyrazole (*methyl-ψ-3-thiopyrine*),  $NPh \begin{smallmatrix} \text{N}=\text{C} \cdot \text{SMe} \\ | \\ \text{CMe}:\text{CMe} \end{smallmatrix}$ , prepared by heating the preceding methiodide

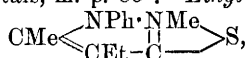
under reduced pressure, crystallises in long, white needles, m. p.  $40^{\circ}$ , b. p.  $205-208^{\circ}/20$  mm.

1-*Phenyl-5-methyl-4-ethyl-3-pyrazolone*, prepared by the action of phosphorus oxychloride and acetylphenylhydrazine on ethyl ethyl-acetoacetate, forms white needles, m. p.  $172^{\circ}$ . The following substances derived from this pyrazolone are described. The *benzene-sulphonyl* derivative,  $C_{12}H_{13}N_2 \cdot O \cdot SO_2Ph$ , forms slender needles, m. p.  $74^{\circ}$ . The *3-chloropyrazole*,  $C_{12}H_{13}N_2Cl$ , forms yellow needles, m. p.  $92^{\circ}$ . The *methiodide* of the *3-iodopyrazole*,  $C_{13}H_{16}N_2I_2$ , m. p.  $196^{\circ}$ .

*Ethyl-3-antipyrine*,  $CMe \begin{array}{c} \diagup NPh \cdot NMe \\ || \\ C \\ \diagdown \end{array} O$ , forms white prisms, m. p.  $64^{\circ}$ ;

the *hydriodide*,  $C_{13}H_{16}ON_2 \cdot HI$ , m. p.  $175^{\circ}$ , when recrystallised from water loses half of its hydrogen iodide and yields the *salt*,  $C_{20}H_{33}O_2N_4I$ , m. p.  $130^{\circ}$ , which has a constitution analogous to that of the corresponding methyl-3-antipyrine derivative. The *picrate*,

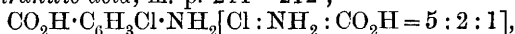
$C_{13}H_{16}ON_2 \cdot C_6H_3O(NO_2)_3$ ,  
forms large, yellow crystals, m. p.  $83^{\circ}$ . *Ethyl-3-thiopyrine*,



crystallises in slender needles, m. p.  $120^{\circ}$ ; the *methiodide*,

$C_{13}H_{16}N_2S \cdot MeI$ ,  
forms white crystals, m. p.  $108^{\circ}$ . *Ethyl-ψ-3-thiopyrine* (3-thiomethyl-1-phenyl-5-methyl-4-ethylpyrazole),  $C_{12}H_{13}N_2 \cdot SMe$ , forms a colourless oil, b. p.  $160-165^{\circ}/12$  mm. G. Y.

**o-Carboxylic Azo-compounds and their Transformation into 3-Hydroxyindazolyl Derivatives.** PAUL FREUNDLER (*Compt. rend.*, 1906, 143, 909—911).—The author has shown (Abstr., 1906, i, 544) that benzene-*o*-azobenzoic acid is converted into chloro-3-hydroxy-2-phenylindazole by the action of phosphorus pentachloride or thionyl chloride. The meta- and para-isomerides under similar conditions yield the normal acid chlorides. The benzene-*o*-azochlorobenzoic acid, obtained by oxidising chloro-3-hydroxy-2-phenylindazole, is identical with benzene-2-azo-5-chlorobenzoic acid obtained synthetically as follows. *Methyl-3-chloroacetyl-anthranilate*, m. p.  $127^{\circ}$ , obtained by the action of sodium hypochlorite on methyl acetyl-anthranilate, yields 5-chloro-anthranilic acid, m. p.  $211-212^{\circ}$ ,



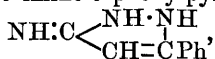
on hydrolysis, which is converted into *p*-chloroaniline when heated at  $200^{\circ}$ ; *methyl-5-chloroanthranilate*, m. p.  $69^{\circ}$ , b. p.  $168-170^{\circ}/22$  mm., condenses with nitrosobenzene to form methyl benzene-2-azo-5-chlorobenzoate, and the corresponding acid is identical with the oxidation product of 5-chloro-3-hydroxy-2-phenylindazole,  $C_7N_2H_3PhCl \cdot OH$ . Benzene-2-azo-5-chlorobenzoic acid yields a dichloro-3-hydroxy-2-phenylindazole, m. p.  $186-187^{\circ}$ , by the action of phosphorus pentachloride in which the second chlorine atom probably occupies position 7.

3-Hydroxy-2-phenylindazole,  $C_7N_2H_4Ph \cdot OH$ , m. p.  $216-217^{\circ}$ , can be prepared from the acetal derivative of benzene-2-azobenzoic acid by the action of dilute sulphuric acid. The lactone of 3-hydroxy-*o*-indazolyl-benzoic acid (Abstr., 1904, i, 667; Carré, Abstr., 1906, i, 705) can be



obtained by reducing *o*-nitrobenzyl alcohol in alkaline medium, or by the action of heat on *o*-hydrazobenzoic acid, or *o*-azobenzoic acid; or by the action of acetic acid on *o*-azoxybenzaldehyde (Bamberger, *private communication*).  
M. A. W.

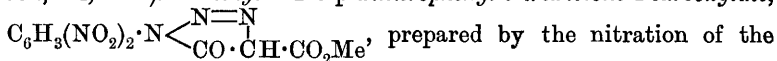
**Condensation of Hydrazines with Acetylenic Nitriles. General Method of [Synthesising Pyrazolonimines [5-Imino-pyrazolines].** CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 143, 1239—1242. Compare Abstr., 1906, i, 702—956).—Phenylpropionitrile condenses readily with hydrazine hydrate in alcoholic solution to form 5-imino-3-phenylpyrazoline,



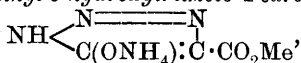
identical with the compound obtained by Seidel (Abstr., 1899, i, 138) by the action of hydrazine hydrate on cyanoacetophenone; it is probable that the hydrazone  $\text{NH}_2\cdot\text{N}:\text{CPh}\cdot\text{CH}_2\cdot\text{CN}$  or  $\text{NH}_2\cdot\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$  is first formed and subsequently converted into the isomeride iminopyrazoline, and this explanation of the reaction is supported by the fact that *as*-diphenylhydrazine condenses with phenylpropionitrile to form the diphenylhydrazone  $\text{NPh}_2\cdot\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$ , identical with the hydrazone prepared by Seidel (*loc. cit.*) by the action of cyanoacetophenone on diphenylhydrazine.

The following iminopyrazolines were prepared. 5-*Imino-3-amylylpyrazoline*, m. p. 41°, b. p. 205—208°/18 mm. (corr.), and the *picrate*, m. p. 142—144°. 5-*Imino-1-phenyl-3-amylylpyrazoline*, b. p. 231—233°/18 mm. (corr.),  $D_4^{20}$  1.047. 5-*Imino-3-hexylpyrazoline*, m. p. 32°, b. p. 214—217°/18 mm. (corr.). 5-*Imino-3-phenylpyrazoline*, m. p. 125—126°; the *hydrochloride*, m. p. 78—80°; the *platinichloride*, m. p. 225° (decomp.); the *picrate*, m. p. 202—203° (corr.). 5-*Imino-1:3-diphenylpyrazoline*, m. p. 127—129° (compare Seidel, Abstr., 1899, i, 138); the *hydrochloride* is dissociated by excess of water and the *platinichloride* decomposes at 153—155°.  
M. A. W.

**5-Hydroxy-1:2:3-triazole.** OTTO DIMROTH and HANS AICKELIN (*Ber.*, 1906, 39, 4390—4392. Compare Curtius and Thompson, this vol., i, 95).—*Methyl 1-o-p-dinitrophenyl-5-triazolone-4-carboxylate*,



ester at  $-5^\circ$  with fuming nitric acid, crystallises from glacial acetic acid in white needles, m. p. 195°, and is explosive. When this compound is heated with a methyl alcoholic solution of ammonia at 100° for ten hours in a sealed tube, 2:4-dinitroaniline and the ammonium salt of *methyl 5-hydroxytriazole-4-carboxylate*,

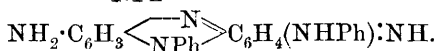


are formed. The *barium salt*,  $(\text{C}_4\text{H}_4\text{O}_3\text{N}_3)_2\text{Ba}\cdot 5\text{H}_2\text{O}$ , crystallises in long, colourless needles. The *ester* crystallises in colourless aggregates and is easily soluble in water, the solution giving with ferric chloride an intense brownish-red coloration, indicating an enolic constitution. By hydrolysing with barium hydroxide and acidifying,

a solution of 5-hydroxytriazole-4-carboxylic acid is obtained, and its alkaline solution with a diazotoluene salt yields 4-tolueneazo-5-hydroxytriazole (Curtius and Thompson, *ibid.*). W. R.

**Formation of *s*-Safranines.** PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1906, [iii], 35, 1278—1282. Compare Abstr., 1906, i, 51, 989).—The method employed is essentially that used by Fischer and Hepp (Abstr., 1903, i, 134), which consists in condensing *p*-aminoazo-compounds under the influence of heat.

When a mixture of *p*-aminoazobenzene and its hydrochloride is heated in phenol at 140—150°, *s*-anilinophenosafranine is produced; it is a black, microcrystalline powder with a bronze sheen. It cannot be obtained by condensing aniline with *s*-phenosafranine. It dyes mordanted cotton and silk in bluish-violet shades. The mechanism of the reaction is represented as follows:  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 + \text{NH}\cdot\text{C}_6\text{H}_3(\text{NHPh})\cdot\text{NH} \rightarrow \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{NHPh})\cdot\text{NH} + \text{NH}_3 \rightarrow \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\langle\text{N}\rangle_{\text{NPh}}\text{C}_6\text{H}_3\cdot\text{NH} + \text{H}_2 \rightarrow$



This reaction is possible because in *p*-aminoazobenzene there is, relatively to the amino-group, an *ortho*-position free, which permits the introduction of the aniline residue. This is not the case when *p*-aminoazotoluene is used as a starting point, and consequently when this substance is condensed in the manner just described the product obtained is *s*-tolusafranine, which after purification forms reddish-brown crystals with a metallic sheen. Along with the tolusafranine there is produced a violet colouring matter, which after prolonged heating is converted into a red dye and a reddish-yellow substance which appears to be *o*-azotoluene.

*p*-Amincazobenzene condenses with benzenediazo-*a*-naphthylamine, in the manner described, to form *naphthaphenosafranine*, which can be purified by recrystallisation from warm water. Its hydrochloride forms slender, brown needles with a bronze sheen. It dyes mordanted silk and cotton a fine red with shades more bluish than those given by the pheno- and tolu-safranines. T. A. H.

**Formation of *as*-Safranines.** PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1906, [iii], 35, 1282—1285. Compare Abstr., 1906, i, 51, 989, and preceding abstract).—When a mixture of *p*-diaminoazobenzene hydrochloride and aniline hydrochloride in alcohol is heated in an autoclave at 160—170°, two products are formed, the one having the reactions and properties of *as*-phenosafranine and the other, which is a dark, microcrystalline powder with a metallic sheen, is *as*-anilinophenosafranine,  $\text{C}_{24}\text{H}_{19}\text{N}_5$ . It gives fine, bluish-violet shades on silk and cotton mordanted with tannin and tartar emetic. The mechanism of the reaction which gives rise to *as*-anilinophenosafranine is supposed to be the following:  $2\text{C}_6\text{H}_5\cdot\text{NH}_2 + \text{NH}\cdot\text{C}_6\text{H}_3(\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)\cdot\text{NH} \rightarrow \text{N}=\text{C}_6\text{H}_2(\text{NHPh})\cdot\text{NH} \text{ } \text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 + \text{NH}_3 + 2\text{H}_2.$

*p*-Diaminoazotoluene, obtained by careful reduction of *p*-nitro-*o*-toluidine, when condensed with *o*-toluidine, as just described, furnishes *as-tolusafranine*,  $C_{21}H_{20}N_4$ , which is crystalline, has a metallic sheen, and gives superb rose-red shades on silk or cotton, the tones being always more bluish than those of the corresponding phenosafranine. The *platinichloride* is a crystalline powder with a metallic lustre.

T. A. H.

### Action of Alkali Hydroxides on *s*-Tribromodiazobenzene.

EUGEN BAMBERGER and E. KRAUS (*Ber.*, 1906, **39**, 4248—4252. Compare Orton, *Trans.*, 1903, **83**, 796; 1905, **87**, 99; Hantzsch, *Abstr.*, 1903, i, 665).—3 : 5-Dibromo-2-aminophenol,  $OH \cdot C_6H_2Br_2 \cdot NH_2$ , is prepared by the action of aqueous sodium hydroxide on diazotised 2 : 4 : 6-tribromoaniline and reduction of the resulting quinonediazide with stannous chloride and glacial acetic acid in hydrochloric acid solution, or by hydrolysis of dibromo-*o*-phenetidine by means of aluminium chloride; it crystallises in long, glistening, colourless, broad needles, m. p.  $145^\circ$ , is readily soluble in aqueous alkali hydroxides, and forms a *hydrochloride* which crystallises in glistening needles, is sparingly soluble in water or dilute hydrochloric acid, and is decomposed by much boiling water. The base gives with alcoholic ferric chloride a violet coloration rapidly becoming brown, and deposits a flocculent precipitate; with calcium hypochlorite it gives a brownish-red coloration, becoming reddish-brown, or, in dilute acetic acid solution, a violet coloration becoming brown, and forms a dark brown, flocculent precipitate.

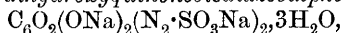
3 : 5-Dibromo-*o*-quinonediazide, prepared by the action of nitrous acid on the dibromoaminophenol, crystallises from ether in glistening, orange-yellow prisms, or from light petroleum in compact, yellow needles, m. p.  $130^\circ$  (decomp.), and can be recrystallised from water, but decomposes on prolonged boiling; it couples with the naphthols or resorcinol in alkaline, or with  $\alpha$ -naphthylamine in acetic acid solution. When boiled with hydrobromic acid and copper powder, the quinonediazide yields 2 : 3 : 5-tribromophenol,  $C_6H_2Br_3 \cdot OH$ , which crystallises from light petroleum in glistening needles, m. p.  $91.5-92.5^\circ$ , is readily volatile in a current of steam, gives a brownish-violet coloration with alcoholic ferric chloride, and forms a voluminous, crystalline precipitate (2 : 3 : 4 : 5-tetrabromophenol?) with bromine water.

G. Y.

3 : 6-Dihydroxyquinonebis-diazoanhydride. FRANZ HENLE (*Annalen*, 1906, **350**, 344—367).—The substance obtained by Nietzki and Benckiser (*Abstr.*, 1885, 779, 1127) as a residue on dissolving crude triquinoyl in sulphurous acid, and considered by these authors to be di-iminodiquinoyl, is now shown to be 3 : 6-dihydroxyquinonebis-diazoanhydride,  $N \leq \begin{array}{c} O \cdot C \cdot CO \cdot C \cdot N \\ | \quad | \\ N \cdot C \cdot CO \cdot C \cdot O \end{array} \geq N$ . This, like the diazo-anhydride of tetric acid, as a colourless *syndiazoanhydride* resembles ethyl diazoacetoacetate anhydride (Wolff, *Abstr.*, 1903, i, 203), whilst on the other hand it forms a sulphonate as does the yellow *o*-diazo-phenol.

3 : 6-Dihydroxyquinonebisdiazooanhydride is obtained also as an insoluble residue when crude triquinoyl is extracted with aqueous sodium chloride, or in a 70—80% yield by the action of sodium nitrite on diaminotetrahydroxybenzene hydrochloride in 80% sulphuric acid solution; it crystallises slowly from nitric acid, D 1.4, in long, white prisms, detonates at 128°, becomes yellow on exposure to light, is decomposed by prolonged boiling with water, forming a cherry-red solution, and yields diaminotetrahydroxybenzene hydrochloride when reduced with stannous chloride and fuming hydrochloric acid. In sodium carbonate solution the bisdiazooanhydride couples with R-salt,  $\beta$ -naphthol, or resorcinol, but not with phenol, giving an intense violet-red coloration, which becomes blue and fluorescent on addition of dilute sodium hydroxide, red on addition of acetic acid, and is destroyed by hot sulphuric acid.

*Tetrasodium 3 : 6-dihydroxyquinonebisdiazosulphonate,*

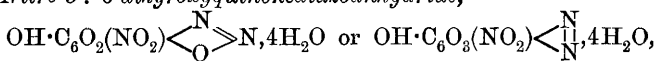


formed with development of heat by the successive action of sodium hydrogen sulphite and sodium hydroxide on the bisdiazooanhydride, crystallises in orange-yellow leaflets, loses  $3\text{H}_2\text{O}$  slowly in a vacuum over sulphuric acid, is very hygroscopic when anhydrous, and is decomposed, evolving gas when heated with water or dilute acids.

With an excess of aniline, the bisdiazooanhydride forms an *additive* compound, probably  $\text{C}_6\text{O}_2(\text{OH})_2(\text{N}_2\cdot\text{NHPh})_2$ , which is obtained as a dark red, crystalline powder, and decomposes into its generators slowly over sulphuric acid in a vacuum, more quickly when treated with organic solvents or acids. A similar *compound* is obtained on adding the bisdiazooanhydride to fused  $\alpha$ -naphthylamine.

The action of concentrated aqueous ammonia on the bisdiazooanhydride leads to the formation of 3 : 6-dioxyquinonebistriazen,  $\begin{matrix} \text{NH}_3\cdot\text{O} \\ \text{N}=\text{N} \end{matrix} > \text{C}_6\text{O}_2 < \begin{matrix} \text{N}:\text{N} \\ \text{O}\cdot\text{NH}_3 \end{matrix}$  (?), which crystallises in colourless prisms, m. p. 167°, decomposes above its melting point, and detonates when quickly heated. It is decomposed by aqueous sodium hydroxide, and when treated with concentrated aqueous or methyl-alcoholic hydrochloric acid or with hydrogen chloride in ethereal solution, evolves 4N and yields a *substance*,  $\text{C}_6\text{H}_8\text{O}_4\text{N}_2\text{Cl}_2, 2\text{H}_2\text{O}$ .

*5-Nitro-3 : 6-dihydroxyquinonediazooanhydride,*



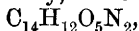
prepared by the action of nitrosulphuric acid on 5-nitro-2-amino-tetrahydroxybenzene hydrochloride in cooled 80% sulphuric acid solution, crystallises in lemon-yellow leaflets or long, thin needles, m. p. 70°, decomposes above 100° or when heated with a solvent, and detonates when heated rapidly; it is decomposed by concentrated aqueous ammonia or alkali hydroxides, but with dilute sodium carbonate and dilute ammonia forms highly explosive, yellow *salts*.

When treated with ethereal ammonia, 4 : 6-dibromo-2-diazophenol is partially decomposed evolving gas, whilst 4 : 6-dinitro-2-diazophenol forms a voluminous, red *product* which decomposes slowly in contact with ethereal ammonia, rapidly when exposed to air.

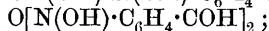
*Chlorotriketocyclopentane*,  $\text{CO} \begin{array}{c} \text{CCl}=\text{C}\cdot\text{OH} \\ \text{CH}_2\cdot\text{CO} \end{array}, \text{H}_2\text{O}$ , is formed when 3:6-dihydroxyquinonebisdiazoanhydride is boiled with 20% hydrochloric acid; it crystallises from moist chloroform in nodular aggregates of colourless needles, m. p. 72—74°, loses  $\text{H}_2\text{O}$  over sulphuric acid in a vacuum or when boiled with chloroform and calcium chloride, forming a white, hygroscopic, crystalline powder, m. p. 119°. It is a strong monobasic acid, is decomposed by concentrated alkali hydroxides, reduces ammoniacal silver solutions, and behaves towards bromine and potassium permanganate as an unsaturated substance. The *sodium*,  $\text{C}_5\text{H}_2\text{O}_3\text{ClNa}\cdot\frac{1}{2}\text{H}_2\text{O}$ , and *ammonium*,  $\text{C}_5\text{H}_2\text{O}_3\text{Cl}\cdot\text{NH}_4$ , salts are described. The *acetate*,  $\text{C}_5\text{H}_5\text{O}_4\text{Cl}$ , forms colourless crystals, m. p. 57°; the *semi-carbazone*,  $\text{C}_6\text{H}_6\text{O}_3\text{N}_3\text{Cl}$ , is obtained as an infusible, white, crystalline precipitate. When heated with bromine water, chlorotriketocyclopentane is converted into chloropentabromoacetone, m. p. 99° (m. p. 92°, Hantzsch, Abstr., 1889, 854). G. Y.

**Hexanitroazobenzene.** EUGÈNE GRANDMOUGIN and H. LEEMANN (*Ber.*, 1906, 39, 4384—4385).—*Hexanitrohydrazobenzene*, prepared either by heating picrylhydrazine and picryl chloride for four hours at 120° or by heating an alcoholic solution of picryl chloride (2 mols.), hydrazine hydrate (1 mol.), and potassium hydroxide (3 mols.), forms bright yellow needles, m. p. 201°. The *monopotassium* salt dissolves in acetone to a deep red solution whilst the solution of the *dipotassium* salt is blue. *Hexanitroazobenzene*, prepared by the oxidation of the above compound with nitric acid, D 1.3, crystallises from glacial acetic acid in red prisms, m. p. 215°. W. R.

**Anthranil. X. A New Reduction Product of *o*-Nitrobenzaldehyde.** EUGEN BAMBERGER (*Ber.*, 1906, 39, 4252—4276. Compare Bamberger and Elger, Abstr., 1904, i, 93; Heller, Abstr., 1906, i, 585).—In the reduction of *o*-nitrobenzaldehyde a new intermediate product has been found to be formed between *o*-hydroxylaminobenzaldehyde and anthranil.—[With E. W. REMMERT.]—If *o*-nitrobenzaldehyde is shaken with ether and aqueous ammonium chloride in a freezing mixture, while zinc dust is added gradually, there is formed a *product*,



which for the present is termed *agnetobenzaldehyde*. It may have the constitution  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{COH}$  or

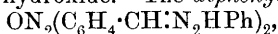


of these the latter is preferred. It crystallises in glistening, white needles, m. p. 94° if heated slowly from 65°, or 98.5—99° if heated rapidly from 85°, and decomposes slowly at the ordinary temperature, more quickly when treated with cold, dilute sulphuric acid or when boiled with water. It gives with alcoholic copper acetate a deep brown coloration rapidly becoming a dirty green, cuprous oxide being precipitated, reduces Fehling's solution, and when treated with 17% aqueous sodium hydroxide and ice becomes orange-red changing to yellow, and forms *o*-azoxybenzaldehyde, *o*-azobenzoic acid, *o*-nitrobenzaldehyde, *o*-nitrobenzyl alcohol, *o*-nitrobenzoic acid, traces of *o*-aminobenzaldehyde, and 2-carboxybenzeneazoxy-2'-benzyl alcohol.

Agnotobenzaldehyde does not form an *N*-aldoxime ether, whereas *o*-nitrobenzaldehyde condenses with phenylhydroxylamine, forming the *N*-aldoxime ether,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ \diagup \text{O} \end{smallmatrix} \text{NPh}$ , which crystallises in slender, yellow needles, m. p.  $93.5^\circ$ .

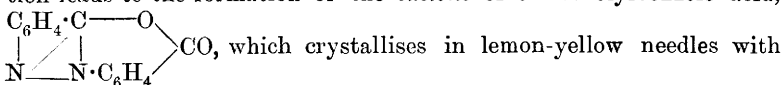
When reduced with aluminium amalgam and water in presence of ether, agnotobenzaldehyde yields anthranil and *o*-aminobenzyl alcohol; with phenylhydrazine in cooled pyridine solution it forms *o*-nitrobenzaldehydephenylhydrazone, m. p.  $156.5\text{--}157^\circ$ , together with the product  $\text{C}_{13}\text{H}_{13}\text{ON}_3$ , obtained by Buhlmann and Einhorn by the action of phenylhydrazine on anthranil (Abstr., 1901, i, 94).

*o*-Azoxybenzaldehyde,  $\text{ON}_2(\text{C}_6\text{H}_4 \cdot \text{COH})_2$  (compare Bamberger and Demuth, Abstr., 1902, i, 95), crystallises from alcohol in golden-yellow needles, m. p.  $118.5\text{--}119^\circ$  when rapidly heated from  $110^\circ$ , intumesces at  $130\text{--}140^\circ$ , and yields a sublimate of slender needles; it reduces silver nitrate only slowly in ammoniacal solution, but rapidly in presence of sodium hydroxide. The *diphenylhydrazone*,



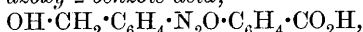
crystallises in light orange needles, m. p.  $185.5\text{--}186^\circ$  (decomp.).

The action of direct sunlight on *o*-azoxybenzaldehyde in acetone solution leads to the formation of the lactone of *o*-indazolybenzoic acid,

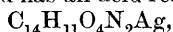


which crystallises in lemon-yellow needles with bronze lustre, m. p.  $295^\circ$ . The lactone is formed also together with *o*-azobenzoic acid (Maier, Abstr., 1902, i, 192) by oxidation of *o*-azobenzaldehyde with chromium trioxide in glacial acetic acid solution.

*2'*-Benzyl alcohol-azoxy-2-benzoic acid,



crystallises from water or alcohol in strongly refracting, small, hard, almost colourless prisms, m. p.  $160\text{--}161^\circ$ , forms a lemon-yellow solution in water or alcohol and has an acid reaction. The *silver*,



*copper*,  $(\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}_2)_2\text{Cu}$ , and *lead*,  $(\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}_2)_2\text{Pb}$ , salts are described.

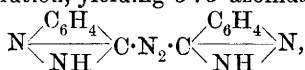
*2'*-Benzaldehydeazoxy-2-benzoic acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{COH}$ , prepared by oxidation of the alcohol with potassium dichromate in dilute sulphuric acid solution, crystallises in golden-yellow needles, m. p.  $179\text{--}180^\circ$  (decomp.), and reduces silver nitrate and Fehling's solutions on prolonged boiling in presence of sodium hydroxide. The *phenylhydrazone*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}_2\text{HPh}$ , crystallises in orange-red leaflets with bronze lustre, m. p.  $156^\circ$ ; the *sodium* salt forms golden-yellow leaflets.

On prolonged boiling with potassium dichromate in dilute sulphuric acid solution, *2'*-benzyl alcohol-azoxy-2-benzoic acid or its aldehyde yields *o*-azoxybenzoic acid.

G. Y.

**Oxidation of Aminoindazoles and a Remarkable Method of Formation of Dichloroindazole.** EUGEN BAMBERGER and S. WILDI (*Ber.*, 1906, 39, 4276—4285).—Whilst indazoles containing an amino-

group in the pyrazole nucleus are converted by various oxidising agents in acid solution into 4-hydroxy- $\beta$ -phenotriazine (Bamberger and v. Goldberger, Abstr., 1899, i, 170; Bamberger, *ibid.*, 543), 3-aminoindazole is oxidised by potassium ferricyanide or atmospheric oxygen in alkaline solution, yielding 3:3'-azoindazole,



ammonia, and a small amount of a brown acid.

3:3'-Azoindazole,  $\text{C}_{14}\text{H}_{10}\text{N}_6$ ,  $\text{C}_2\text{H}_6\text{O}$ , crystallises from alcohol in dark red, glistening needles with intense green lustre, m. p.  $229.5^\circ$  (corr.), and gives a light blood-red coloration with concentrated sulphuric acid. It dissolves in aqueous alkali hydroxides, forming a bluish-red solution, dyes silk and wool in an acid bath a rose colour, and is readily reduced by zinc dust, forming 3-aminoindazole. The *nitrate*,  $\text{C}_{14}\text{H}_{10}\text{N}_6 \cdot 2\text{HNO}_3$ , forms slender, red needles with green lustre. The *diacetyl* derivative,  $\text{N}_2(\text{C}_7\text{H}_4\text{N}_2\text{Ac})_2$ , crystallises in slender, orange needles, m. p.  $210^\circ$  (corr.), gives with concentrated sulphuric acid a dark blue coloration becoming red on addition of water, and is readily hydrolysed by dilute alkali hydroxides. The *dibenzoyl* derivative,  $\text{C}_{28}\text{H}_{18}\text{O}_2\text{N}_6$ , crystallises in glistening needles, m. p.  $195-196^\circ$  (corr.).

Azoindazole reacts with aniline at the laboratory temperature, forming 3-aminoindazole, 3-benzeneazoindazole, and a *substance* (azoindazole hydrate?),  $\text{C}_{14}\text{H}_{12}\text{ON}_6$ , which crystallises in glistening, bronze needles, m. p.  $338.5^\circ$ .

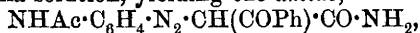
3-Benzeneazoindazole, m. p.  $190.5-192.5^\circ$  (corr.), is identical with the dye obtained by Bamberger (*loc. cit.*) by the action of diazobenzene chloride on indazole.

3-Amino-5:7-dimethyl- and 3-amino-5-methyl-indazole are oxidised by atmospheric oxygen in aqueous alkaline solution in the same manner as is 3-aminoindazole. Along with the corresponding *dye*, 3:3'-azo-5:5'-dimethylindazole forms an *acid* which crystallises in glistening, colourless needles, m. p. about  $160^\circ$ . The red coloration, formed on shaking these substances with air in alkaline solution, constitutes an extremely delicate reaction for 3-aminoindazoles.

*Dichloroindazole*,  $\text{C}_6\text{H}_2\text{Cl}_2 \begin{array}{c} \text{CH} \\ | \\ \text{N} \end{array} \text{NH}$ , is formed together with indazole, a *substance* which is soluble in cold dilute sodium hydroxide, and a sparingly soluble, indifferent *substance* (trichloroindazole?) by the action of alkali hydroxides on an *o*-diazotoluene salt. It crystallises in matted, white needles, m. p.  $242-242.5^\circ$ , sublimes in woolly needles, is only slightly volatile in a current of steam, has feeble basic properties, and is soluble in boiling dilute sodium hydroxide (compare Abstr., 1899, i, 720). G. Y.

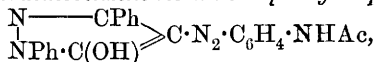
**Diazo-compounds from *p*-Phenylene nediamine with Heterocyclic Side-chains.** CARL BÜLOW and FRITZ BUSSE (*Ber.*, 1906, 39, 3861-3868. Compare Abstr., 1906, i, 717).—*Ethyl p*-acetylaminobenzeneazobenzoylacetate,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH}(\text{COPh}) \cdot \text{CO}_2\text{Et}$ , obtained by condensing a diazo-salt of acetyl-*p*-phenylenediamine with an

alcoholic solution of ethyl benzoylacetate, crystallises from alcohol in yellow needles, m. p.  $95^{\circ}5'$ . The ester reacts with an aqueous alcoholic ammonia solution, yielding the *amide*,

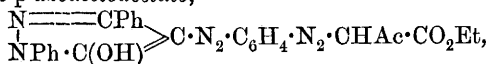


in the form of pale yellow needles, m. p.  $252^{\circ}$ .

Phenylhydrazine reacts with an acetic acid solution of the ester, yielding 4-*p*-acetylaminobenzeneazo-1 : 3-diphenyl-5-pyrazolone,



which crystallises from dilute acetic acid in red needles, readily soluble in most organic solvents and in dilute alkalis, but insoluble in ether, light petroleum, or water. 4-*p*-Aminobenzeneazo-1 : 5-diphenyl-5-pyrazolone,  $\text{C}_{21}\text{H}_{17}\text{ON}_5$ , obtained by hydrolysing the acetyl derivative with sodium hydroxide solution, crystallises from alcohol in reddish-brown needles, m. p.  $208\text{--}209^{\circ}$ . The diazo-chloride derived from this amine reacts with an alcoholic solution of ethyl acetoacetate in the presence of sodium acetate, yielding ethyl 1 : 3-diphenyl-5-pyrazolone-4-azobenzene-*p*-azoacetoacetate,



which crystallises from alcohol in pale red needles, m. p.  $195\text{--}196^{\circ}$  (decomp.).

1 : 3-Diphenyl-5-pyrazolone-4-azobenzene-*p*-4'-azo-1'-phenyl-3'-methyl-5'-pyrazolone,  $\begin{array}{c} \text{N} \text{---} \text{CPh} \\ | \\ \text{NPh} \cdot \text{C}(\text{OH}) \end{array} \text{>} \text{C} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C} \begin{array}{c} \text{CMe} \text{---} \text{N} \\ \text{C}(\text{OH}) \cdot \text{NPh} \end{array}$ , obtained by the action of phenylhydrazine on the preceding compound, may be recrystallised from hot benzene or by solution in hot nitrobenzene and precipitation with acetic acid. It forms reddish-brown plates with a green, metallic lustre, m. p. about  $270^{\circ}$  (decomp.).

The constitution of the last-mentioned compound has been established by its formation by the following stages : 1-phenyl-3-methyl-5-pyrazolone-4-azobenzene-diazo-chloride  $\rightarrow$  ethyl 1-phenyl-3-methyl-5-pyrazolone-4-azobenzene-*p*-4'-azobenzoylacetate,  $\text{C}_{27}\text{H}_{24}\text{O}_4\text{N}_6$ , m. p.  $203^{\circ}$   $\rightarrow$  1'-phenyl-3'-methyl-5'-pyrazolone-4-azobenzene-*p*-4'-azo-1 : 3-diphenyl-5-pyrazolone. J. J. S.

**Reduction of Nitroazo-compounds with Sodium Hypo-sulphite.** EUGÈNE GRANDMOUGIN (*Ber.*, 1906, 39, 3929—3932, Compare Abstr., 1906, i, 716, 967).—The reduction of nitroazo-compounds with sodium hyposulphite does not always proceed normally; *o*-nitroazo-compounds in particular are only partially reduced, whilst azoimino-oxides are also formed.

Benzeneazosalicylic acid undergoes normal reduction with formation of aniline and 5-aminosalicylic acid.

*m*-Nitrobenzeneazosalicylic acid is reduced to aminosalicic acid and *m*-phenylenediamine, whilst *p*-nitrobenzeneazosalicylic acid yields aminosalicic acid and *p*-phenylenediamine.

*o*-Nitrobenzeneazophenol, on reduction with sodium hyposulphite, forms *p*-hydroxyphenylazoiminobenzene oxide,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \text{---} \\ \text{NO} \end{array} \text{>} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ ,



which crystallises in colourless needles, m. p. 232—233°; its *acetyl* derivative separates from dilute alcohol in needles, m. p. 176°. When *p*-hydroxyphenylazoiminobenzene oxide is reduced by stannous chloride, it forms *p*-hydroxyphenylbenzotriazole,  $C_6H_4 \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ N \end{smallmatrix} N \cdot C_6H_4 \cdot OH$ , which separates from alcohol in colourless needles, m. p. 219°. A. McK.

**Digestion of Egg and Serum Proteids by Papain.** D. JONESCU (*Biochem. Zeit.*, 1906, 2, 177—187).—Digestion of the proteids named with papain stops short at peptone; amino-acids are not found. Coagulated egg-white and fibrin are not digested at all. The influence of temperature is discussed; reversibility of action was not discovered, and the questions of pro-ferment and activation suggested.

W. D. H.

**Albumin Extracted from Fishes' Eggs, and a comparison of it with the Vitellin of Hens' Eggs.** LOUIS HUCOUNENQ (*Compt. rend.*, 1906, 143, 693—694. Compare Abstr., 1906, i, 324).—The albumin extracted from the eggs of *Clupea harengus* and called *clupeovin* by the author, yields on hydrolysis arginine, histidine, lysine, tyrosine, leucine, aminovaleric acid, alanine, serine, phenylalanine, and aspartic acid; it follows therefore that the vitellin obtained from the egg-albumin of birds or fishes is formed of the same compounds associated in comparable if not almost identical proportions (Abstr., 1906, i, 85, 776).

M. A. W.

**Occurrence of *iso*Leucine in Casein.** R. WEITZENBÖCK (*Monatsh.*, 1906, 27, 831—837).—The first phosphotungstate precipitate, obtained from a large amount (3 kilos) of casein, contains leucine, *isoleucine* (Ehrlich, Abstr., 1904, i, 56), and small amounts of arginine, histidine, lysine, and probably aminovaleric acid and phenylalanine.

If the phosphotungstate precipitate is distilled with aqueous potassium hydroxide, and the distillate evaporated with hydrochloric acid and redistilled with aqueous baryta, leucine and *isoleucine* are present in the final distillate and can be separated by Ehrlich's method.

G. Y.

**The Homogeneous Nature of Hæmatin and Attempts to Remove Iron from Blood-colouring Matter.** RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1906, 49, 472—481. Compare Abstr., 1900, i, 711).—Hæmin obtained by the pepsin-hydrochloric acid method closely resembles hæmin obtained by other methods. It may be crystallised from acetic acid and the analytical data agree fairly well with the formula  $C_{34}H_{33}O_4N_4ClFe$ .

When the blood-colouring matter is left in contact with pepsin-hydrochloric acid for some months, the yield of crystallised hæmin is small, and considerable amounts of residues are left in the pyridine-chloroform solutions, but the percentage of iron is not reduced. Hæmin prepared by the pepsin-hydrochloric acid method is more readily decomposed by dilute acid or by water at 180° than is ordinary

hæmin. It is also more readily decomposed when a feeble electric current is passed through its alkaline solution.

When a suspension of hæmin in sulphurous acid solution is exposed to light, the aqueous liquid becomes purple-red in colour and shows the characteristic bands of hæmatoporphyrin. The iron has been removed from the hæmin and is contained in the solution in the ionic state.

J. J. S.

**Nucleic Acids. XI.** PHÆBUS A. LEVENE and JOHN A. MANDEL (*Zeit. physiol. Chem.*, 1906, **49**, 262—265. Compare Abstr., 1906, i, 468).—The nuclein substance obtained from the egg of the shell-fish, *Gadus æglefinus*, appears to be a mixture of ichthulic and nucleic acids. It yields on hydrolysis the purine bases, guanine and adenine, the pyrimidine bases, cytosine and uracil. It gives a positive orcinol reaction, but the yield of lævulic acid is very small.

W. D. H.

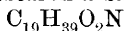
**Composition of Nucleic Acids of Thymus and Herring-roë.** HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1906, **49**, 406—409. Compare Abstr., 1906, i, 125).—The four nitrogenous components of these nucleic acids seem to be present in molecular proportion. They are guanine, adenine, cytosine, and thymine.

W. D. H.

**Cleavage of Gelatin.** PHÆBUS A. LEVENE and WALLACE A. BEATTY (*Zeit. physiol. Chem.*, 1906, **49**, 247—251, 252—261. Compare Abstr., 1904, i, 357; 1906, i, 469).—The following are the percentage amounts of cleavage products obtained from gelatin: glycine, 19.25; alanine, 3.00; leucine, 6.75;  $\alpha$ -proline, 6.25; oxyproline, 6.4; phenylalanine, traces; aspartic acid, absent, and glutamic acid, 1.75.

W. D. H.

**Cerebrone. III.** F. KITAGAWA and HANS THIERFELDER (*Zeit. physiol. Chem.*, 1906, **49**, 286—292. Compare Abstr., 1906, ii, 183).—A new method for the separation of cerebrone is described. In a 5% solution in 75% chloroform,  $[\alpha]_D^{20} + 7.6$ . Sphingosine was the name given by Thudichum to a basic cleavage product of his phrenosin. In the present research a base with the formula



was prepared, but its relationship to sphingosine is at present uncertain.

W. D. H.

**Diffusion of Enzymes through Cellulose Membranes.** ALB. J. J. VANDEVELDE (*Biochem. Zeit.*, 1906, **1**, 408—412).—Leune's cellulose membrane and pig's intestinal membrane were employed. Invertase does not diffuse through the former, but easily diffuses through the latter. Maltase, rennet, and blood-catalase behave like invertase. Zymase diffuses through neither, but the isolated enzyme was not employed, only yeast cells.

W. D. H.

## Organic Chemistry.

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**A New Octane [ $\delta$ -Methylheptane].** LATHAM CLARKE (*Ber.*, 1907, 40, 352—355).—This is the fourth octane to be prepared; the three at present known are *n*-octane, di-*isobutyl* ( $\beta$ -dimethylhexane), and  $\gamma$ -methylheptane. The synthesis was accomplished by first preparing *ethyl  $\beta$ -amylacetoacetate*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{CHMePr}^a) \cdot \text{CO}_2\text{Et}$ , from  $\beta$ -iodopentane and ethyl sodioacetoacetate; the oil, b. p.  $226^\circ$ , has a characteristic almond-like odour. On hydrolysis with 10% potassium hydroxide,  $\delta$ -methyl- $\beta$ -heptanone,  $\text{CH}_3 \cdot [\text{CH}_2]_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$ , is obtained as an oil, b. p.  $156^\circ$ . The ketone, on being reduced with sodium in the presence of ether and water, gives  $\delta$ -methyl- $\beta$ -heptanol,  $\text{CHMe} \cdot \text{Pr}^a \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$ , an oil, b. p.  $168^\circ$ , and a pinacone, b. p.  $285\text{—}290^\circ$ .  $\beta$ -Iodo- $\delta$ -methylheptane was obtained, but not isolated, by the reduction of the alcohol by hydrogen iodide at  $100^\circ$ , and on replacing the iodine by means of zinc and hydrochloric acid  $\delta$ -methylheptane was obtained as a colourless, almost odourless, mobile oil, b. p.  $118^\circ$ .  
W. R.

**Preparation of Tetra- and Hexa-chloroethanes from Acetylene.** SALZBERGWERK NEU-STASSFURT (D. R.-P. 174068).—The direct addition of chlorine to acetylene takes place with explosive violence, carbon being eliminated and hydrogen chloride formed, owing to the great affinity of this halogen for hydrogen. The catalytic processes hitherto in vogue are not entirely satisfactory, but the difficulties of this chlorination are overcome by passing acetylene into sulphur chloride in the presence of iron powder or some iron compound. When the mixture is cooled, tetrachloroethane is produced, and when heated to boiling ( $138^\circ$ ), hexachloroethane is obtained. The former product is isolated by distillation alone or in steam, whilst the latter crystallises from hot sulphur chloride and is collected, and either sublimed, distilled, or recrystallised from alcohol.

When the absorption of acetylene slackens, the mixture is saturated with chlorine, and in this way, by alternating with acetylene and chlorine, the process is rendered continuous. In the absence of the catalyst, the sulphur chloride has no action on the acetylene.

G. T. M.

**Preparation of Methyl and Ethyl Iodides.** WEINLAND and K. SCHMID (D. R.-P. 175209).—Although dry potassium chloride yields methyl chloride on heating with methyl sulphate, yet potassium bromide and iodide when similarly treated do not undergo a like change, methyl bromide is not the exclusive product, and methyl iodide is not obtained by this process. It has now been found that by slowly adding methyl or ethyl sulphate to a warm concentrated aqueous solution of an alkali iodide, the alkyl iodide is produced quantitatively.

G. T. M.

**Application of the Principle of Partition. VIII. Constitution of the Hexyl Iodide obtained from Mannitol.** ARTHUR MICHAEL and ROBERT N. HARTMAN (*Ber.*, 1907, 40, 140—146. Compare Erlenmeyer and Wanklyn, *Zeitsch. Chem.*, 1863, 6, 564; Combes and Le Bel, *Abstr.*, 1893, i, 246).—From theoretical considerations, the conclusion is drawn that the hexyl iodide from mannitol contains a considerable amount of  $\beta$ -iodohexane, and a certain amount of  $\gamma$ -iodohexane, but little or no  $\alpha$ -iodohexane. The amounts of the  $\beta$ - and  $\gamma$ -iodo-derivatives actually found were respectively 65—60% and 35—40%.

The hexyl iodide was prepared by Domac's method (*Abstr.*, 1881, 1113), and purified by distillation under reduced pressure. It was transformed into the acetate by means of silver acetate and glacial acetic acid. One hundred and ten grams of hexyl iodide gave 18 grams of hexene and 42 grams of hexyl acetate, b. p. 150—158°.

The acetate on hydrolysis gave 26 grams of hexyl alcohol, b. p. 136—140°, which when oxidised by Lieben's method gave 17.8 grams of ketone. When analysed by the semicarbazide method, this indicated the presence of some 60% of  $\beta$ -hexanone. J. J. S.

**$\alpha\alpha$ -Dichloroisopropyl Alcohol and the Preparation of Dichloroacetaldehyde.** ALFRED WOHL and H. ROTH (*Ber.*, 1907, 40, 212—218. Compare Jocitsch and Faworsky, *Abstr.*, 1899, i, 786; Fourneau and Tiffeneau, *Abstr.*, 1905, i, 591; Höring, *Abstr.*, 1905, i, 903; Oddo and Mameli, *Abstr.*, 1904, i, 280).—The authors have attempted to prepare dichloroisopropyl alcohol by reduction of trichloroisopropyl alcohol, but unsuccessfully, as the reaction proceeds beyond the first stage. Reduction of the trichloro-alcohol by means of zinc dust and glacial acetic acid in cooled aqueous solution leads to the formation of  $\alpha\alpha$ -dichloropropylene, or by means of sodium and boiling absolute alcohol to the formation of ethyl  $\alpha$ -ethoxypropionate, b. p. 73°/42 mm.

When treated with zinc ethyl in cooled ethereal solution in an atmosphere of carbon dioxide, dichloroacetone evolves gas and yields a mixture of chlorinated products, b. p. 35—50° and 50—57°/19 mm. The action of magnesium *tert.*-butyl bromide, prepared by slowly adding magnesium to *tert.*-butyl bromide in ethereal solution, on dichloroacetone leads to the formation of isobutylene.

Dichloroacetaldehyde is prepared in a 70.8% yield by heating dichloroacetal with benzoic anhydride and concentrated sulphuric acid at 170—180° and finally at 200°. When treated with magnesium methyl bromide in cooled ethereal solution it yields *dichloroisopropyl alcohol*,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHCl}_2$ , b. p. 146—148°/765 mm. G. Y.

**Synthesis of Alcohols by Means of Organomagnesium Compounds. III.** MICHAEL I. KONOWALOFF, K. MILLER, and TIMTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1906, 38, ii, 447—448. Compare *Abstr.*, 1904, i, 496; Grignard, *Abstr.*, 1900, i, 382).—*Methylethyltert.-amylcarbinol* or *8-hydroxy- $\gamma\gamma$ -dimethylhexane*,



prepared by the action of methyl ethyl ketone on magnesium  $\beta$ -bromo-

$\beta$ -methylbutane, has m. p. 165—166°,  $D_D^{21}$  0.8323,  $n_D^{21}$  1.43407, is only sparingly soluble in water, but absorbs it rapidly and has the ordinary odour of a tertiary alcohol. In the synthesis of alcohols by Grignard's method, the ketone or aldehyde employed is often itself reduced to the corresponding alcohol; thus fenchone when treated with magnesium ethyl iodide yielded chiefly fenchyl alcohol, whilst *tert*-bromobutane and pentane with benzophenone gave 38.5% of benzhydrol or its ester. Z. K.

**Preparation of  $\beta$ -Glycols from Aldols by the Action of Organomagnesium Compounds.** ADOLF FRANKE and MORITZ KOHN (*Monatsh.*, 1906, 27, 1097—1128. Compare Abstr., 1905, i, 111; Lieben, Abstr., 1896, i, 403).— $\beta\beta$ -Dimethylbutane- $\alpha\gamma$ -diol, formed together with pentylene glycol, which on oxidation yields hydroxypivalic acid, by the action of magnesium methyl iodide (2 mols.) on formylisobutaldol, is identical with Fossek's glycol (Abstr., 1884, 37).

$\beta\beta$ -Dimethylpentane- $\alpha\gamma$ -diol, formed by the action of magnesium ethyl iodide (2 mols.) on formylisobutaldol, m. p. 60—63° (55°, Abstr., 1905, i, 111), b. p. 112—114°/11 mm., could not be completely purified.

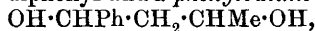
The glycols described in this paper have been prepared by the action of organomagnesium compounds on aldols. Full details are given as to the methods of purification, which are mostly complicated and tedious.

$\gamma$ -Phenyl- $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -diol (Swoboda and Fossek, Abstr., 1891, 31) is formed together with diphenyl by the action of magnesium phenyl bromide on formylisobutaldol.

[With EUGEN THIEL.]—Acetaldol is obtained in a 55% yield by the action of aqueous potassium hydrogen carbonate on acetaldehyde below 10°; with magnesium methyl iodide it forms pentane- $\beta\gamma$ -diol, b. p. 201—202°/748 mm. (Poray-Koschitz, Abstr., 1904, i, 363); the *diphenylcarbamate*,  $C_{19}H_{22}O_4N_2$ , forms a white powder, m. p. 141°.

The action of magnesium ethyl iodide on acetaldol leads to the formation of *hexane- $\beta\delta$ -diol*,  $OH\cdot CHMe\cdot CH_2\cdot CHEt\cdot OH$ , which is obtained as a viscid oil, b. p. 103°/11 mm. or 210—211°/750 mm. (corr.). The *diphenylcarbamate*,  $C_{20}H_{24}O_4N_2$ , m. p. 144°; the *diacetate*, b. p. 101—102°/13 mm. or 211°/750 mm. (partial decomp.).

The product of the action of magnesium phenyl iodide on acetaldol yields on distillation diphenyl and  *$\alpha$ -phenylbutane- $\alpha\gamma$ -diol*,



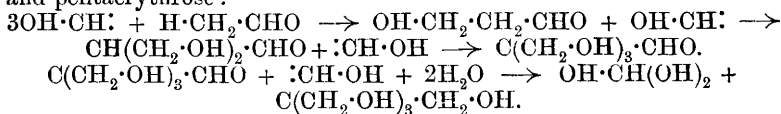
which forms a white, crystalline powder, m. p. about 73.5°, b. p. 162—164°/11 mm.; the *diacetate*,  $C_{14}H_{18}O_4$ , is a transparent, mobile liquid, b. p. 157°/10 mm., which decomposes partially when boiled under atmospheric pressure.

[With KARL ZWIAUER.]—Propaldol is obtained from propaldehyde in a 70% yield by Lieben's method. It reacts with magnesium methyl iodide, forming  *$\gamma$ -methylhexane- $\beta\delta$ -diol*,  $OH\cdot CHEt\cdot CHMe\cdot CHMe\cdot OH$ , which is obtained as a colourless, viscid oil, b. p. 112.5°/9 mm.; the *diacetate*,  $C_{11}H_{20}O_4$ , forms a transparent, mobile liquid, b. p. 103.5—105.5°/11 mm.

*δ-Methylheptane-γε-diol*,  $\text{OH}\cdot\text{CHEt}\cdot\text{CHMe}\cdot\text{CHEt}\cdot\text{OH}$ , formed from propaldol and magnesium ethyl iodide, is obtained as a transparent, odourless liquid, b. p. 120—123°/14 mm.; the *diacetate*,  $\text{C}_{12}\text{H}_{22}\text{O}_4$ , is a mobile, transparent liquid, b. p. 112—113°/13 mm.

*α-Phenyl-β-methylpentane-αγ-diol*,  $\text{OH}\cdot\text{CHEt}\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{OH}$ , formed together with benzene and diphenyl from magnesium phenyl iodide and propaldol, is obtained as a transparent, extremely viscid substance, b. p. 169—173°/14 mm., which solidifies to a white mass when cooled with solid carbon dioxide and alcohol, and cannot be completely purified. The *diacetate*,  $\text{C}_{16}\text{H}_{22}\text{O}_4$ , is a mobile, transparent oil, b. p. 169·5—170°/14 mm., which has a pleasant odour. G. Y.

**Aldol, Pentaerythrose, and the Action of Copper Acetate on the Hexoses.** A. F. McLEOD (*Amer. Chem. J.*, 1907, 37, 20—50).—It has been shown by Tollens (Abstr., 1892, 127; 1893, 617) that considerable quantities of pentaerythritol can be obtained by the condensation of acetaldehyde (1 mol.) with formaldehyde (4 mols.). From a consideration of Nef's work, it is probable that this change is effected by the following successive reactions, involving the intermediate formation of hydracrylaldehyde,  $\beta\beta'$ -dihydroxyisobutaldehyde, and pentaerythrose:



The present investigation has been carried out with the object of obtaining experimental proof that the condensation does take place in the stages indicated. It has been found that considerable quantities of pentaerythrose can be isolated, and indications have been obtained of the presence of relatively large amounts of  $\beta\beta'$ -dihydroxyisobutaldehyde in the reaction product. Further, it is shown that mixtures of hydracrylaldehyde (1 mol.) and formaldehyde (2 mols.) in presence of traces of sodium hydroxide give an almost quantitative yield of pentaerythrose.

Experiments with acetaldehyde have shown that when this compound is left in contact at the ordinary temperature with solutions of sodium or calcium hydroxide of concentration below 0·1%, little or no condensation of the aldehyde occurs. The conditions under which the best yields of aldol and of crotonaldehyde can be obtained from acetaldehyde have been carefully studied. Acetaldehyde cannot be regenerated from aldol or crotonaldehyde by treatment with water, with very dilute alkalis, or with acids in sealed tubes at 100°. Under these conditions, aldol is readily transformed into crotonaldehyde, which, in turn, is converted into insoluble, yellow, volatile and non-volatile oils, and finally into aldehyde-resin.

The behaviour of acetaldehyde and of hydracrylaldehyde towards alkalis has been investigated. Nef's statement (Abstr., 1905, i, 4) that crotonaldehyde is formed under these conditions is incorrect. The addition of traces of any alkali to a cold aqueous solution of acetaldehyde results in the formation of an insoluble, amorphous polymeride, which decomposes at 94—95° and is analogous to that

obtained by Nef by the action of barium hydroxide. These polymerides are neutral to sodium carbonate, but dissolve in 10% sodium hydroxide, and, after heating the solution for a short time at 100° and adding the calculated quantity of hydrochloric acid, yield a light brown, amorphous, substance of high melting point of about half the molecular weight of the original polymeride. On treating hydracrylaldehyde with sodium hydroxide, an insoluble polymeride is not formed in the cold, but on further treatment as in the previous case an insoluble polymeride is produced.

A quantitative estimation has been made of the amounts of cuprous oxide, carbon dioxide, and of formic, glycollic, and oxalic acids formed from 100 grams of *d*-dextrose, *d*-lævulose, or *d*-galactose when heated for eight hours on the water-bath with excess of copper acetate solution, but the results so far obtained are not sufficiently complete to enable a theory of the oxidation of hexoses to be put forward.

Experiments on the action of copper acetate solution on formaldehyde and on formic, glycollic, and oxalic acids have led to the following conclusions. The formic and carbonic acids obtained on oxidising the hexoses are not produced as the result of the decomposition of the oxalic acid formed as an intermediate product; the oxalic acid is not produced by an oxidation of glycollic acid, and the formation of carbonic acid is not due to the oxidation of formic acid.

E. G.

**Synthesis of Natural Erythritol.** ROBERT LESPIEAU (*Compt. rend.*, 1907, 144, 144—146. Compare *Abstr.*, 1905, i, 566).—The inactive erythrolactone previously described proves to be a racemic mixture, for on treating it in the presence of water with an equivalent quantity of brucine, and fractionally crystallising the product, a separation (probably incomplete) into brucine salts of rotatory power varying from  $-25.3^{\circ}$  to  $-34^{\circ}$  is effected. The salt of rotatory power  $-25.3^{\circ}$  gives a lactone of rotatory power  $-35^{\circ}$ .

When the lactone is reduced by sodium amalgam (containing 2.6% of sodium) in a solution kept slightly acid, a syrup is obtained, which with phenylhydrazine gives, not erythrosazone, but a hydrazone identical with that obtained directly from the lactone. This syrup on keeping for three months deposits crystals identical with natural erythritol. The identity was established by the melting point, both alone and when mixed with the natural substance, by analysis, and by the production of a dibenzoylacetal, m. p. 195—196°, identical with that described by Fischer.

E. H.

**Preparation of Alkyl Ethers.** TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1906, 650—668).—By heating propyl alcohol or *isoamyl* alcohol with quinoline hydrochloride in closed tubes at 180° during six days, the author has obtained a mixture of products containing in each case the corresponding alkyl ether, alkyl chloride, and di- and tri-alkyl quinolines. The yield of pure propyl ether so obtained is 35% of the theoretical and of the *isoamyl* ethyl, 53%. When these alcohols are heated with quinoline alone, under the above conditions, no change occurs, whence it appears that the reaction, which takes place in the

presence of quinoline hydrochloride, is due to the hydrolysis of this salt, the hydrochloric acid liberated forming the alkyl chloride, which then reacts in part with the alcohol and in part with the quinoline.

The alkylquinolines produced are separated by conversion into the picrates. *Dipropylquinoline*, b. p.  $329^{\circ}$  (corr.), yields a crystalline *picrate*, m. p.  $189-190^{\circ}$ . *Tripropylquinoline*, b. p.  $348^{\circ}$  (corr.), furnishes a crystalline *picrate*, m. p.  $133^{\circ}$ . A third amorphous basic product is obtained in this reaction, which also yields an amorphous *picrate*.

*iso*Amyl ether, b. p.  $172.2^{\circ}$ , has  $D_{19}^{20} 0.7767$ . From the mixture of bases obtained in the reaction with *iso*amyl alcohol, *diisoamylquinoline picrate* was obtained in slightly fluorescent tufts, m. p.  $180^{\circ}$ . In this reaction also a small amount of amylene is formed. T. A. H.

**Ethyl *aa*-Dichloroisopropyl Ether and Dibromoacetaldehyde.** PAUL FREUNDLER (*Compt. rend.*, 1907, 144, 272-273).—By condensing dibromoacetaldehyde with magnesium methyl iodide, the author obtains a liquid denser than water, which he considers to be *aa*-dibromoisopropyl alcohol. This, however, is much less stable than the corresponding dichloro-compound obtained by Wohl (this vol., i, 170), undergoing partial decomposition when distilled, and its examination was not proceeded with.

*Ethyl aa-dichloroisopropyl ether*,  $\text{CHCl}_2 \cdot \text{CHMe} \cdot \text{OEt}$ , formed as a by-product in the preparation of trichlorobutyric acetal (this vol., i, 13), is liquid, b. p.  $145-146^{\circ}$ . When heated with lead oxide and water in a sealed tube at  $180-200^{\circ}$ , it gives, not  $\beta$ -ethoxypropaldehyde, but a mixture of ethyl chloride (or ethyl alcohol) and lead propionate. It is suggested that the propionic acid arises from an internal transposition of the oxide,  $\text{O} \begin{smallmatrix} \text{CHMe} \\ < \\ \text{CH} \cdot \text{OH} \end{smallmatrix}$ , first formed, and that in any case

the reaction contradicts Nef's theories on ethylenic dissociation, whilst leading to the conclusion that it will not be possible to obtain lactaldehyde from an *aa*-dichloro- $\beta$ -hydroxypropyl derivative as a starting point. E. H.

**Butylene Nitrosite and Butylenediamine.** NICOLAUS J. DEMJANOFF (*Ber.*, 1907, 40, 245-246).—When nitrous fumes are passed into a well-cooled ethereal solution of butylene, *butylene nitrosite*,  $(\text{C}_4\text{H}_8\text{O}_3\text{N}_2)_2$ , m. p.  $103-104^{\circ}$ , is precipitated in colourless, glistening prisms. From the ethereal residue, after reduction with tin and hydrochloric acid, butaldehyde and *butylenediamine*,  $\text{C}_4\text{H}_8(\text{NH}_2)_2$ , are obtained; the *hydrochloride*, *platinichloride*, *aureichloride*, and *picrate* of the latter are described. C. S.

**Structure of Phosphorous Acid and its Derivatives. III. The Compounds of the Tervalent Phosphorus Derivatives with the Monohalogen Compounds of Copper.** ALEXANDER E. ARBUSOV (*J. Russ. Phys. Chem. Soc.*, 1906, 38, ii, 293-319. Compare this vol., i, 8).—Compounds of the type  $\text{CuX}_2\text{P}(\text{OR})_3$  (where X stands for a halogen, R for Et, Ph, &c.) have been prepared by the gradual addition of an equivalent weight of copper halide to a weighed quantity of the phosphorous ester. On warming gently, the copper salt dissolves completely, and the solution crystallises immediately on



cooling. Most of the salts thus formed are nearly insoluble in ether and ethyl and methyl alcohols, but they are readily soluble in chloroform and ethyl bromide. When exposed to the air they decompose, but they can be preserved indefinitely in a sealed tube in an atmosphere of carbon dioxide. Pure water has no action, whilst nitric acid oxidises them rapidly. The following compounds have been prepared. *Methyl* compounds,  $\text{CuCl}, \text{P}(\text{OMe})_3$ , m. p.  $190-192^\circ$ ;  $\text{CuBr}, \text{P}(\text{OMe})_3$ , m. p.  $180-182^\circ$ ;  $\text{CuI}, \text{P}(\text{OMe})_3$ , m. p.  $175-177^\circ$ , can only be obtained at temperatures above  $100^\circ$ ; at a low temperature the substance,  $\text{CuI}, 2\text{P}(\text{OMe})_3$ , m. p.  $69-70^\circ$ , is formed. *Ethyl* compounds are formed with greater difficulty.  $\text{CuCl}, \text{P}(\text{OEt})_3$  is a colourless, oily, unstable liquid which does not solidify at  $-18^\circ$ ;  $\text{CuBr}, \text{P}(\text{OEt})_3$ , m. p.  $27-28^\circ$ ;  $\text{CuI}, \text{P}(\text{OEt})_3$ , m. p.  $109-110^\circ$ , are soluble in most organic solvents and are fairly stable in air. *Propyl* compounds,  $\text{CuI}, \text{P}(\text{OPr}^a)_3$ , m. p.  $64-65^\circ$ , the chloride and bromide are liquids difficult to purify;  $\text{CuCl}, \text{P}(\text{OPr}^s)_3$ , m. p.  $112-114^\circ$ ;  $\text{CuBr}, \text{P}(\text{OPr}^s)_3$ , m. p.  $149-150^\circ$ ;  $\text{CuI}, \text{P}(\text{OPr}^s)_3$ , m. p.  $184-185^\circ$ , are soluble in most organic solvents, but are very unstable. *Phenyl* compounds,  $\text{CuCl}, \text{P}(\text{OPh})_3$ , m. p.  $95-96^\circ$ , strongly refractive;  $\text{CuCl}, 2\text{P}(\text{OPh})_3$ , m. p. about  $70^\circ$ ;  $\text{CuBr}, \text{P}(\text{OPh})_3$ , m. p.  $90.5-91.5^\circ$ ;  $\text{CuBr}, 2\text{P}(\text{OPh})_3$ , m. p.  $73-74^\circ$ ;  $\text{CuI}, 2\text{P}(\text{OPh})_3$ , m. p.  $73-76^\circ$ ;  $\text{CuI}, \text{P}(\text{OPh})_3$ , has not been obtained. *isoButyl* compounds,  $\text{CuCl}, \text{P}(\text{OC}_4\text{H}_9)_3$ , prepared from the esters,  $\text{P}(\text{OC}_4\text{H}_9)_3$ ,  $\text{P}(\text{OC}_4\text{H}_9)_2 \cdot \text{OH}$ , was not obtained pure, but the corresponding compounds,  $\text{CuCl}, \text{P}(\text{OC}_4\text{H}_9)_3, \text{P}(\text{OPh})_3$ , m. p.  $54-55^\circ$ , and  $\text{CuBr}, \text{P}(\text{OC}_4\text{H}_9)_3, \text{P}(\text{OPh})_3$ , m. p.  $58-59^\circ$ , were prepared in a pure state.

*Copper cyanide* compounds have been prepared in an impure form; they exhibit a tendency to polymerise.

*Triethylphosphine* compounds,  $\text{CuCl}, \text{PEt}_3$ , m. p.  $103-104^\circ$ , and  $\text{CuI}, 2\text{PEt}_3$ , m. p.  $37-39^\circ$ , are also described; the latter yields  $\text{CuI}, \text{PEt}_3$  on heating.

Cuprous chloride, bromide, and iodide are also dissolved by the chloroanhydrides of phosphorous acids of the type  $\text{P}(\text{OR})\text{Cl}_2$  and by  $\text{P}(\text{OPh})_2\text{Cl}, \text{P}(\text{OMe})_2\text{Cl}$ , yielding crystalline substances.

Phosphorous tribromide or chloride reacts with cuprous bromide, forming the substance,  $\text{CuBr}, \text{PBr}_3$ , which could not be purified. It is insoluble in practically all solvents, and fumes strongly in air, yielding hydrogen bromide, cuprous bromide, and phosphorous acid.

None of the derivatives of quinquivalent phosphorus reacts with the cuprous halogen compounds even when the substances are heated together for several days at  $250^\circ$ . Since neither phosphorous acid nor its acid derivatives form compounds with the cuprous halides, the phosphorus in this acid must be quinquivalent, and the structure of the acid must consequently be represented thus:  $\text{O}:\text{P} \begin{smallmatrix} < \\ \text{H} \end{smallmatrix} \begin{smallmatrix} (\text{OH})_2 \\ \end{smallmatrix}$ , and the derivatives,  $\text{O}:\text{P} \begin{smallmatrix} < \\ \text{H} \end{smallmatrix} \begin{smallmatrix} (\text{OR})_2 \\ \end{smallmatrix}$ .

Z. K.

**Acetyl Nitrate.** AMÉ PICTET and EUGÈNE KHOTINSKY (*Compt. rend.*, 1907, 144, 210-212).—*Acetyl nitrate*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{NO}_2$ , is obtained by dissolving nitric pentoxide in acetic anhydride; it is separated from excess of acetic anhydride by distillation under reduced pressure. If the mixture of acetyl nitrate and acetic

anhydride is heated at the ordinary pressure, it undergoes a violent reaction at 60° with evolution of nitrous fumes and formation of tetranitromethane. Acetyl nitrate is a colourless, very mobile and hygroscopic liquid, b. p. 22°/70 mm., which fumes strongly in air and explodes violently on rapid heating. Analysis was effected by decomposition with water and estimation of the nitric and acetic acids formed. It reacts with alcohols, giving nitric or acetic esters according to the nature of the alcohol and the temperature. Aniline is converted into a mixture of molecular quantities of acetanilide and aniline nitrate. It is a very powerful nitrating agent towards aromatic compounds, benzene, toluene, anthracene, and thiophen being nitrated below 0°. With substituted benzenes, it has a tendency to give ortho- rather than para-nitro-derivatives. Thus toluene gives ten times as much o-nitro- as p-nitro-toluene. Acetanilide gives solely o-nitroacetanilide. E. H.

**Hydrolysis of Sodium Palmitate.** DAVID HOLDE and F. SCHWARZ (*Ber.*, 1907, 40, 88—92. Compare Cohn, *Zeitsch. öffentl. Chem.*, 1905, 11, 58; Abstr., 1906, ii, 58; Schwarz, Abstr., 1905, ii, 657).—The authors dispute Cohn's views on the hydrolysis of sodium palmitate. Palmitic acid (0.5—1 gram) was dissolved in 20 c.c. of aqueous *N*/2 alkali and the excess of alkali titrated with *N*/2 hydrochloric acid. It was shown that in aqueous solution 100% of palmitic acid cannot be formed in this manner by Cohn's method using phenolphthalein; that is, that the amount of excess of alkali and the amount of alkali, obtained by the hydrolysis of the salt, cannot be separately distinguished by this method. A. McK.

**Occurrence of Dierucin in Rape Oil.** C. L. REIMER (*Ber.*, 1907, 40, 256—257. Compare Abstr., 1887, 233).—The separation of dierucin from rape oil occasionally occurs before refining (compare Marcusson, Abstr., 1906, i, 924; Lewkowitsch, this vol., i, 10), due possibly to a reaction between trierucin and water caused by fermentation. C. S.

**$\Delta$ -Chloro- $\gamma$ -valerolactone and some Related Compounds.** HERMANN LEUCHS and OSKAR SPLETTSTÖSSER (*Ber.*, 1907, 40, 301—310).—Whilst the chlorine of ethyl  $\delta$ -chloro- $\gamma$ -valerolactone- $\alpha$ -carboxylate is replaced by hydroxyl on warming with alkali (Traube and Lehmann, Abstr., 1901, i, 501), at 0° hydrolysis occurs, the chlorine for the most part remaining intact. The hydrolysis is effected much better, however, by hydrochloric acid, when a 90% yield of  $\delta$ -chloro-

$\gamma$ -valerolactone,  $\text{CH}_2\text{Cl}\cdot\underset{\text{O} \text{---} \text{CO}}{\text{CH}}\cdot\text{CH}_2\cdot\text{CH}_2$ , is obtained as a colourless, almost odourless oil of b. p. 132—135°/12 mm.,  $D^{25}$  1.625, sparingly soluble in sodium carbonate. It dissolves in ammonia, forming a salt of chlorohydroxyvaleric acid, and when this solution is heated at 100° for one hour in a sealed tube, Emmerling's 3-hydroxy-6-piperidone is formed (Abstr., 1900, i, 16).  $\delta$ -( $\beta$ )-*N*-phthalenesulphonamino- $\gamma$ -valerolactone,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\underset{\text{O} \text{---} \text{CO}}{\text{CH}}\cdot\text{CH}_2\cdot\text{CH}_2$ , is obtained in good

yield by heating the hydroxypiperidone for three hours with *N* sodium hydroxide (2 mols.) and then shaking the solution with  $\beta$ -naphthalene-sulphonic chloride (2 mols.) dissolved in ether and 2 mols. more of the alkali. The lactone precipitated from its sodium salt by acid, crystallises from 50% alcohol in small rectangular plates, m. p. 143—144° (corr.); it dissolves easily in sodium hydroxide, but is insoluble in sodium carbonate.

3-Hydroxy-1-methyl-6-piperidone,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \\ | \qquad \qquad | \\ \text{NMe} - \text{CO} - \text{CH}_2 \end{array}$ , obtained by heating the chlorovalerolactone with aqueous methylamine in a sealed tube at 100°, is a thick, colourless oil, b. p. 193—195°/13 mm. It is characterised by forming the  $\beta$ -naphthalenesulphonamino-compound,  $\text{C}_{16}\text{H}_{17}\text{O}_4\text{NS}$ , crystallising in very small hexagonal plates, m. p. 82—83°.

The dilactone,  $\begin{array}{c} \text{O} \qquad \qquad \text{CO} \\ | \qquad \qquad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \\ | \qquad \qquad | \\ \text{O} \qquad \qquad \text{CO} \end{array}$ , derived from  $\gamma$ - $\delta$ -dihydroxypropylmalonic acid, was isolated in small quantity from the product of the hydrolysis of ethyl chlorovalerolactonecarboxylate. If, however, the sodium salt in alcohol is heated in a closed tube at 100° for four hours, and the residue, left after evaporation of the alcohol, boiled with hydrochloric acid, a 14% yield of the dilactone is obtained; it forms colourless prisms, m. p. 179—180° (corr.). An ester cannot be prepared by heating it with an alcoholic solution of hydrogen chloride, nor is it soluble in alkali carbonates although it is easily soluble in alkali hydroxides.  $\gamma$ - $\delta$ -Dihydroxypropylmalonamide, obtained by heating the dilactone in a methyl alcohol solution of ammonia for twenty minutes, crystallises in slender prisms, m. p. 168—169° (corr.). That Traube and Lehmann's amide (m. p. 140°, *loc. cit.*) was impure is proved by the fact that both the dilactone and ethyl  $\delta$ -hydroxy- $\gamma$ -valerolactonecarboxylate give the same *bisphenylhydrazide*,  $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$ , crystallising in colourless needles, m. p. 214° (corr. decomp.).

The dilactone,  $\begin{array}{c} \text{O} \qquad \qquad \text{CO} \\ | \qquad \qquad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CBr} \\ | \qquad \qquad | \\ \text{O} \qquad \qquad \text{CO} \end{array}$ , of  $\alpha$ -bromo- $\gamma$ - $\delta$ -dihydroxypropylmalonic acid, prepared by heating a solution of the parent di-lactone in hydrobromic acid and bromine (2.2 mols.) in a sealed tube at 70° for one hour, crystallises from alcohol in hexagonal plates, m. p. 186—187° (corr.). When, however, the dilactone is heated with 4.4 mols. of bromine at 85° for four to five hours, *aa*- $\delta$ -tribromo- $\gamma$ -valerolactone,  $\begin{array}{c} \text{CH}_2\text{Br} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CBr}_2 \\ | \qquad \qquad | \\ \text{O} \qquad \qquad \text{CO} \end{array}$ , is the product obtained, crystallising from aqueous alcohol in aggregates of needles, m. p. 84—85°.

W. R.

**Desmotropic Forms of Ethyl Acetoacetate at Low Temperatures.** HANS STOBBE (*Annalen*, 1907, 352, 132—146).—By working at low temperatures (−78° to −64°) and using the characteristic

red coloration which is obtained with ferric chloride when a definite quantity of the ketonic form of ethyl acetoacetate has changed into the enolic form, it has been possible to show that the velocity with which the ketonic form changes into the enolic is greatest in amyl alcohol, becoming smaller in the following alcohols in the order given: butyl, ethyl, methyl. For example, the red coloration appears in the case of amyl alcohol in thirty-nine secs., and in the case of methyl alcohol in fifty-six secs. after the addition of equal quantities of the ester to equal volumes of the respective alcoholic solutions at  $-78^{\circ}$  containing ferric chloride in equal concentration. Since methyl alcohol possesses the greatest, and amyl alcohol the smallest, dielectric constant, it is obvious that the velocity of the change of the ketonic into the enolic form is greatest in the least dissociating medium. This result is contrary to that usually observed, with the one exception discovered by Dimroth (Abstr., 1905, i, 98). It is further shown, in agreement with Traube (Abstr., 1896, i, 593), but in contradiction to Brühl (Abstr., 1905, i, 407), that the proportion of the enolic form present is greater in alcoholic solutions than in the undissolved ester. W. H. G.

**Determination of the Molecular Weight of Ethyl Acetoacetate in Freezing Chloroform.** HANS STOBBE and ERNST MÜLLER (*Annalen*, 1907, 352, 147—151).—The apparatus employed was a slightly modified form of the ordinary Beckmann's apparatus. The constant for chloroform, m. p.  $-62^{\circ}$ , using ethyl benzoate as the solute, was found to be 499. The mol. weight found for ethyl acetoacetate showed it to be unimolecular in freezing chloroform. The authors therefore consider it probable that the ester is also unimolecular in alcoholic solutions at  $-78^{\circ}$ , and that the slow rate with which the ketonic form of the ester changes into the enolic form at this temperature is not due to the formation of associated molecules, but merely to the low temperature (compare preceding abstract). W. H. G.

**New Synthesis of Ethyl  $\gamma$ -Chloroacetoacetate.** M. PICHA [completed by RICHARD DOHT and S. WEISL] (*Monatsh.*, 1906, 27, 1245—1249).—The action of aluminium amalgam on ethyl chloroacetate in presence of traces of alcohol leads with development of heat to the formation of ethyl  $\gamma$ -chloroacetoacetate, ethyl alcohol, and hydrogen chloride; the temperature of the reaction must not be allowed to rise above  $120^{\circ}$ . The  $\gamma$ -chloroacetoacetate is isolated in the form of its copper derivative, m. p.  $163^{\circ}$  (corr.) ( $168^{\circ}$ : Lespieau, Abstr., 1899, i, 243), from which it is obtained by heating with dilute sulphuric acid. G. Y.

**Preparation of  $\beta\beta$ -Disubstituted Glycidic Acids.** GEORGE DARZENS (D.R.-P. 174279).—Disubstituted glycidic acids having the general formula  $\begin{array}{c} \text{CRR}' \\ | \\ \text{O} \end{array} \text{---} \text{CH} \cdot \text{CO}_2\text{H}$  are readily obtained by condensing a ketone with a halogenated ethyl acetate in the presence of an alkaline reagent and then hydrolysing the resulting ester.

A mixture of methyl nonyl ketone and ethyl chloroacetate was treated with alcoholic sodium ethoxide; *ethyl methylnonylglycidate*

thus obtained was distilled under reduced pressure, b. p. 165—170°/16 mm. *Ethyl p-tolylmethylglycidate* (b. p. 160—164°/16 mm.) and *ethyl benzylmethylglycidate* (b. p. 175—180°/16 mm.) were obtained respectively from *p*-tolyl methyl ketone and benzyl methyl ketone.

G. T. M.

**Disubstituted Ethyl Acetoacetates and Malonates.** HANS MEYER (*Monatsh.*, 1906, 27, 1083—1096. Compare Abstr., 1906, i, 137, 358).—It has been shown previously that whilst methyl dimethyl- and methylethyl-malonates are converted into the corresponding diamides by the action of aqueous ammonia, methyl diethyl- and ethyl dimethyl-malonates remain unchanged. The action of ammonia on a number of other compounds of similar structure has been investigated with the object of throwing light on the relation of the stability of the system  $CR'R''R'''\cdot CO_2Alk$  to the nature of the groups  $R'$ ,  $R''$ , and  $R'''$ .

Ethyl diethylacetoacetate remains unchanged when shaken with aqueous ammonia, but under the same conditions methyl dimethyl-, ethyl methylethyl-, and ethyl dimethyl-acetoacetates yield the corresponding amides.

Dimethylacetoacetamide,  $COMe\cdot CMe_2\cdot CO\cdot NH_2$ , m. p. 120—121°, crystallises from water or methyl alcohol.

Methylethylacetoacetamide,  $COMe\cdot CMeEt\cdot CO\cdot NH_2$ , separates from water in compact crystals, m. p. 123—124°.

The preparation described as commercial ethyl dimethylacetoacetate is usually the methyl ester (compare Peters, Abstr., 1891, 1097) which has the hydrolysis constant,  $k=2.25$  at 25° (Goldschmidt and Oslan, Abstr., 1900, i, 373); the ethyl ester which must be prepared in two distinct stages, the intermediate ethyl methylacetoacetate being carefully fractionated, has the hydrolysis constant,  $k=0.75$  at 25°.

Methyl diethylacetoacetate is hydrolysed partially by aqueous ammonia, but does not form the amide. On the other hand, methyl and ethyl ethylacetoacetates react with aqueous ammonia, forming the amide in a few hours, and ethyl benzylacetoacetate undergoes the reaction in two days, forming the amide, whilst methyl benzylacetoacetate, m. p. 291—293° (corr.), dissolves only in aqueous ammonia in six days, the product obtained on evaporation being identical with benzylmethylacetamide, m. p. 109°, prepared by the action of thionyl chloride and ammonia on benzylmethylacetic acid, m. p. 275—277°.

Ethyl diallylmalonate does not react with aqueous ammonia; the *methyl ester*, b. p. 235° (corr.), which is obtained on boiling the acid with methyl alcohol and sulphuric acid as an oil having an odour of pears, dissolves slowly in ammonia, and if evaporated after five days yields *diallylmalonamide*,  $C(CH_2\cdot CH:CH_2)_2(CO\cdot NH_2)_2$ , m. p. 201—202°; this gives the biuret reaction, decolorises potassium permanganate in sodium carbonate solution, and yields ammonia when treated with cold aqueous potassium hydroxide.

Ethyl methylpropylmalonate does not react with ammonia in aqueous solution; the *methyl ester*, b. p. 206—209°, yields *methylpropylmalonamide*, m. p. 182°, ammonium methylpropylmalonate, and *ethyl methylpropylmalonamate* (?), m. p. 67°, subliming.

Whilst ethyl benzylmethylmalonate does not react with aqueous ammonia, ethyl benzylmalonate rapidly forms the amide, m. p. 225°.

*Methyl benzylmethylmalonate* crystallises in large plates, m. p. 63°, has a pleasant odour, and is converted by ammonia into *benzylmethylmalonamide*, which crystallises in needles, m. p. 202—203°, and gives the biuret reaction.

*Methyl cetylmalonate*, m. p. 44°, crystallises from ether and does not react with ammonia.

Methyl triphenylacetate, m. p. 182°, is formed quantitatively by the action of diazomethane on the acid; it does not react with ammonia in aqueous solution at 120°, but when heated at 180° explodes.

The action of aqueous ammonia on ethyl diethylmalonate for several months leads to the formation of a clear solution; this on evaporation leaves a syrupy residue, which when heated yields ethyl diethylmalonate and ammonium diethylmalonate in accordance with the equation:  $2\text{CO}_2\text{Et} \cdot \text{C}(\text{Et})_2 \cdot \text{CO}_2\text{NH}_4 = \text{C}(\text{Et})_2(\text{CO}_2\text{Et})_2 + \text{C}(\text{Et})_2(\text{CO}_2\text{NH}_4)_2$ .  
G. Y.

**Carbon Suboxide.** II. OTTO DIELS and GEORG MEYERHEIM (*Ber.*, 1907, 40, 355—363. Compare *Abstr.*, 1906, ii, 227).—It has been found that carbon suboxide is formed when methyl, benzyl, or phenyl malonates, as well as ethyl malonate, are heated with phosphoric oxide; ethyl oxalacetate and ethyl methanetricarboxylate also yield it. The most interesting reaction studied, however, is that of malonic acid itself, as in addition to its giving acetic acid and carbon dioxide (the known fission of an *aa*-dicarboxylic acid), it also gives a 10—12% yield of carbon suboxide when heated at 140—150°, and serves as the most convenient method of preparing the compound. A description of the apparatus is given. Carbon suboxide has m. p. -107° and  $D_4^{20}$  1.11.

When conducted through a heated constricted tube, carbon suboxide forms a characteristic metallic mirror like that given by arsine. At low temperatures the suboxide is stable, and the change into the dark red product at 0—15°, due to polymerisation, is hastened by traces of impurity. This polymeride or mixture of polymerides is very hygroscopic; with cold water, heat is developed, an eosin-red solution is formed, carbon dioxide being evolved at the same time. On heating the polymerised product, carbon monoxide, carbon dioxide, and carbon suboxide are obtained. Heating the suboxide to a higher temperature, or working with larger quantities, results in an evolution of carbon monoxide and dioxide; the residue, probably a complicated mixture, contains more carbon than the suboxide.

The authors consider that carbon suboxide is to be represented as a malonic anhydride,  $\text{OC}:\text{C}:\text{CO}$ , and not as the lactone of  $\beta$ -hydroxypropionic acid,  $\text{C} \begin{smallmatrix} \diagup \text{C} \\ \diagdown \text{CO} \end{smallmatrix} \text{O}$  (Michael, *Abstr.*, 1906, ii, 442).

Dehydracetic acid is formed when acetic anhydride is heated with phosphoric oxide.  
W. R.

**Action of Reducing Agents on Cholic Acid.** ALFRED EKBOM (*Zeitsch. physiol. Chem.*, 1906, 50, 97—124).—Vahlen's conclusion (*Abstr.*, 1897, i, 648) that deoxycholic acid is formed by the reduction of

cholic acid with alkaline reducing agents has not been confirmed; in all cases unaltered cholic acid was obtained. It is probable that the acid used by Vahlen contained a reduction product. When heated with acetic acid or with zinc dust and acetic acid, cholic acid yields a mixture of mono- and diacetyl derivatives, which may be obtained as a flocculent precipitate on the addition of water. These acetyl derivatives do not give Mylius's reaction.

J. J. S.

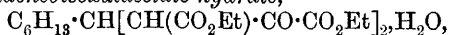
**The Pyran Series.** IV. H. GAULT (*Bull. Soc. chim.*, 1907, [iv], 1, 40—48. Compare this vol., i, 148).—*Ethyl ethylidenebisoxalacetatehydrate*,  $\text{CHMe}[\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CO}_2\text{Et}]_2\cdot\text{H}_2\text{O}$ , m. p. about  $112^\circ$ , obtained by condensing acetaldehyde with ethyl oxalacetate as already described (*loc. cit.*), crystallises from dilute alcohol, and gives a coloration with ferric chloride on warming. The anhydrous ester could not be isolated. The *monophenylhydrazone*, m. p.  $135^\circ$ , crystallises from alcohol; the *monosemicarbazone*, m. p.  $185^\circ$ , crystallises from boiling water. Cold sulphuric acid hydrolyses the hydrated ester, forming

*ethylidenebisoxalacetic dianhydride*,  $\text{CHMe}\left(\text{CH}\begin{array}{c} \text{CO}\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{CO}\cdot\text{O} \end{array}\right)_2$ , which forms

a very soluble hydrate with cold water, and on warming with water decomposes, evolving 2 mols. of carbon dioxide and forming diketomethylpimelic acid; a similar decomposition of the dianhydride is brought about by alcohol, whilst aniline furnishes a dianilide which decomposes on contact with water, forming the dianilide of diketomethylpimelic acid. Boiling dilute mineral acids convert the hydrated ester directly into diketomethylpimelic acid.

*Ethyl propylidenebisoxalacetate hydrate*, m. p.  $118^\circ$ , is prepared similarly from propaldehyde and ethyl oxalacetate. The anhydrous ester could not be isolated. The *monophenylhydrazone*, m. p.  $129^\circ$ , crystallises from dilute alcohol, and the *monosemicarbazone*, m. p.  $160^\circ$ , separates in crystals from the same solvent. *Propylidenebisoxalacetic dianhydride*, m. p. about  $170^\circ$  (decomp.), obtained on treating the hydrated ester with cold sulphuric acid and with cold water, yields the corresponding unstable tetra-acid, which rapidly decomposes, yielding diketoeethylpimelic acid. With alcohol the dianhydride yields ethyl diketoeethylpimelate and with aniline the corresponding dianilide, which readily decomposes, forming the dianilide of diketoeethylpimelic acid. The latter acid is produced in minute quantities when the hydrated ester is boiled with dilute mineral acids.

*Ethyl heptylidenebisoxalacetate hydrate*,



m. p.  $115^\circ$ , obtained from heptaldehyde (ænanthaldehyde) and ethyl oxalacetate, crystallises from dilute alcohol, and when heated at  $110^\circ$  decomposes without yielding the anhydrous ester. The *monophenylhydrazone*, m. p.  $115$ — $116^\circ$ , crystallises from dilute alcohol, and the *monosemicarbazone*, m. p.  $153^\circ$ , crystallises from ether or from a mixture of this solvent with light petroleum. *Heptylidenebisoxalacetic dianhydride*, m. p.  $89$ — $90^\circ$ , obtained by the action of cold sulphuric acid on the hydrated ester, is less stable than its lower homologues, furnishes a very unstable hydrate with cold water, and is decomposed by warm water, forming diketohexylpimelic acid, whilst alcohol and

aniline furnish similarly the diethyl ester and the dianilide of the same acid respectively. Diketohexylpimelic acid is not produced when ethyl heptylidenebisoxalacetate hydrate is boiled with dilute mineral acids.

T. A. H.

**The Action of Aluminium Alkylloxides on Aldehydes. Complex Ethereal Condensations considered as a New Form of Aldehyde Condensation.** V. E. TISTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1906, 38, ii, 355—418).—A historical survey of previous work on condensation is given. By the prolonged action of a small quantity of dry aluminium ethoxide on dry paraformaldehyde at the ordinary temperature, a mixture of ethyl and methyl formates are formed. Aluminium or magnesium methoxide with the same aldehyde yield chiefly methyl formate together with a little formic acid and possibly the compound  $\text{Mg}[\text{O}\cdot\text{CH}(\text{OMe})_2]_2$ . Benzaldehyde behaves similarly, benzyl benzoate being the chief product; the main course of the reaction being  $2\text{CH}_2\text{O} = \text{H}\cdot\text{CO}_2\cdot\text{CH}_3$ ;  $2\text{C}_6\text{H}_5\cdot\text{CHO} = \text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ . The following substances are formed by the interaction of aluminium ethoxide and acetaldehyde. Ethyl acetate, aldol, crotonaldehyde, ethyl alcohol, ethyl  $\beta$ -hydroxybutyrate and its acetyl derivative, mono- and diacetyl derivatives of  $\beta\delta$ -dihydroxybutane, crotonic acid, and possibly also para-acetaldehyde and acetal. The main product is, however, ethyl acetate, but in the presence of water considerable quantities of aldol are also formed. As the amount of aluminium ethoxide employed is increased, the amount of aldehyde remaining unchanged diminishes, whilst the amount of ethyl acetate formed increases until the mixture contains 15% of ethoxide, after which any further addition of the latter diminishes the yield of ester. The temperature at which the experiment is performed exerts but little influence on the course of the reaction. About 80% of the ethoxide remains unchanged, the rest being converted into aluminium hydroxide, or, possibly, into more complex alkoxide compounds of aluminium. Z. K.

**Preparation of Aldehydes containing a Secondary Alkyl Group.** GEORGES DARZENS (D.R.-P. 174239. Compare preceding abstract).—Aldehydes having the general formula  $\text{CHRR}'\cdot\text{CHO}$  can be obtained from the  $\beta\beta$ -substituted glycidic acids by heating these substances either alone or in the presence of water.

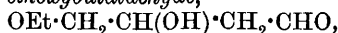
*Methylnonylacetaldehyde*,  $\text{C}_9\text{H}_{19}\cdot\text{CMe}\cdot\text{CHO}$ , b. p. 119—122°/16 mm., obtained by heating in a vacuum at 120° the glycidic acid produced from methyl nonyl ketone and ethyl chloroacetate, furnishes a semicarbazone, m. p. 101—102°.

*p*-Methylhydratropaldehyde, b. p. 107—108°/19 mm., was obtained by heating *p*-tolylmethylglycidic acid with water at 150°; it furnishes a semicarbazone, m. p. 159—160°. Ethyl benzylmethylglycidate when hydrolysed yields an acid which when heated at 140° in a vacuum gives rise to  $\beta$ -phenyl- $\alpha$ -methylbutaldehyde,  $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CHO}$ , b. p. 129—130°/19 mm., it yields a semicarbazone, m. p. 70—72°. Many other aldehydes of this series have been prepared in a similar manner.

G. T. M.



**Condensation Product of Ethoxyacetaldehyde with Acetaldehyde.** BRUNO EISSLER and ALEXANDER POLLAK (*Monatsh.*, 1906, 27, 1129—1144; Abstr., 1905, i, 683).—Ethoxyacetaldehyde condenses with acetaldehyde in presence of anhydrous potassium carbonate, forming  $\beta$ -hydroxy- $\gamma$ -ethoxybutaldehyde,



which is obtained as a yellow, viscid oil, b. p. 122—125°/18 mm., gives the aldehyde reactions, and when oxidised with alkaline potassium permanganate yields ethoxyacetic and oxalic acids. When heated with anhydrous sodium acetate at 120—130°, the aldol yields  $\gamma$ -ethoxycrotonaldehyde,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CHO}$ , which forms a transparent liquid, b. p. 157°, and combines with 1 mol. of bromine. The aldol is oxidised by potassium permanganate in neutral solution, forming  $\beta$ -hydroxy- $\gamma$ -ethoxybutyric acid,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which is isolated in the form of its calcium salt,  $(\text{C}_6\text{H}_{11}\text{O}_4)_2\text{Ca}$ .

The glycol,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 210°/760 mm., is prepared by reduction of the aldol with aluminium amalgam.

G. Y.

**Fermentability of Methylglyoxal.** PAUL MAYER (*Biochem. Zeitsch.*, 1907, 2, 435—437. Compare Büchner and Meisenheimer (*Ber.*, 1906, 39, 3201).—Methylglyoxal in 1, 2, or 5% aqueous solution is not fermented by living yeast cells.

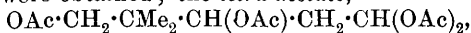
J. J. S.

**Unimolecular and Termolecular Glyoxal.** CARL HARRIES and PAUL TEMME (*Ber.*, 1907, 40, 165—172).—A unimolecular glyoxal,  $\text{CHO}\cdot\text{CHO}$ , is obtained when commercial glyoxal (Debus's polyglyoxal) is heated with phosphoric oxide, and the product collected in a vessel surrounded with a mixture of solid carbon dioxide and ether or with liquid air, care being taken to prevent the admission of atmospheric moisture. It forms golden yellow crystals, m. p. 15° and b. p. 51°/776 mm. or 50°/742 mm. Its vapour has an intense green colour, and condenses to a green liquid, which changes to yellow on cooling. The odour is similar to that of formaldehyde, and the vapour burns with a violet flame. Even at low temperatures it polymerises to an insoluble *paraglyoxal*, and in the presence of small amounts of water this change occurs instantaneously. The glyoxal dissolves in an excess of water, and the molecular weight determined by the cryoscopic method indicates that in such a solution the aldehyde is still unimolecular.

A termolecular glyoxal is obtained when cinnamaldehyde ozonide is warmed with water at 60—70°. It dissolves readily in water, and may be obtained from the aqueous solution by evaporating at 25—30° after the removal of benzaldehyde, benzoic acid, &c. If the temperature is raised above 30° a polymeric modification resembling the commercial product is obtained. The termolecular compound forms a yellow, amorphous mass insoluble in ether; it changes colour at 175° and decomposes at about 200°. Its aqueous solution is distinctly acid, and also reduces Fehling's solution. Its aqueous or alcoholic solutions yield derivatives of the unimolecular glyoxal; the *disemicarbazone*,  $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$ , crystallises in rhombohedral prisms; the phenylosazone has

m. p. 167—168°; the diphenylosazone, 203°, and the phenylmethyl-osazone, 221°. The *tetraethyl acetal*,  $\text{CH}(\text{OEt})_2 \cdot \text{CH}(\text{OEt})_2$ , is a mobile liquid, b. p. 88—89°/14 mm., sparingly soluble in water. J. J. S.

**Preparation of an Unsaturated Aldehyde from Formylisobutacetaldol and an Attempt to Condense Formylisobutacetaldol with Formaldehyde.** HANS BUSCH and KLARA GOLDENTHAL (*Monatsh.*, 1906, 27, 1157—1166. Compare Weis, *Abstr.*, 1905, i, 17; Schachner, *ibid.*, 171).—In one experiment the action of acetic anhydride and sodium acetate on formylisobutacetaldol led to the formation of only a small amount of the unsaturated  $\delta$ -acetoxy-aldehyde,  $\text{OAc} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH} : \text{CH} \cdot \text{CHO}$ , which is obtained as a yellow oil, b. p. 83°/16 mm., reduces ammoniacal silver solutions, and forms an *additive* product with bromine,  $\text{C}_9\text{H}_{14}\text{O}_3\text{Br}_2$ . In another experiment two products were obtained; the *tetra-acetate*,

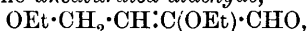


which forms a colourless, mobile liquid, b. p. 83—90°/12 mm., and the *diacetate*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OAc})_2$ , which is a slightly yellow, more viscid liquid, b. p. 137—138°/12 mm. When heated with potassium carbonate in an atmosphere of carbon dioxide in a reflux apparatus at 110—115°, the aldol yields the *acid*,  $\text{C}_7\text{H}_{12}\text{O}_3$ , which is obtained in yellow crystals, m. p. 104—105°, and forms an *additive* compound with bromine; the *calcium* salt,  $(\text{C}_7\text{H}_{11}\text{O}_3)_2\text{Ca}$ , forms white crystals. The corresponding unsaturated *aldehyde*,  $\text{C}_7\text{H}_{12}\text{O}_2$ , is prepared by heating the aldol with potassium carbonate in an atmosphere of carbon dioxide in a sealed tube at 110°; it crystallises in slender, yellow needles, m. p. 49—50°, sublimes at 65°/15 mm., gives the aldehyde reactions, forms an *additive* compound with bromine, and is oxidised on exposure to air yielding the preceding acid.

The condensation of the aldol with formaldehyde in potassium carbonate solution leads to the formation of  $\beta\beta$ -dimethyltrimethylene glycol (Just, *Abstr.*, 1896, i, 403). G. Y.

**Preparation of the Corresponding Aldol from Ethoxyacetaldehyde.** WALTER FRIED (*Monatsh.*, 1906, 27, 1251—1258. Compare Klüger, *Abstr.*, 1905, i, 683; Eissler and Pollak, this vol., i, 183).—The action of potassium carbonate on ethoxyacetaldehyde and isobutaldehyde in concentrated aqueous solution leads to the formation of a mixture of aldols, b. p. 112—115°/18 mm.

The *aldol* of ethoxyacetaldehyde [ $\beta$ -hydroxy- $\alpha$ -diethoxybutaldehyde],  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OEt}) \cdot \text{CHO}$ , prepared by the action of potassium carbonate on ethoxyacetaldehyde in concentrated aqueous solution cooled by ice, is obtained as a mobile, transparent liquid, b. p. 115—117°/18 mm., which gives the aldehyde reactions, and when heated with anhydrous sodium acetate in a current of carbon dioxide at 120—130° yields the *unsaturated aldehyde*,



b. p. 148° This reduces ammoniacal silver solutions, and forms in ethereal solution an *additive* compound with two atoms of bromine.

G. Y.

**Peroxide of Methyl Ethyl Ketone.** PASTUREAU (*Compt. rend.*, 1907, 144, 90—93).—*Methyl ethyl ketone peroxide*,  $C_8H_{16}O_4$ , obtained as a thick, colourless oil when methyl ethyl ketone is treated with hydrogen peroxide in the presence of sulphuric acid, has  $D^{15}_D$  1.042, possesses an agreeable odour, is stable at the ordinary temperature, but very explosive when heated above  $100^\circ$ , and cannot therefore be distilled even under reduced pressure. When distilled with steam under reduced pressure, it yields a mixture of constant b. p.  $48^\circ/80$  mm. or  $56^\circ/130$  mm. It is completely reduced to methyl ethyl ketone by the action of nascent hydrogen in the cold; explodes violently when placed in contact with concentrated sulphuric acid, and is partially transformed into the original ketone and acetylmethylcarbinol by the action of dilute sulphuric acid. It yields the tetrabromo-derivative of methyl ethyl ketone,  $CH_2Br \cdot CO \cdot CH_2 \cdot CBr_3$ , when treated with bromine. The acid mother liquor from which the peroxide is separated in the above preparation contains acetylmethylcarbinol,  $CHMeAc \cdot OH$ , which yields the yellow osazone, m. p.  $243^\circ$ , and the blood-red osotetrazone (von Pechmann, *Abstr.*, 1888, 1287). M. A. W.

**Transformation of Aldehydes into Ketones by Means of Diazomethane.** FRITZ SCHLOTTERBECK (*Ber.*, 1907, 40, 479—483).—The author has studied the formation of ketones from aldehydes by means of diazomethane. Furodiazoles are probably formed as intermediate products, thus:  $R \cdot CHO + CH_2N_2 \rightarrow R \cdot CH \begin{smallmatrix} O-N \\ | \\ CH_2 \cdot N \end{smallmatrix} \rightarrow R \cdot CO \cdot CH_3 + N_2$ .

Methyl hexyl ketone was obtained from heptaldehyde, acetophenone from benzaldehyde, and methyl isobutyl ketone from isovaleraldehyde, the ketones having been identified in each case by means of their semicarbazones. A. McK.

**New Synthesis of  $\alpha$ -Diketones.** LEO TSCHUGAEFF (*Ber.*, 1907, 40, 186—187).—Diacetyl and dipropionyl are formed by the action of magnesium methyl and magnesium ethyl bromides respectively on vinylideneoxanilide (von Pechmann, *Abstr.*, 1898, i, 135).

*Nickel diethylglyoximine*,  $Ni(NO \cdot CET \cdot CET \cdot N \cdot OH)_2$ , has also been prepared, and crystallises in orange-red needles. G. Y.

**Solubility of Sucrose in Water in Presence of Invert-sugar.** HENRI PELLET and CH. FRIBOURG (*Chem. Centr.*, 1906, ii, 1722; from *Bull. Assoc. Chim. Sucr. Dist.*, 24, 304—315).—Experiments have shown that a saturated solution of sucrose can dissolve invert-sugar and that a saturated solution of crystalline sucrose can after inversion dissolve sucrose. In a saturated solution containing equal weights of sucrose and invert-sugar, 1 part of water holds 3.5 of dry substances in solution at  $29^\circ$ , whilst under similar conditions in a solution of pure sucrose, 2.18—2.22 are dissolved by 1 part of water. A solution of invert-sugar saturated with sucrose at  $29^\circ$  contains 69 parts of sucrose per 100 of invert-sugar, and 3.9 of dry substances are dissolved by 1 part of water.

The viscosity of a saturated solution of sucrose increases in proportion to the quantity of invert-sugar contained in it. E. W. W.

**Cellulose.** HERMANN WICHELHAUS and WALTHER VIEWEG (*Ber.*, 1907, 40, 441—443).—The view that in mercerising cellulose only the cuticle of the fibre is removed (compare Fränkel and Friedlander, *Mitt. K. K. Techn. Gewerbemus., Wien*, 1898, 326) is incorrect. By comparing the esters of nitric and benzoic acids derived from the natural and mercerised cellulose the change is shown to be chemical in character. The yield of benzoate, obtained from 100 parts of cellulose by the action of benzoyl chloride and sodium hydroxide, is :

	Before.	After mercerising.
Cotton wool .....	112	139
Flax .....	121	137

Again, although the % of nitrogen in the nitrates derived from cotton, cotton wool, or flax both before and after treatment is practically constant (13%), the products are chemically different, as the portion soluble in a mixture of alcohol and ether is increased by mercerisation. W. R.

**Constituents of Lignocelluloses which Yield Furfuraldehyde and Methylfurfuraldehyde.** KONRAD FROMHERZ (*Zeitsch. physiol. Chem.*, 1906, 50, 209—240).—Lignocellulose has been prepared from the wood of the aspen (*Populus tremula*) by Lange's method, the yield being 55%. Certain of the constituents which yield furfuraldehyde and methylfurfuraldehyde are dissolved when heated with water under pressure at 150°. These constituents probably resemble the "furoids" obtained by Cross and Bevan from straw. The mannans and galactans are also dissolved during this process. Dextrose could not be detected, and lævulose was present in small quantities only.

Part of the furfuraldehyde is derived from the cellulose of the wood, and is formed mainly from oxidised groups. The cellulose also yields methylfurfuraldehyde, whereas cellulose from filter paper, when heated with water under pressure, yields only the minutest traces of this aldehyde.

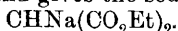
The yields of furfuraldehyde from lignocellulose or cellulose and the yield of methylfurfuraldehyde from rhamnose decrease with the process of heating, whereas the yields of methylfurfuraldehyde from the lignocellulose and cellulose of the wood increase, up to a certain point, on heating with water. J. J. S.

**Some Reactions of Sodamide.** LOUIS MEUNIER and E. DESPARET (*Compt. rend.*, 1907, 144, 273—275).—The action of sodamide on polyhaloid derivatives of the hydrocarbons is very similar to that of alcoholic potash. With ethylene dibromide, it gives acetylene. With chloroform, the reaction is slower in commencing, but becomes explosive, bromoform reacts similarly and even more violently; if, however, powdered sodamide is added in small quantities to excess of chloroform and the latter warmed slightly, ammonia is

evolved and a mixture of sodium chloride and cyanide precipitated. This reaction can be expressed by an equation  $\text{CHCl}_3 + 4\text{NaNH}_2 = \text{NaCN} + 3\text{NaCl} + 3\text{NH}_3$ , precisely similar to that for the preparation of the carbylamines. Moreover, chloroform diluted with anhydrous benzene, when heated with aniline (1 mol.) and sodamide (3 mols.), gives phenylcarbylamine, thus:  $\text{NH}_2\text{Ph} + \text{CHCl}_3 + 3\text{NaNH}_2 = 3\text{NaCl} + 3\text{NH}_3 + \text{PhNC}$ .

Sodamide can be employed for the preparation of sodium derivatives (compare Alexéeff, *Journ. Russ. Phys. Chim. Soc.*, 1902, **34**, 526; Titherley, *Proc.*, 1902, **18**, 186; Haller, *Abstr.*, 1905, **i**, 214; and Claisen and Feyerabend, *Abstr.*, 1905, **i**, 286). Aniline, diphenylamine, and diazoaminobenzene readily give sodium derivatives. Addition of diphenylamine in ethereal solution to benzyl chloride in the same solvent containing a slight excess of sodamide causes a vigorous reaction with evolution of ammonia and formation of diphenylbenzylamine.

Ethyl malonate, when treated in cold benzene solution with sodamide, forms a transparent jelly probably consisting of the additive compound,  $\text{NH}_2\cdot\text{C}(\text{OEt})(\text{ONa})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which, when heated, evolves ammonia and gives the sodium derivative,



When anhydrous acetaldehyde is added to sodamide covered with dry ether, a white, crystalline precipitate, stable in dry air, is formed, whilst ammonia is evolved and combines with the aldehyde, forming aldehyde-ammonia. The evolution of ammonia can only be explained by the dehydration of the aldehyde and formation of the sodium derivative of the corresponding imine,  $\text{CH}_3\cdot\text{CHO} + 2\text{NaNH}_2 = \text{CH}_3\cdot\text{CH:NNa} + \text{NaOH} + \text{NH}_3$ . The crystalline precipitate is therefore probably a mixture of aldehyde-ammonia and the sodimino-derivative. This explanation agrees with Delepine's work on aldehyde-ammonia (*Abstr.*, 1898, **i**, 462). E. H.

**Relative Stability of some Metalamine Compounds.** LEO TSCHUGAEFF (*Ber.*, 1907, **40**, 173—181. Compare *Abstr.*, 1904, **i**, 478; 1905, **i**, 865; 1906, **i**, 814).—The capacity of a number of primary, secondary, and tertiary amines to form complex compounds with copper, silver, platinum, and nickel salts in *N*/10 solution has been investigated qualitatively and found to diminish as the number of *N*-hydrogen atoms substituted is increased.

On addition of methyl-, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, isobutyl-, *tert*-butyl-, *sec*-butyl-, *n*-amyl-, isoamyl-, *tert*-amyl-, or vinyl-amine to aqueous copper chloride, copper hydroxide is precipitated and dissolves on addition of an excess of the amine, forming the characteristic blue solution; with camphylamine, fenchylamine, or thujylamine the addition of alcohol is necessary for complete solution of the blue compound, which may be extracted with ether, chloroform, or benzene. The red compounds,  $(\text{Su})_2\text{Cu}_2\text{a}$ ,  $[\text{Su} = \text{C}_2\text{H}_4(\text{CO})_2\text{N}$ ; **a** = an amine], is formed on addition of succinimide to the blue solutions.

Under the same conditions, secondary amines such as diethyl-, di-*n*-propyl-, di-isobutyl-, di-isoamyl-, and dibenzylamine dissolve only small quantities of the precipitated copper hydroxide, whilst this is

completely insoluble in tertiary amines: trimethyl-, triethyl-, tri-*n*-propyl-, triisobutyl-, and triisoamyl-amines, which do not form complex metallic compounds in either aqueous or alcoholic solution. On prolonged contact with trimethylamine, copper hydroxide is converted into the black oxide.

The aliphatic amines react in the same manner with dilute silver nitrate, forming a black precipitate of silver oxide which is dissolved by an excess of the primary amines. Camphylamine forms with silver oxide a crystalline compound which is soluble in alcohol.

The primary aliphatic amines form complex compounds with silver succinimide with development of heat (compare Landsberg, Abstr., 1883, 476). *Benzylamine silver succinimide*, (Su)Ag, CH<sub>2</sub>Ph·NH<sub>2</sub>, crystallises from alcohol in nacreous leaflets, and commences to become brown in a sealed capillary tube at 160°, m. p. about 190° (decomp.).

Silver oxide precipitated by addition of secondary or tertiary amines to dilute silver nitrate is dissolved by an excess of the secondary amines to a less extent than is copper hydroxide, whilst it is almost insoluble in excess of the tertiary amines in which even silver chloride is barely soluble.

The behaviour of silver salts with pyridine and quinoline bases is completely analogous with that of the copper salts (Jørgensen, Abstr., 1886, 857).

Whilst the action of primary aliphatic amines on potassium platinochloride in aqueous solution leads to the formation of platoso-diamine chlorides and platoso-diamine platinosochlorides (Jørgensen, *loc. cit.*), tertiary amines precipitate metallic platinum slowly at the ordinary temperature or quickly on boiling, trimethylamine yielding an odour of acetaldehyde.

With nickel salts and aliphatic amines there have been obtained in addition to the succinimide compounds derived from primary amines, (Su)<sub>2</sub>Ni<sub>2</sub>a (Abstr., 1906, i, 814), only an unstable derivative of dimethylamine.

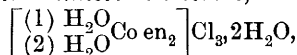
[With J. SURENJANZ.]—Tetramethylethylenediamine does not form complex compounds with nickel salts (compare Werner, Abstr., 1899, i, 856; Kurnakoff, Abstr., 1900, i, 209).

The difference of the behaviour of the pyridine bases from that of the aliphatic secondary amines is discussed and considered to support Euler's views on the formation of complex ions (Abstr., 1904, ii, 379).

G. Y.

**Stereoisomeric Diaquodiethylenediaminecobalt Salts.** ALFRED WERNER [and, in part, G. JANTSCH] (*Ber.*, 1907, 40, 262–271).—The salts of this series are obtained initially from complex ethylenediaminecobalt compounds, which are formed by atmospheric oxidation of aqueous cobalt nitrate or sulphate in the presence of ethylenediamine, and which will be described in a future paper.

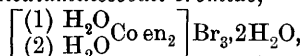
*cis-Diaquodiethylenediaminecobalt chloride*,



is obtained by triturating the preceding compounds with hydrochloric acid, saturated at 0°, or from *hydroxoquadiethylenediaminecobalt*

*bromide* in a similar manner. ("Hydroxo" indicates the hydroxyl group in direct union with the metallic atom.) This basic bromide,  $\left[ \begin{smallmatrix} \text{HO} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right] \text{Br}_2, 2\text{H}_2\text{O}$ , is precipitated in red crystals by the addition of pyridine and powdered potassium bromide to the syrup obtained by the evaporation of an aqueous solution of dinitratodiethylenediaminecobalt nitrate (*A. Lieben. Festschrift*, 211).

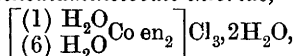
*cis-Diaquodiethylenediaminecobalt bromide*,



is obtained by the same methods as the chloride. The two salts form red crystals and are extremely soluble in water, forming solutions with an acid reaction. At  $115^\circ$  the salts lose  $4\text{H}_2\text{O}$ , the chloride forming *cis*-dichlorodiethylenediaminecobalt chloride (violetochloride) and a small quantity of the green *trans*-isomeride, whereas the bromide yields chiefly *trans*-dibromodiethylenediaminecobalt bromide (praseobromide). The *cis*-diaquo-chloride or bromide in boiling aqueous solution is converted by hydrochloric or hydrobromic acid into *trans*-dichlorodiethylenediaminecobalt chloride or the corresponding bromide, whilst potassium hydroxide converts them into *cis*-hydroxo-aquodiethylenediaminecobalt chloride (or bromide).

The configuration of the two salts is ascertained by treating them with sodium nitrite and acetic acid, whereby an unstable dinitritodiethylenediaminecobalt salt,  $[(\text{ON}\cdot\text{O})_2\text{Co en}_2]\text{X}$ , is obtained, which changes into 1:2-dinitrodiethylenediaminecobalt nitrite.

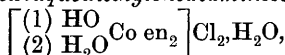
*trans-Diaquodiethylenediaminecobalt chloride*,



and the corresponding *bromide*,  $[(\text{H}_2\text{O})_2\text{Co en}_2]\text{Br}_3, 2\text{H}_2\text{O}$ , are obtained by treating 1:6-hydroxo-aquodiethylenediaminecobalt bromide (compare following abstract) with the concentrated halogen acid, or from Werner and Bräunlich's *di-isothiocyanodiethylenediaminecobalt thiocyanate* (*Abstr.*, 1900, i, 86) in the following way. An aqueous solution of the thiocyanate is heated with potassium hydroxide, cooled, and treated with hydrobromic acid; the reddish-brown precipitate of 1:6-hydroxo-aquodiethylenediaminecobalt thiocyanate is dissolved in 50% acetic acid and treated with sodium nitrite, whereby 1:6-dinitritodiethylenediaminecobalt thiocyanate is obtained, which by trituration with concentrated hydrochloric or hydrobromic acid yields the required salt. The *trans*-diaquo-chloride forms glistening, reddish-brown needles, the bromide violet-brown leaflets. Both contain  $2\text{H}_2\text{O}$ , which is lost readily. By stronger heating, the chloride is converted mainly into the dichlorovioletochloride, whilst the bromide yields only the dibromopraseobromide.

C. S.

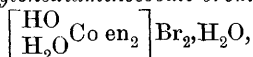
**Theory of Hydrolysis and Stereoisomeric Hydroxo-aquodiethylenediaminecobalt Salts.** ALFRED WERNER (*Ber.*, 1907, 40, 272—287).—*cis-Hydroxo-aquodiethylenediaminecobalt chloride*,



obtained by the addition of pyridine or, less suitably, of potassium

hydroxide to an aqueous solution of *cis*-diaquodiethylenediaminecobalt chloride, is a brownish-red, crystalline powder, and is reconverted into the diaquochloride by concentrated hydrochloric acid. From an aqueous solution of the substance which has been heated at 115° before solution, triethylenediaminecobalt salts and ethylenediaminecobalt salts can be obtained.

*cis*-Hydroxoquaquodiethylenediaminecobalt bromide,

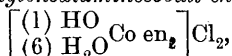


is obtained (1) like the preceding compound; (2) by treating *trans*-dichlorodiethylenediaminecobalt chloride (praseo-chloride) with concentrated potassium hydroxide and neutralising the resulting solution with cold concentrated hydrobromic acid; (3) in a similar manner from *cis*-dichlorodiethylenediaminecobalt chloride (violeo-chloride). It forms a red, crystalline powder and possesses properties similar to those of the chloride.

The *iodide*,  $\left[ \begin{array}{c} (1) \text{HO} \\ (2) \text{H}_2\text{O Co en}_2 \end{array} \right] \text{I}_2, \text{H}_2\text{O}$ , is obtained in small, brownish-red needles by treating an aqueous solution of *cis*-diaquodiethylenediaminecobalt bromide with pyridine and powdered potassium iodide.

The *dithionate*,  $\left[ \begin{array}{c} (1) \text{HO} \\ (2) \text{H}_2\text{O Co en}_2 \end{array} \right] \text{S}_2\text{O}_6$ , crystallises in slender, violet-red needles, and is prepared by adding pyridine and saturated sodium dithionate to the solution of the syrup obtained by the evaporation, after prolonged boiling, of an aqueous solution of dinitratodiethylenediaminecobalt nitrate.

*trans*-Hydroxoquaquodiethylenediaminecobalt chloride,



is obtained from aqueous *trans*-diaquodiethylenediaminecobalt chloride in pearly-bluish-red leaflets by the addition of potassium hydroxide, or, less readily, in needles by the addition of pyridine.

The *bromide*,  $\left[ \begin{array}{c} (1) \text{HO} \\ (6) \text{H}_2\text{O Co en}_2 \end{array} \right] \text{Br}_2$ , is obtained similarly, or better, by boiling an aqueous solution of the *cis*-compound for two minutes with potassium hydroxide and neutralising the well-cooled solution with hydrobromic acid. It is a light red, crystalline powder; the cryoscopic method in aqueous solution indicates the presence of three ions,  $\left[ \begin{array}{c} \text{HO} \\ \text{H}_2\text{O Co en}_2 \end{array} \right]$  and 2Br.

The *iodide*,  $\left[ \begin{array}{c} (1) \text{HO} \\ (6) \text{H}_2\text{O Co en}_2 \end{array} \right] \text{I}_2$ , is obtained in pearly reddish-brown leaflets by decomposing an aqueous solution of *trans*-diaquodiethylenediaminecobalt chloride with concentrated potassium hydroxide followed by the addition of potassium iodide.

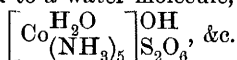
The *dithionate*,  $\left[ \begin{array}{c} (1) \text{HO} \\ (6) \text{H}_2\text{O Co en}_2 \end{array} \right] \text{S}_2\text{O}_6$ , obtained by the addition of saturated sodium dithionate to an aqueous solution of *trans*-hydroxoquaquodiethylenediaminecobalt chloride, crystallises in glistening, red needles.

The salts of the *cis*- and *trans*-hydroxoquaquodiethylenediaminecobalt

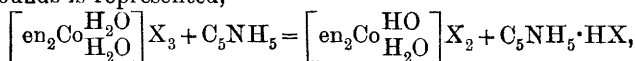


series have a faintly alkaline reaction, but do not precipitate silver oxide from silver nitrate solution or absorb carbon dioxide; mineral acids convert them into salts of the diaquo-series. They are, as a rule, sparingly soluble in water, but dissolve readily in the presence of acetic acid, forming solutions from which metallic salts precipitate the corresponding hydroxoquo-salt.

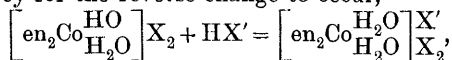
The properties of these salts of the basic diethylenediaminecobalt series, those of Pfeiffer's pyridine chromium compounds (Abstr., 1906, i, 531), and those even of Jörgensen's pentammine and tetrammine cobalt and chromium salts (Abstr., 1883, 554; 1891, 1325; 1898, ii, 226) cannot be rationally interpreted by Jörgensen's theory that the hydroxyl group is linked to a water molecule, thus:



By the author's theory the formation of hydroxoquo- from diaquo-compounds is represented,



and the tendency for the reverse change to occur,



serves to account for many of the properties of the hydroxoquo-salts.

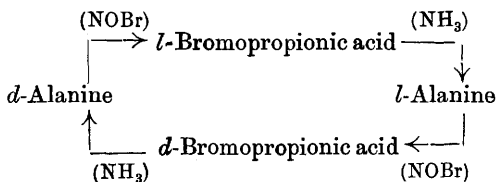
An attempt is made to explain the formation and reactions of hydroxo-salts by the aid of the ionic hypothesis. C. S.

**Synthesis of  $\alpha$ -Amino- $\gamma$ -hydroxybutyric Acid.** EMIL FISCHER and HERBERT BLUMENTHAL (*Ber.*, 1907, 40, 106—113).— *$\alpha$ -Bromo- $\gamma$ -phenoxyethylmalonic acid*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CBr}(\text{CO}_2\text{H})_2$ , obtained by the gradual addition of bromine to an ethereal solution of  $\gamma$ -phenoxyethylmalonic acid (prepared according to Perkin, Bentley, and Haworth, *Trans.*, 1896, 69, 165) separates from benzene in rhombic crystals, m. p.  $148^\circ$  (corr.) with evolution of gas. When heated at  $150$ — $155^\circ$  it evolves carbon dioxide and is converted into  *$\alpha$ -bromo- $\gamma$ -phenoxybutyric acid*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$ , which separates from a mixture of ether and light petroleum in stellate prisms and has m. p.  $101.5^\circ$  (corr.).

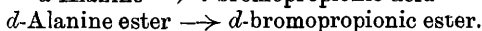
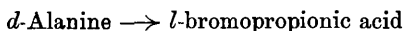
*$\alpha$ -Amino- $\gamma$ -phenoxybutyric acid*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , obtained by agitating the preceding compound with aqueous ammonia and then either allowing the mixture to remain at the ordinary temperature for four to five days or heating in a closed vessel for three hours at  $100^\circ$ , separates from water in colourless needles, m. p.  $233^\circ$  (decomp.). When boiled with strong hydrobromic acid, phenol and  $\alpha$ -amino- $\gamma$ -hydroxybutyric acid,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , are formed, the latter readily passing into its lactone which crystallises out in the form of its hydrobromide.  *$\alpha$ -Aminobutyrolactone hydrobromide*,  $\text{C}_4\text{H}_8\text{O}_2\text{NBr}$ , separates from alcohol in glistening, almost colourless pyramids, m. p.  $227^\circ$  (corr.) (decomp.); when treated with silver carbonate, it forms either the lactone or the free acid according to the conditions.  *$\alpha$ -Amino- $\gamma$ -hydroxybutyric acid*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , crystallises from aqueous alcohol in silky, colourless needles, m. p.  $187^\circ$  (corr.) (decomp.), it has a very faint acid reaction towards litmus. Its copper salt forms dark blue prisms. Its hydrochloride,  $\text{C}_4\text{H}_8\text{O}_2\text{NCl} \cdot \text{H}_2\text{O}$ ,



(Abstr., 1905, i, 692), leucine (Abstr., 1906, i, 808), and phenyl-alanine :



The active  $\alpha$ -bromopropionic acid or its ester is converted into the amino-acid of the same sign by aqueous or liquid ammonia or by potassium phthalimide, whereas by the action of nitrosyl bromide,  $d$ -alanine and its ester yield bromopropionic acid and ester of opposite signs.



This result, which has been observed in the case of other amino-acids, indicates that optical inversion is caused by the action of nitrosyl chloride or bromide.

Walden's contention that potassium hydroxide or phosphorus pentachloride causes an optically normal reaction is supported by his own observation that active haloid acids and their esters are changed into hydroxy-acids and esters of the same sign by the former, whereas  $d$ -lactic acid or its ester yields  $d$ -chloropropionic acid by the action of the latter. Moreover, aqueous  $d$ -chloropropionic acid is converted by silver oxide into  $l$ -lactic acid (Purdie and Williamson, Trans., 1896, 69, 837), whilst natural  $d$ -alanine yields  $d$ -lactic acid by the action of nitrous acid (Fisher and Skita, Abstr., 1901, i, 783). The author confirms these results by showing that  $l$ -bromopropionic acid is converted into  $d$ -lactic acid by silver oxide or carbonate and into  $l$ -lactic acid by dilute potassium hydroxide.

The ester of  $l$ -bromopropionic acid does not react with silver oxide at low temperatures;  $l$ -bromopropionylglycine, however, yields a substance which is hydrolysed to  $l$ -lactic acid. The action of silver oxide on an haloid acid and its esters is similar to that of nitrosyl bromide on active hydroxy-acids and their esters.

Little can be said at present concerning the mechanism whereby optical inversion is produced. Walden regards the abnormal reactions caused by silver or mercuric oxide as due to the formation of unstable additive products by the decomposition of which a change of configuration is rendered possible. Evidence of the formation of additive compounds has been obtained by the author in a few cases which are described below.

The new compounds recorded are :

Ethyl  $l$ - $\alpha$ -phthalylalanine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , containing

about 42% of the racemic form, is obtained by heating ethyl  $l$ - $\alpha$ -bromopropionate and powdered potassium phthalimide for five hours at  $125^\circ$  to prevent racemisation as much as possible (compare Gabriel and Colman, Abstr., 1900, i, 358); it has m. p.  $58\text{--}60^\circ$  and  $[\alpha]_D^{20} 7.15^\circ$  in alcoholic solution.

*Phthalyl-d-alanine*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot CHMe \cdot CO_2H$ , m. p. 150—151° (corr.) softening at 139°, is obtained by heating *d*-alanine and phthalic anhydride for seven hours at 120—125°; it separates from hot water in small, quadrangular leaflets, has  $[\alpha]_D^{20} - 17.84^\circ$  in alcoholic solution, and yields *d*-alanine by hydrolysis with 20% hydrochloric acid; the *ethyl* ester has m. p. 54—56° (corr.) and  $[\alpha]_D^{20} - 12.46^\circ$ .

By the action of excess of bromine on *ethyl d*-alanine or *ethyl l*-leucine in a minimal quantity of 20% hydrobromic acid, in a freezing mixture, red oils are obtained, which seem to consist of additive compounds of bromine and the ester; they are decomposed by nitric oxide, yielding respectively *ethyl d*- $\alpha$ -bromopropionate and *ethyl d*- $\alpha$ -bromo-*isohex*oate.

*Ethyl l*- $\alpha$ -bromo*isohex*oate, prepared from *l*- $\alpha$ -bromo*isohex*oic acid, obtained from *l*-leucine and nitrosyl bromide, has b. p. 49—54°/0.5 mm.,  $[\alpha]_D^{20} - 43.1^\circ$ , and contains some of the racemic form.

*l*-*Bromopropionylglycine*,  $CHMeBr \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , m. p. 120° (corr.), is obtained conveniently from glycine and *l*- $\alpha$ -bromopropionyl chloride; it crystallises in large prisms,  $[\alpha]_D^{20} - 35.27^\circ$  in aqueous and  $-46.6^\circ$  in alcoholic solution. By treatment with water and silver carbonate it yields at first slender needles of a silver salt, but after long keeping and evaporation a viscous liquid is obtained, probably consisting of the active lactylglycine, which by hydrolysis yields *l*-lactic acid.

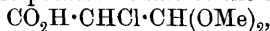
*r*-*Lactylglycine*,  $OH \cdot CHMe \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , prepared from *r*- $\alpha$ -bromopropionylglycine in a similar manner, has m. p. 108.5—109.5° (corr.). C. S.

**Aminolactaldehyde.** ALFRED WOHL and H. SCHWEITZER (*Ber.*, 1907, 40, 92—102).— *$\alpha$ -Chloro- $\beta$ -hydroxypropaldehyde methyl acetal*,  $OH \cdot CH_2 \cdot CHCl \cdot CH(OMe)_2$ , best obtained by preparing the requisite hypochlorous acid by passing a current of chlorine into an aqueous solution of sodium hydrogen carbonate and then adding acraldehyde dimethyl acetal (compare Abstr., 1898, i, 555), has b. p. 97—98°/11 mm. Its *benzoyl* derivative has b. p. 68°/0.25 mm.

*$\alpha$ -Chloro- $\beta$ -benzoylhydroxypropaldehyde ethyl acetal*,  
 $OBz \cdot CH_2 \cdot CHCl \cdot CH(OEt)_2$ ,

has b. p. 128°/0.3 mm.

The constitution of  *$\alpha$ -chloro- $\beta$ -hydroxypropaldehyde methyl acetal* is indicated by its behaviour on oxidation with alkaline potassium permanganate, when the potassium salt of the acid,



is formed. By the action of methyl iodide, the latter salt was converted into the *methyl ester*,  $CO_2Me \cdot CHCl \cdot CH(OMe)_2$ , b. p. 86°/11 mm. The corresponding *ethyl ester*,  $CO_2Et \cdot CHCl \cdot CH(OEt)_2$ , has b. p. 116—117°/11 mm.

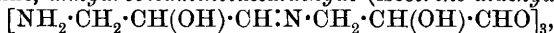
*Aminolactaldehyde methyl acetal*,  $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH(OMe)_2$ , obtained by heating a mixture of  *$\alpha$ -chloro- $\beta$ -hydroxypropaldehyde methyl acetal* and sodium iodide with methyl alcoholic ammonia at 120° for forty-eight hours, has b. p. 100—111°/11 mm. and separates from ethyl acetate in needles, m. p. 55—58°.

*Aminolactaldehyde ethyl acetal*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OEt})_2$ , has b. p.  $120-121^\circ/14$  mm.

*Aminolactaldehyde hydrochloride*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHO} \cdot \text{HCl}$ , obtained by the action of fuming hydrochloric acid on aminolactaldehyde methyl acetal, crystallises in needles and begins to decompose at  $137^\circ$ . It reduces both Fehling's solution and ammoniacal silver nitrate. Its *semicarbazone*,  $\text{CH}_2(\text{NH}_2\text{Cl}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}:\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \cdot 2\text{MeOH}$ , is hygroscopic, softens at  $72^\circ$ , and has m. p.  $74-75^\circ$ . Its *platinichloride* begins to decompose at  $155^\circ$ .

When aminolactaldehyde hydrochloride is oxidised by bromine it forms *isoserine*.

When aminolactaldehyde hydrochloride is dissolved in ethyl alcohol and a few drops of chloroform are added and the mixture agitated for twenty-four hours at the ordinary temperature with diethylamine, *anhydrobisaminolactaldehyde (isoserine aldehyde)*,



is obtained as a white powder. The aqueous solution of the latter compound gives an alkaline reaction; it reduces ammoniacal silver nitrate and boiling Fehling's solution, and begins to decompose at  $125^\circ$ . When its molecular weight is determined by the cryoscopic method in aqueous solution, values are obtained for a termolecular compound; after standing two days, the values indicate a bimolecular structure and finally, after five days, a unimolecular structure. Dilute hydrochloric acid converts the anhydro-compound, either in its unimolecular or in its termolecular form, at the ordinary temperature into the aminoaldehyde hydrochloride.

A. McK.

**Constitution of Cyanic Acid.** F. CARLO PALAZZO and EDUARDO CARAPELLE (*Chem. Centr.*, 1906, ii, 1723—1724; from *Estr. Giorn. Sci. Nat. Econ.*, 26. Compare Nef, *Abstr.*, 1896, i, 71).—Since the action of diazomethane (compare Meyer, *Abstr.*, 1906, i, 108) on cyanic acid yields a derivative of a carbamide, the author concludes that free cyanic acid is not tautomeric, but has the formula  $\text{O}:\text{C}:\text{NH}$ , and that its salts are also carbimides. The action of the acid on diazomethane is somewhat energetic. When the ethereal solution of the acid at  $-12^\circ$  is poured into the ethereal solution of diazomethane at  $-5^\circ$  and the mixture treated with dry ammonia, methylcarbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NHMe}$ , m. p.  $101-102^\circ$ , is the main product. Diazoethane yields ethylcarbamide; methyl ethylcarbamate,  $\text{NHEt} \cdot \text{CO}_2\text{Me}$ , b. p.  $96-100^\circ/50$  mm.,  $70-73^\circ/19$  mm. (compare Klobbie, *Rec. trav. chim.*, 1888, 7, 355), is also formed from the methyl alcohol which always accompanies diazoethane (compare von Pechmann, *Abstr.*, 1899, i, 134).

E. W. W.

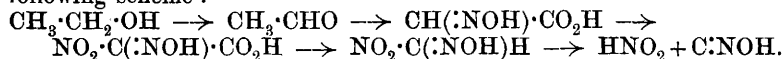
**Preparation of Cyanoacetylcarbamide and its Alkyl and Amyl Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 175415).—It has been found that cyanoacetylcarbamide and its derivatives can be readily obtained by condensing cyanoacetic acid and carbamide or one of its alkyl or acyl derivatives with an acid anhydride. A mixture of carbamide, cyanoacetic acid, and acetic

anhydride when warmed on the water-bath furnishes pure cyanoacetylcarbamide. Methylcarbamide, cyanoacetic acid, and propionic anhydride give cyanoacetylmethylcarbamide. Dimethylcarbamide, cyanoacetic acid, and acetic anhydride yield cyanoacetyldimethylcarbamide, whilst phenylcarbamide, cyanoacetic acid, and benzoic anhydride give rise to *cyanoacetylphenylcarbamide* (m. p. 216°).

G. T. M.

**New Synthesis of Fulminic Acid. The Formation of Fulminic Acid from Alcohol and Nitric Acid.** HEINRICH WIELAND (*Ber.*, 1907, 40, 418—422).—When methylnitrolic acid is boiled for a short time with dilute nitric acid and silver or mercuric nitrates, the corresponding salt of fulminic acid crystallises out; the by-products of the interaction are formic acid, nitrous oxide, carbon dioxide, ammonia, and a small quantity of nitrous acid and nitric oxide.

The interaction of nitric acid and alcohol is explained by the following scheme:



The experimental support for the above hypothesis is as follows. Wöhler (*Abstr.*, 1905, i, 418) found aldehyde a more suitable agent than alcohol for the preparation, whilst the formation of methyl-nitrolic acid from isonitrosoacetic acid has been accomplished by Ponzio (*Abstr.*, 1903, i, 453).

W. R.

**Iron-Cyanogen Compounds. IV.** KARL A. HOFMANN [with H. ARNOLDI and H. HIENDLMAIER] (*Annalen*, 1907, 352, 54—72).—With the object of showing the truth of the former statement (*Abstr.*, 1906, i, 75) that the blue iron-cyanogen compounds, formed either from ferric salts and ferrocyanide or ferrous salts and ferricyanides, are derivatives of potassium ferrocyanide in which potassium is either wholly or partly replaced by trivalent iron, the reduction of mixed solutions of ferric salts and potassium ferricyanide has been studied. It has been further shown that those compounds, believed by several investigators to be ferrous cyanide, are really complex iron-cyanogen compounds. The compound  $\text{Fe}_2\text{C}_6\text{N}_6\text{H}_2\frac{1}{2}\text{H}_2\text{O}$  is obtained by treating a solution containing molecular proportions of potassium ferricyanide and ferric alum with hydrogen peroxide; since this compound differs only from that obtained by treating soluble Prussian blue with dilute acid in the percentage of water present, it is evident that soluble Prussian blue contains the ferrocyanide complex.

When a solution containing potassium ferricyanide and ferric chloride is acted on by free hydroxylamine, soluble Prussian blue alone is formed; from this it follows that soluble Turnbull's blue is identical with soluble Prussian blue; in other words, Turnbull's blue is not a ferrous ferricyanide. Ferrous cyanide is not obtained by adding ammonia to a solution containing ferrous chloride and prussic acid; the precipitates thus obtained on oxidation are converted into complex substances in which the atomic ratio of iron to carbon is

1 : 3, and not 1 : 2 as it would be were the original precipitate ferrous cyanide.

The compound  $\text{Fe}_2\text{C}_6\text{N}_6\text{NH}_4, 1\frac{1}{2}\text{H}_2\text{O}$  is obtained by oxidising the precipitate formed by the interaction of ferrous chloride (1 mol.), hydrocyanic acid (6 mols.), and ammonia (4 mols.), and similarly the compound  $\text{Fe}_2\text{C}_6\text{N}_6\text{H}, 2\text{H}_2\text{O}$  when the proportions, ferrous chloride (1 mol.), prussic acid (6 mols.), and ammonia (2 mols.) are used. These compounds are blue powders, decomposed by 4% ammonia in four minutes at  $15^\circ$ , insoluble in water, soluble, however, in a saturated aqueous solution of oxalic acid. Similar compounds were obtained by using hydroxylamine instead of ammonia.

When the compound,  $\text{Fe}_2\text{C}_6\text{N}_6\text{H}_2$ , obtained by boiling an aqueous solution of hydroferrocyanic acid with exclusion of air, is oxidised, a blue compound,  $\text{Fe}_2\text{C}_6\text{N}_6\text{H}, \text{H}_2\text{O}$ , insoluble in water, oxalic acid, and ammonium oxalate solutions, is formed. Although similar to Williamson's violet, it differs from it in that it is decomposed by ammonia. Attempts to prepare a Williamson's violet containing sodium were unsuccessful. The compound,  $\text{Fe}_2\text{C}_6\text{N}_6\text{K}_2$ , obtained as a residue in the preparation of hydrocyanic acid, is also formed by heating a solution of potassium ferrocyanide with excess of oxalic acid.

All soluble blue iron-cyanogen compounds of the general formula  $\text{FeC}_6\text{N}_6\text{FeMe}_x, x\text{H}_2\text{O}$  are reduced by ammonium oxalate in direct sunlight to a yellowish-white substance which is converted by hydrogen peroxide into Monthier's blue (Berzelius, *Jahresb.*, 27, 173). The latter compound,  $\text{Fe}_2\text{C}_6\text{N}_6\text{NH}_4, \text{H}_2\text{O}$ , is, however, best prepared by oxidising with hydrogen peroxide the green precipitate obtained by acting on a solution containing potassium ferrocyanide, ammonium chloride, and ammonia with fine iron wire; it dissolves in water and oxalic acid, forming blue solutions, not, however, in ammonium tartrate solution; it is precipitated from its aqueous solution by ammonium oxalate, and is decomposed by 4% ammonia in five to seven minutes. It is therefore very similar to the blue iron-cyanogen compound obtained from an acidified solution containing potassium ferrocyanide (1 mol.) and a ferrous salt (1 mol.) (compare Abstr., 1905, i, 756). A compound of the same formula,  $\text{Fe}_2\text{C}_6\text{N}_6\text{NH}_4, \text{H}_2\text{O}$ , is obtained by oxidising in a neutral solution the compound formed by the reduction of Prussian blue with hydrogen sulphide. Robiquet [Dammer, *Handbuch III.* (1893), 364] considered the substance obtained by reducing Prussian blue with hydrogen sulphide to be ferrous cyanide, but this cannot be correct, since by oxidation in neutral solution only an oxy-cyanide and not the above compound,  $\text{Fe}_2\text{C}_6\text{N}_6\text{NH}_4, \text{H}_2\text{O}$ , should be obtained.

W. H. G.

**Conditions of Stability of the Carbylamines.** H. GUILLEMARD (*Compt. rend.*, 1907, 144, 141—143. Compare this vol., ii, 141).—When a mixture of excess of ethylcarbylamine with a small quantity of ethyl iodide is kept at the ordinary temperature for a prolonged period, a brown, crystalline additive compound,  $2\text{EtNC}, 3\text{EtI}$ , may be isolated by distillation in a vacuum. It is very soluble in water and organic solvents and is easily decomposed by heat, by acids, and by alkalis; with the latter the products include diethylamine and alkali

oxalate. If the action takes place at a high temperature, a tarry product, apparently either a mixture of the above compound and a polymeride of the carbylamine or a compound of this polymeride with ethyl iodide, is obtained.

The carbylamines are instantly destroyed by normal alkyl sulphates and by those sulphovinates which are not strictly neutral. They combine with metallic cyanides, giving compounds the stability of which varies with the cyanide employed, but all are dissociated by heat. The silver compound,  $\text{AgNC,CNEt}$ , which can be considered as the ethyl ester of hydroargentocyanic acid, dissociates into silver cyanide and ethyl carbylamine below  $140^\circ$ . Above  $140^\circ$  a mixture of nitrile and carbylamine is formed, the proportion of nitrile increasing with rise of temperature.

The silver compound, when heated to  $160^\circ$  in a sealed tube for four hours, is completely converted into silver cyanide and the nitrile.

When the carbylamines are heated in sealed tubes, the molecular weight rises gradually at temperatures from  $100^\circ$  to  $160^\circ$  and falls between  $160^\circ$  and  $240^\circ$ , whilst the quantity of nitrile formed increases regularly from  $140^\circ$  to  $240^\circ$ , at which temperature the conversion into nitrile is complete. Hence it follows that, on heating, the carbylamine polymerises first, and the product dissociates into carbylamine and nitrile, the proportion of the latter increasing as the temperature is raised, because the reaction is not reversible. A small quantity of the polymeride was isolated as a very explosive, oily substance, which from a cryoscopic determination appears to be termolecular.

The conclusion is drawn that in their preparation the carbylamines may combine with the alkylating agent, and under the action of heat may give rise to nitriles after polymerisation or combination with the cyanide.

E. H.

**Complex Compounds of Oxalenediamino-oxime.** LEO TSCHUGAEFF and JAC. SURENJANZ (*Ber.*, 1907, 40, 181—185. Compare *Abstr.*, 1905, i, 743; 1906, i, 814).—Oxalenediamino-oxime, which resembles on the one hand the ethylenediamines in having two amino-groups in the  $\alpha\beta$ -position to each other, and, on the other hand, the  $\alpha$ -dioximes in having two oxime groups in the same relative positions, has, as was to be expected, a strong tendency to the formation of two series of complex metallic compounds. In the present paper the nickel compounds are described.

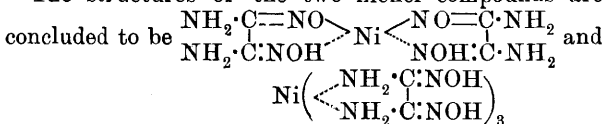
The action of slightly more than 2 mols. of oxalenediamino-oxime on nickel acetate (1 mol.) in aqueous solution, or on other nickel salts in presence of ammonia, pyridine, or ammonium acetate, leads to the formation of the compound,  $\text{Ni}(\text{OxH})_2 \cdot 2\text{H}_2\text{O}$   $\left( \text{Ox} = \begin{array}{c} \text{NH}_2 \cdot \text{C} : \text{NO} \cdot \\ | \\ \text{NH}_2 \cdot \text{C} : \text{NO} \cdot \end{array} \right)$ , which crystallises in orange-red needles, loses  $2\text{H}_2\text{O}$  at  $110^\circ$ , and decomposes with explosive violence at about  $270^\circ$ . It dissolves in dilute mineral acids or acetic acid, forming a blue solution, is decomposed by an excess of mineral acid, gives a brownish-red coloration with concentrated aqueous alkalis, yields nickel sulphide when treated with hydrogen or ammonium sulphide, and on solution in aqueous



potassium cyanide forms oxalenediamino-oxime and potassium nickel cyanide.

In concentrated solution and in presence of acetic acid, 1 mol. of nickel chloride reacts with 3—4 mols. of oxalenediamino-oxime, forming the *chloride*,  $\text{Ni}(\text{OxH}_2)_3\text{Cl}_2$ , which crystallises in bluish-violet needles, decomposes suddenly at  $230^\circ$ , and is moderately stable in acid solutions; towards ammonium sulphide, excess of mineral acid, or potassium cyanide solution it behaves in the same manner as the orange-red compound into which it is converted by the action of water. Both chlorine atoms are ionised, being removed as silver chloride on addition of silver nitrate. The nitrate,  $\text{Ni}(\text{OxH}_2)_3(\text{NO}_3)_2$ , forms bluish-violet prisms, behaves towards reagents in the same manner as the chloride, and yields the whole of its nitric acid as nitron nitrate on addition of nitron acetate solution (Busch, Abstr., 1900, ii, 282).

The structures of the two nickel compounds are discussed, and



respectively.

G. Y.

**Study of a Case of Isomerism among the Oxonium Compounds of Grignard and Baeyer.** WLADIMIR TSCHELINZEFF (*Compt. rend.*, 1907, 144, 88—90).—If the oxonium derivatives obtained by the condensation of organomagnesium compounds with ethers possess the structure suggested by Baeyer (Abstr., 1902, i, 355), isomerides of the types  $\text{OR}_2\text{X} \cdot \text{MgR}'$  and  $\text{ORR}'\text{X} \cdot \text{MgR}$  should be possible, and the author has prepared a series of compounds in which  $\text{R} = \text{C}_2\text{H}_5$  and  $\text{R}' = \text{C}_3\text{H}_7$ ,  $\text{C}_4\text{H}_9$ ,  $\text{C}_5\text{H}_{11}$ , or  $\text{C}_6\text{H}_5$  by adding one equivalent of the ether to the organomagnesium compound in benzene solution, and has measured the heat developed when the compounds are decomposed by water. Ethylmagnesiummethylpropyloxonium iodide,  $\text{OEtPrI} \cdot \text{MgEt}$ , obtained from ethyl propyl ether and magnesium ethyl iodide, has a heat of decomposition 62.3 cal., and the isomeride propylmagnesiumdiethyloxonium iodide,  $\text{OEt}_2\text{I} \cdot \text{MgPr}$ , has 62.5 cal.; similarly, ethylmagnesiummethylisobutyloxonium iodide,  $\text{C}_4\text{H}_9 \cdot \text{OEtI} \cdot \text{MgEt}$ , has 58.7 cal., and isobutylmagnesiumdiethyloxonium iodide has 60.2 cal.; ethylmagnesiummethylisoamyloxonium iodide,  $\text{C}_5\text{H}_{11} \cdot \text{OEtI} \cdot \text{MgEt}$ , yields ethane when decomposed by water with a heat development of 62.9 cal., whilst the decomposition of isoamylmagnesiumdiethyloxonium iodide,  $\text{OEt}_2\text{I} \cdot \text{Mg} \cdot \text{C}_5\text{H}_{11}$ , is not accompanied by any evolution of gas, and the heat equivalent is 60.5 cal.; ethylmagnesiumphenylethyloxonium iodide,  $\text{OEtPhI} \cdot \text{MgEt}$ , is decomposed by water with evolution of ethane and a heat equivalent of 62.1 cal., and phenylmagnesiumdiethyloxonium iodide,  $\text{OEt}_2\text{I} \cdot \text{MgPh}$ , yields benzene on decomposition with water and a heat equivalent of 59.2 cal.

No conclusions as to the possible isomerism among the oxonium derivatives can be drawn from the results of the thermochemical investigation given above, as the thermal values are practically

identical, but the nature of the products of decomposition show that the compounds do show isomerism of the type suggested by Baeyer.

M. A. W.

**$\beta$ -Mercuridipropionic Acid.** EMIL FISCHER (*Ber.*, 1907, 40, 386—389. Compare Pesci, *Abstr.*, 1901, i, 624).—This work was undertaken to fill a gap in the organo-mercuric derivatives amongst which previously no compounds of the fatty acids have been described.

*Ethyl  $\beta$ -mercuridipropionate*,  $\text{Hg}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , prepared by shaking ethyl  $\beta$ -iodopropionate with sodium amalgam in cooled ethereal solution, is obtained on evaporation of the ethereal solution in a vacuum as a yellow oil having an unpleasant odour. The *acid*,  $\text{Hg}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , formed by shaking the ester with *N*-sodium hydroxide, crystallises from water in slender, colourless, odourless prisms, m. p.  $148.5$ — $149.5^\circ$  (corr.), can be titrated with sodium hydroxide in presence of phenolphthalein, is readily decomposed by halogens or strong acids, and yields with iodine mercuric iodide, with a limited amount of boiling hydrobromic acid, a crystalline *substance* which may be *bromomercuripropionic acid*, or with an excess of hydrobromic acid mercuric bromide; when warmed gently with iodine in aqueous potassium iodide solution, mercuridipropionic acid yields a dark crystalline *periodide*. The *copper*, *lead*, and *silver* salts are described.

$\beta$ -Mercuridipropionic acid is decomposed by water at  $100^\circ$  yielding propionic acid and the *anhydride* of  $\beta$ -hydroxymercuripropionic acid,  $\text{Hg}\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{matrix}$ , which separates in colourless crystals, becomes grey at about  $190^\circ$ , gradually decomposes at higher temperatures, and is soluble in dilute alkalis or warm dilute acids.

G. Y.

**The Benzene Nucleus, its Reactivity, and the Valency Strength of its Substituting Groups and of Carbon.** JULIUS OBERMILLER (*J. pr. Chem.*, 1907, [ii], 75, 1—61. Compare Flürscheim, *Abstr.*, 1905, i, 614).—The argument of this theoretical paper is based on the following conceptions of valency.

(1) The valencies of an atom are the directions in which the force constituting the total affinity of the atom acts. The valencies act in straight lines but may be diverted to a certain extent. The valency of an atom is the number of directions in which the affinity acts and the number of valencies of other elements which must be neutralised in the formation of a chemical compound.

(2) The total affinity of the atom varies for different elements and is not proportional to the valency, that is, the average affinities of the valencies of the atom are different for different elements.

(3) It is not necessary in a chemical compound that the total affinity of an atom should be completely neutralised; any excess of affinity expresses itself in the so-called secondary valencies, partial valencies, indirect linkings, &c.

(4) The valencies of a multivalent atom may vary in strength, the distribution of the total affinity of the atom depending chiefly on the strength of the valencies neutralised.

(5) The mutual attraction of chemical affinities is to be considered as a special case of mass attraction,  $m.m'/r^2$ . The force forming the linking is the product of the two valencies which are mutually neutralised and which are not necessarily of the same strength.

(6) The affinity necessary for the formation of a given linking is constant within certain limits, outside of which unstable compounds are formed or combination does not take place; this necessary affinity varies for different combinations of atoms and depends on the manner in which the remaining valencies of the atoms concerned are occupied. It follows that in a combination of two atoms the affinity of the one atom must be the greater the less that of the second valency forming the linking. In the combination  $AB$ , the affinity required of  $B$  in consequence of that of  $A$  to make the combination, is termed the "valency need- $B$ " of the atom  $A$ , and the possibility of measuring it is discussed.

It is suggested that the "valency need- $C$ " of the carbon atom is greater than the affinity of the average carbon valency, when it follows that in the centric formula for benzene, which agrees best with the above conceptions of valency, with the direct formation of substitution compounds, and the nature of partially reduced benzene derivatives, more than half of the total affinity of the six carbon atoms is required for the formation of the ring, and after expenditure of sufficient affinity for the union with the six hydrogen atoms there remains for the centric valencies less affinity than is necessary for the formation of true C-C linkings; the centric valencies are considered to be of the nature of *pseudo-para*-linkings. If now one of the hydrogen atoms is substituted by a group requiring a greater carbon affinity for combination, the remaining three valencies, forming the two *ortho*- and the one *para*-linkings, of the carbon atom to which the new group is attached, must be weakened with the effect of rendering the two *o*- and the *p*-hydrogen atoms less firmly attached to the nucleus and therefore more reactive. It is for this reason that the introduction of a second substituting group tends to take place in the *o*- and *p*-positions. *Meta*-substitution is considered to be a consequence of steric hindrance. The stability of a benzene derivative must diminish with increasing "valency need" of the substituting group, hence the great stability of benzene is in agreement with the order of "valency need- $C$ " represented by the series given below.

These considerations are shown to apply also to the orientation of substitution in pyridine, naphthalene, and anthracene, and to the mutual influence on each other of two or more substituting groups as modified by their relative positions in the benzene nucleus.

If the orientation of a group is influenced in two directions by two substituting groups already present in the benzene nucleus, the influence of the stronger of these will predominate to the greater extent the more the two groups differ in "valency need- $C$ " and the more easily the introduction of the third group takes place. That the stronger substitution group is that with the greater "valency need" follows from the above exposition of the affinity equilibrium of the benzene nucleus and its disturbance by substitution. From consideration of a number of cases of substitution it is shown that the

"valency need-*C*" diminishes from  $N'''$  to  $H$  in the series:  $N'''$ ,  $C^{IV}$ ,  $NO_2$ ,  $SO_3H$ ,  $OH$ ,  $NH_2$ ,  $Cl(Br)$ ,  $CH_3$ ,  $H$ .

The "valency need-*C*" of carbon being greater than the average affinity of a carbon valency, the stability of methane and its homologues results from the small "valency need-*C*" of hydrogen, on the other hand, for the same reason, whilst in tetranitromethane sufficient carbon affinity is at the disposal of each nitro-group, hexanitroethane must be unstable if capable of existence (compare Hantzsch, Abstr., 1906, i, 617). The properties of acetylene and of the cyanogen group, the existence of both tetraphenylmethane and triphenylmethyl, and the instability of two hydroxyls when attached to the same carbon atom are discussed from the author's point of view.

G. Y.

[Oxidation of Aromatic Hydrocarbons and their Derivatives with Manganese Disulphate.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 175295).—Manganese disulphate,  $Mn(SO_4)_2$ , in acid solution has the property of oxidising the methyl group of toluene and its homologues and derivatives in such a way that aldehydes and, finally, carboxy-acids are obtained. The manganous sulphate resulting from the oxidation can be readily reconverted into the disulphate by electrolytic oxidation. Toluene when oxidised at  $40-50^\circ$  furnishes an almost quantitative yield of benzaldehyde, and when the oxidation is effected at a higher temperature with a further quantity of manganese disulphate, benzoic acid is obtained finally. Benzyl alcohol and chloride may also be oxidised in this manner to yield benzaldehyde and even benzoic acid.

G. T. M.

Oxidation of Substituted Aromatic Hydrocarbons. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 174238).—*o*-Chlorotoluene is readily oxidised to *o*-chlorobenzaldehyde when suspended in 60–65% sulphuric acid at  $50^\circ$  and treated gradually with cerium dioxide, the temperature being slowly raised to  $90^\circ$ . The product now contains a white, pasty mass of cerous sulphate, mixed with *o*-chlorobenzaldehyde and a small quantity of *o*-chlorobenzoic acid, the yield of aldehyde being 66%.

The *o*- and *p*-nitrotoluenes are similarly oxidised at  $80-85^\circ$ , but in this case more of the corresponding nitrobenzoic acids are produced.

The anthracenesulphonic acids are readily oxidised in this way to anthraquinonesulphonic acids even at the ordinary temperature.

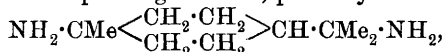
G. T. M.

The Two Modifications of *o*-Nitrotoluene. EMIL KNOEVENAGEL (Ber., 1907, 40, 508–517. Compare Abstr., 1903, i, 785).—The existence of *o*-nitrotoluene in two forms (compare Ostromisslensky, this vol., i, 120) had been discovered by Schmidt and Berndt in 1903 in the Griesheim-Elektron works. The author also showed in 1904 that the  $\alpha$ -form (m. p.  $-9.4^\circ$ ) is transformed exothermally at low temperatures into the  $\beta$ -form (m. p.  $-3.6^\circ$ ). The two modifications exhibit differences in the liquid as well as in the solid state, and are therefore regarded as chemical isomerides and as instances of motoisomerism.

The author proceeds to develop his theory of motoisomerism. The fact that the viscosity of freshly distilled nitrobenzene differs from that of nitrobenzene, determined five hours after distillation, is attributed by the author to motoisomerism. C. S.

**Nitro-derivatives in the Mentane Series. III. MICHAEL I. KONOWALOFF** (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 449—453. Compare Abstr., 1904, i, 513).—Menthane was heated with nitric acid, D 1.1 at 115—120°, in a sealed tube. Three crystalline dinitro-compounds were obtained, melting respectively at 98—100°, 92—95°, and 75—85°. The first fraction yielded *dinitromenthane*,  $C_{10}H_{18}(NO_2)_2$ , probably  $NO_2 \cdot CMe < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} > CH \cdot CMe_2 \cdot NO_2$ , m. p. 107.5—108.5°.

It is readily soluble in benzene, sparingly so in ether, and does not distil but commences to decompose at 210°. Zinc dust and acetic acid reduce it to the corresponding *diamine*, probably



b. p. 231—233°,  $D_0^{20}$  0.9263,  $D_0^{17.5}$  0.9108,  $n_D^{17.5}$  1.47955, a colourless liquid which does not solidify at -8°. The *hydrochloride* and *sulphate* are described. The *dibenzoyl* derivative,  $C_{10}H_{18}(NHBz)_2$ , m. p. 232.5—233.5°, crystallises from alcohol in small needles.

Z. K.

[Nitration of 3:4-Dichlorobenzenesulphonic Acid.] **AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION** (D.R.-P. 175022. Compare Abstr., 1904, i, 1065).—The nitration product of 3:4-dichlorobenzene-sulphonic acid in concentrated sulphuric acid is poured on to ice and the nitro-sulphonic acids salted out in the form of their sodium salts. The mixed salts, when redissolved in water and allowed to crystallise, yield a crop of the less soluble sodium 4:5-dichloro-2-nitrobenzenesulphonate, whilst an isomeric salt of the nitro-sulphonic acid, containing the nitro-group either in position 3 or 6, remains in the mother liquors. The calcium, barium, and zinc salts of the latter acid are generally more soluble than those of 4:5-dichloro-2-nitrobenzenesulphonic acid. On reducing the mixture of these two nitro-acids with iron and dilute acetic acid, the corresponding amino-sulphonic acids are obtained. 4:5-Dichloroaniline-*o*-sulphonic acid is by far the less soluble and is precipitated from an acidified solution of its sodium salt. The isomeric acid remains in the mother liquors and is obtained on concentration. When successively diazotised and treated with alkali, one of the chlorine atoms of this more soluble acid is replaced by hydroxyl, showing that the amino-group was originally in the ortho-position to one of the chlorine atoms. It is on account of this reaction that the nitro-group is assumed to enter position 3 or 6. G. T. M.

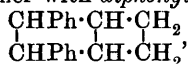
**Unsaturated Acids of the Sorbic Series and their Conversion into Cyclic Hydrocarbons. III. OSCAR DÖBNER** (*Ber.*, 1907, 40, 146—147).—The hydrocarbon,  $C_8H_{12}$ , previously termed *cyclooctadiene* (Abstr., 1902, i, 598) is not identical with Willstätter

and Veraguth's *cyclo*-octadiene (Abstr., 1905, i, 515). As the latter possesses the properties of an unsaturated compound it is probable that the hydrocarbon obtained from  $\beta$ -vinylacrylic acid has the constitution  $\begin{array}{cccc} \text{CH}_2 & \cdot \text{CH} & \cdot \text{CH} & \cdot \text{CH}_2 \\ | & & | & \\ \text{CH}_2 & \cdot \text{CH} & \cdot \text{CH} & \cdot \text{CH}_2 \end{array}$ , and is termed *tricyclooctane*.

J. J. S.

**Unsaturated Acids of the Sorbic Series and their Conversion into Cyclic Hydrocarbons.** IV. OSCAR DÖBNER and G. SCHMIDT (*Ber.*, 1907, 40, 148—152. Compare Abstr., 1902, i, 598; 1904, i, 149, and preceding abstract).—When the yellow modification of cinnamylidenemalonic acid is heated with anhydrous barium hydroxide, it yields phenyl*cyclobutene*, m. p. 25°, b. p. 118—122°/12 mm., together with a considerable amount of diphenyl*tricyclo*-octane, b. p. 204—206°/10 mm., and a small amount of a hydrocarbon,  $\text{C}_{30}\text{H}_{30}$ . The last is a viscous liquid and is not attacked by bromine or permanganate.

The colourless cinnamylidenemalonic acid, m. p. 178° (Liebmann, Abstr., 1895, i, 470), when treated in the same manner yields considerable amounts of diphenyl*tricyclo*octane and small amounts of the hydrocarbon,  $\text{C}_{30}\text{H}_{30}$ , together with *diphenyldicyclohexane*,



m. p. 56°, b. p. 212—215°/12 mm., and an unsaturated hydrocarbon,  $\alpha$ -phenyl- $\Delta^{\gamma}$ -butadiene,  $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2$ , b. p. 93—95°/12 mm., the tetrabromide of which melts at 150° (Klages, Abstr., 1902, i, 669; Riiber, 1903, i, 471).

J. J. S.

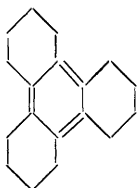
**Synthesis of Aldehydes and Ketones from *as*-Disubstituted Ethylene Glycols and their Ethers.** A Correction. RICHARD STÖRMER (*Ber.*, 1907, 40, 488—489).—It was stated (Abstr., 1906, i, 581) by the author that when phenoxyditolyethylene was heated with alcoholic potassium hydroxide at 240°, di-*p*-tolylethylene was formed together with the corresponding ethoxy-compound. Di-*p*-tolylethylene was described as an oil, b. p. 186°/20 mm. This oil is, however, a mixture of ditolyethylene and ditolylmethane.

Di-*p*-tolylethylene had previously been described correctly by Bistrzycki and Reintke as a solid, m. p. 61°. A. McK.

**Pentaphenylethane and Hexaphenylethane.** ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1907, 40, 367—369. Compare Abstr., 1905, i, 125; Flürscheim, *ibid.*, 614; Hantzsch, Abstr., 1906, i, 617).—Gomberg and Cone's pentaphenylethane (Abstr., 1906, i, 821), m. p. 178—179° (decomp.), determined in an atmosphere of carbon dioxide, which behaves at the ordinary temperature as a saturated hydrocarbon, when heated alone or in nitrobenzene solution, decomposes into tetraphenylethane and triphenylmethyl, and absorbs oxygen. When heated with hydrogen chloride in benzene solution at 150° with exclusion of air, it yields tetraphenylethane, triphenylmethane, and triphenylmethyl chloride. The decomposition in question must result from a weakening of the linking between the diphenylmethyl and the

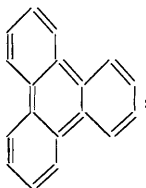
triphenylmethyl groups of the pentaphenylethane; this behaviour resembles closely that of triphenylmethyl which consequently is considered to be hexaphenylethane. Schmidlin's supposed stable hexaphenylethane (this vol., i, 26) was probably impure tetraphenylethane. The experimental results described are opposed to Vorländer's view that two hexaphenylethanes, a stable and a labile form, are capable of existence. G. Y.

**Condensation of *cyclo*Hexanone.** CARL MANNICH (*Ber.*, 1907, 40, 153—158).—*cyclo*Hexanone yields condensation products in much the same manner as aliphatic ketones (compare Wallach, *Abstr.*, 1896, i, 572; 1897, i, 425). A condensation, similar to the formation of mesitylene from acetone, occurs when *cyclo*hexanone is boiled for some ten to twelve hours with its own weight of concentrated sulphuric acid and 2.5 times its weight of methyl alcohol. The product, *dodecahydrotriphenylene*, the yield of which is some 6%, crystallises from benzene in large, compact prisms, m. p. 232—233°. It may be sublimed in an atmosphere of carbon dioxide or hydrogen. When heated with fuming nitric acid at 180° it yields mellitic acid.



Other products formed during the condensation are a ketone,  $C_{12}H_{18}O$ , probably identical with that obtained by Wallach (*loc. cit.*), and yielding a *semicarbazone*, m. p. 175—177°, and a *ketone*,  $C_{18}H_{26}O$ , b. p. 214—217°/15 mm. The latter condenses with guanidine, and the condensation product yields a *picrate*,  $C_{25}H_{33}O_7N_7$ , m. p. 203° (decomp.). J. J. S.

**Triphenylene.** CARL MANNICH (*Ber.*, 1907, 40, 159—165).—*Triphenylene* is formed when dodecahydrotriphenylene (preceding abstract) is distilled with zinc dust in an atmosphere of hydrogen. It may be isolated in the form of its *picrate*. The hydrocarbon crystallises from benzene or alcohol in colourless needles, m. p. 198—198.5°. A better yield is obtained when the dodecahydro-compound is passed over a layer of copper in an atmosphere of carbon dioxide at 450—500°. When completely oxidised, it yields mellitic acid. With chromic acid, it is oxidised to a mixture of quinones, and with fuming nitric acid yields a *trinitra*-derivative,  $C_{18}H_9(NO_2)_3$ , which crystallises from nitrobenzene in pale yellow, slender needles, and darkens at 335° without melting. The hydrocarbon is identical with the triphenylene obtained in minute quantities by Schmidt and Schultz (*Abstr.*, 1881, 435). J. J. S.



**Use of Acetic Anhydride in Nitrating.** KENNEDY J. P. ORTON (*Ber.*, 1907, 40, 370—376. Compare *Trans.*, 1902, 81, 806; Witt and Utermann, this vol., i, 27).—Nitric acid for use in nitrating in acetic anhydride is freed from nitrous acid by treatment with a limited quantity of carbamide nitrate.

Nitroamines are obtained in a 90% yield, together with nitro-com-

pounds and diazo-salts, from anilines having one or both *o*-hydrogen atoms present if the amine dissolved in glacial acetic acid is run into a mixture of acetic anhydride and nitric and glacial acetic acids cooled in ice-water. The presence of nitrous acid is necessary to the nitration of dialkylanilines, intermediate nitroso-derivatives probably being formed.

Nitrotoluene has been prepared in a quantitative yield by nitration of toluene in presence of acetic anhydride; results are quoted showing that the function of the acetic anhydride is to combine with the water present in the nitric acid and formed during the reaction. Under the same conditions benzoic acid yields *m*-nitrobenzoic acid. G. Y.

**Electrochemical Reduction of *o*-Nitroacetanilide.** KURT BRAND and EDWARD STOHR (*Ber.*, 1907, 40, 364. Compare this vol., i, 100).—References are given to two other *o*-nitrosoanilines which had been overlooked by the authors. W. R.

**Phenylbiurets and the Biuret Reaction.** HUGO SCHIFF (*Annalen*, 1907, 352, 73—87. Compare Abstr., 1902, i, 429).—By acting on phenylbiuret with aniline, Weith (Abstr., 1878, 141) obtained a compound which he describes as diphenylbiuret; it is shown that this compound is really *s*-diphenylcarbamide. When heated in sealed tubes with carbonyl chloride dissolved in toluene, the latter substance is converted into *s*-diphenylbiuret. Pickard and Carter (*Trans.*, 1901, 79, 841; 1902, 81, 1563), by acting on acetylphenylhydroxyloxamide with dilute ammonia, obtained a compound which they thought to be phenylbiuret; this substance is really *as*-phenylbiuret; it crystallises in silvery scales, *m. p.* 167°, and does not give the biuret reaction; at the same time the following by-products are formed: monophenylcarbamide, oxanilide, *s*-diphenylbiuret, and ammonium oxanilate. When *s*-diphenylcarbamide is heated with carbamide, cyanuric acid is formed together with only small quantities of biuret and monophenylcarbamide; that only small quantities of the last are obtained is probably due to the fact that when heated this compound is partially converted into carbamide and *s*-diphenylcarbamide. The author's original supposition (compare Abstr., 1897, i, 144) that asymmetrically substituted biurets, even when only one of the amido-hydrogen atoms is substituted, do not give the biuret reaction, although true in most cases, has not been found to hold good in all cases. After mentioning the cases in which his proposition fails, the author concludes by putting forward the suggestion that only those reactions which are obtained with amino-amides or diamides derived from the parent substances, biuret, oxamide, and malonamide, with copper or nickel salts, should be known as biuret reactions.

W. H. G.

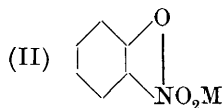
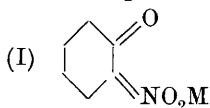
**Action of Phosphorus Pentabromide on Phenol Ethers.** LOUIS HENRY (*Ber.*, 1907, 40, 243—244).—A claim for priority (compare *Ber.*, 1869, 2, 710; Autenrieth and Mühlinghaus, this vol., i, 31). C. S.



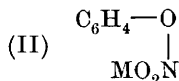
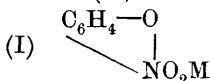
**Isomerism of the Salts of Nitrophenols and the Existence of Metaquinonoid Compounds.** ARTHUR HANTZSCH (*Ber.*, 1907, 40, 330—351. Compare Abstr., 1906, i, 352, 353).—Two series of coloured alkali salts of nitrophenols have been prepared, one yellow, the other red; the red salts are usually unstable and could not be obtained pure. Colourless 2:4:6-tribromo-3:5-dinitrophenol, however, gives a yellow and a red potassium salt of the same composition and of the same molecular weight and electrical conductivity. Although many of these salts crystallise with water or alcohol, their colour is not dependent on the water or alcohol of crystallisation as this may be removed from the red or yellow potassium salts of tribromonitrophenol without any alteration in colour. The fact that the red ammonium salt of *o*-nitrophenol when dehydrated is yellow and the orange-yellow potassium salt, red, whereas, precisely the reverse is the case with the corresponding salts of 2:6-dinitro-*p*-cresol, shows that these are the stable salts under these conditions and that isodynamic change has occurred during the dehydration. The author concludes that the two series of differently coloured salts obtained from colourless nitrophenols have different constitutions and that their colour is independent of the alkali metal present as all the yellow and all the red salts are almost of the same colour intensity.

The yellow and red salts are morphologically different (compare Rabe, Abstr., 1901, i, 697), and generally either the red or the yellow salt is alone formed, but with *m* nitrophenols, orange salts are obtained which are of the nature of solid solutions of the red and yellow varieties.

The nitro-group not conferring colour on a compound, it follows that the real nitrophenols should be colourless, and their salts must possess the constitution represented by either of the two formulæ:



As an analogous series of coloured salts of dinitroparaffins has been prepared, the change in colour from red to yellow and conversely cannot be due to changes in the nature of the benzene ring. Again, the isomerism existing amongst these salts is not due to one salt being represented in constitution by the first, and the other by the second formula, otherwise benzene derivatives free from nitrogen should give also yellow and red salts. This is not the case (compare Abstr., 1906, i, 856) and these salts are concluded to be structurally identical; they are therefore stereoisomeric and are represented by *syn*- and *anti*-configurations. By analogy with the red and yellow salts of benzene diazosulphonates, the red salt is given the *syn*-formula (I), the yellow the *anti*-formula (II), thus:

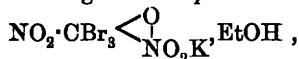


The determination of the actual configuration is not yet possible.

The existence of two classes of coloured *m*-nitrophenol salts is held

to be a proof of their metaquinonoid character, although metaquinones are possibly not capable of existence.

[With N. ROSANOFF.]—The m. p. of 2:4:6-tribromo-3:5-dinitrophenol is 188°, not 194° (compare Jackson and Warren, *Abstr.*, 1894, i, 176), and its *acetyl* derivative forms colourless needles, m. p. 164°. The separation of the orange mixed *potassium* salt,



into the *lemon-yellow* and *red isomerides* must be carried out in absolutely dry solvents. By addition of dry ether and benzene to an alcoholic solution and spontaneous evaporation in a vacuum over sulphuric acid, the yellow salt crystallises out first. From the mother liquor the mixed salt is next precipitated, and, finally, the vermilion-red salt is obtained. After recrystallising the salts two or three times, a yield of 2% of the yellow salt and 4–5% of the red is obtained. The two salts are microcrystalline and their solutions are yellow and dark orange respectively; the solutions gradually change in colour, due to isodynamic change. When in *N/10* solution the yellow solution freshly prepared absorbs light up to a wave length of 508, the dark orange to 523, whereas the orange mixed salt gives absorption up to 521. By following the change in the spectroscope, the yellow solution had changed its absorption from 508 to 519 in ten hours, and in 2·5 months the less unstable red solution from 528 to 523. There is therefore in the equilibrated orange mixture roughly 66% of the red salt. These salts are also labile in the solid state.

The *cæsium* salts are the only alkali salts in addition to the *potassium* capable of separate existence and can be separated into a yellow and red variety from the orange mixture. The red salt is much less stable than the corresponding *potassium* salt.

The *sodium* salt, prepared either at the ordinary temperature or at –75°, is yellow and gives a yellow aqueous solution, the *lithium* and unstable *ammonium* salts are also yellow. The following metals give mixed salts: *rubidium*, *barium*, *calcium*, *thallium*, as also the *pyridine* salt. These salts in solution do not show isodynamic change.

The *potassium* salt is the only salt of 3:5-dinitrophenol to give an indication of two forms, as it alters its colour on heating to 100°; the mixed orange salt could not be separated. The *rubidium* salt is orange; the *barium*, light orange; the *sodium*, *lithium*, *ammonium*, and *silver* salts are pure yellow.

[With E. BORCHERS.]—The *potassium* and *sodium* salts of *m*-nitrophenol are yellow at low temperatures, but change in solution at 0° into the red salt. These salts could not be isolated. An ethereal or benzene solution of 1 mol. of *m*-nitrophenol and 1 mol. of ammonia is practically colourless, but excess of ammonia precipitates the orange-coloured *ammonium* salt.

The *potassium* and *sodium* salts of *o*-nitrophenol when prepared at low temperatures are lemon-yellow, but these salts are very unstable, giving immediately the scarlet salts at –75° with excess of ethoxide. The yellow *ammonium* salt is only stable at low temperatures; at the ordinary temperature it is orange, and scarlet plates have been

obtained from solid *o*-nitrophenol (compare Merz and Ris, *Ber.*, 1886, 19, 1752).

On the other hand, the salts of *p*-nitrophenol behave differently from those of *o*-nitrophenol. The red salts are the exception; at low temperatures, yellowish-white salts are obtained.

The ethyl ester of 2 : 6-dinitro-*p*-cresol is colourless. The potassium and sodium salts of this cresol are orange-yellow and orange when anhydrous; when hydrated they are red. The ammonium salt is red when anhydrous and orange-yellow when hydrated; the *cæsium*, *barium*, and *calcium* salts are anhydrous and orange-yellow, the *silver* salt is red (compare Städel, *Abstr.*, 1883, 662).

*Pentamethylenediamine picrate* when first prepared is red, but in a desiccator it becomes yellow. At  $-80^{\circ}$  ammonium picrate is red, at the ordinary temperature yellow. When prepared in benzene or ether solution, the potassium salts are vermilion-red, the potassium salt becoming yellow. The sodium salt is more stable, but by washing with alcohol below  $0^{\circ}$  it also becomes yellow. W. R.

**Acyl Derivatives of *o*- and *p*-Aminophenol.** J. BISHOP TINGLE and L. F. WILLIAMS (*Amer. Chem. J.*, 1907, 37, 51—71).—*o*-Benzoylamino-phenyl benzoate, m. p.  $180^{\circ}$ , prepared by the action of benzoyl chloride on *o*-acetylaminophenol, crystallises in white, slender needles. The following compounds of *o*-aminophenol are also described. *p*-Nitrobenzoyl-*o*-aminophenol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p.  $220^{\circ}$ , forms small, yellow crystals; its *p*-nitrobenzoate,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , m. p.  $219^{\circ}$ , light, feathery crystals. *m*-Nitrobenzoyl-*o*-aminophenol, m. p.  $206^{\circ}$ , forms small, yellow crystals; the *m*-nitrobenzoate, m. p.  $188^{\circ}$ , light, flaky plates. Benzenesulphonyl-*o*-aminophenol,

$\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p.  $141^{\circ}$ , forms small, white needles; its benzenesulphonate,

$\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{SO}_2\text{Ph}$ , m. p.  $134^{\circ}$  (not  $81-83^{\circ}$ , Georgescu, *Abstr.*, 1900, i, 344), faintly red, columnar crystals.

*p*-Acetylaminophenol, m. p.  $166^{\circ}$  (not  $179^{\circ}$ , Morse, *Abstr.*, 1878, 416), when treated with acetyl chloride, yields the acetate previously obtained by Ladenburg (*Abstr.*, 1877, i, 305) by a less convenient method. *p*-Acetylaminophenol shows a different behaviour with benzoyl chloride from that of the corresponding *o*-derivative, and yields *p*-acetylaminophenyl benzoate,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$ , m. p.  $166.5^{\circ}$ , which forms white, feathery crystals (compare Reverdin, this vol., i, 37). The following compounds of *p*-aminophenol have also been prepared. *p*-Benzoylamino-phenol, m. p.  $227.5^{\circ}$  (not  $205-207^{\circ}$ , as stated by Smith, *Abstr.*, 1892, i, 490). *p*-Nitrobenzoyl-*p*-aminophenol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p.  $258^{\circ}$ , forms small, lustrous, orange-red, monoclinic crystals; its *p*-nitrobenzoate,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , m. p.  $264^{\circ}$ , light yellow, microscopic crystals. *m*-Nitrobenzoyl-*p*-aminophenol, m. p.  $215-216^{\circ}$ , forms light yellow, slender needles; its *m*-nitrobenzoate, m. p.  $264-265^{\circ}$ , a light grey powder. By the action

of benzenesulphonic chloride on *p*-aminophenol, benzenesulphonyl-*p*-aminophenol is produced, but the di-benzenesulphonyl derivative described by Georgescu (*loc. cit.*) could not be obtained.

Experiments have been made at 0°, at the ordinary temperature, and at 240–250° with the object of obtaining tribenzoyl derivatives of *o*- and *p*-aminophenol, but without success. E. G.

**Preparation of Thio-derivatives of Quinol and its Chloro-compounds.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 175070).—*Potassium quinolthiosulphonate* separates as a colourless, crystalline powder on adding aqueous sodium thiosulphate to a warm acetic acid solution of *p*-benzoquinone, and subsequently salting out with potassium chloride. The corresponding *mercaptan*,  $\text{SH} \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , m. p. 119–120°, is obtained in colourless needles on reducing the preceding compound with zinc dust and an acid. The sodium derivative of the mercaptan, on treatment with iodine, furnishes the *disulphide*, m. p. 185°. The mercaptan and benzoquinone together form the *mono-sulphide*, m. p. 227–229°. Quinolthiosulphonic acid on oxidation with potassium dichromate yields the corresponding quinonethiosulphonic acid.

*Potassium  $\alpha$ -quinoldithiosulphonate*, obtained from benzoquinone and a larger proportion of sodium thiosulphate, is very soluble in water, but dissolves only sparingly in alcohol. The mercaptan forms colourless leaflets, m. p. 190–192°.

*Potassium  $\beta$ -quinolthiosulphonate*, isomeric with the preceding salt, was obtained by dissolving benzoquinonethiosulphonic acid in dilute acetic acid at 65–70°, and pouring this solution into aqueous sodium thiosulphate at 10°; on adding potassium chloride the moderately soluble potassium salt separated, and when crystallised from water formed white needles. The mercaptan forms white needles, m. p. 165–166°. These two quinoldithiosulphonic acids when oxidised by acidified dichromate yield the corresponding benzoquinonethio-acids.

*Potassium quinoltetrathiosulphonic acid* is the ultimate product of the action of excess of thiosulphate on quinol or benzoquinone in the presence of oxidising agents; it forms white, felted needles sparingly soluble in cold and readily so in hot water.

*2 : 6-Dichloroquinol-3-thiosulphonic acid*, from dichloroquinol and sodium thiosulphate, forms soluble, yellowish-white needles; the mercaptan has m. p. 171–172°. It is readily oxidised to the corresponding quinone.

*Potassium 2 : 6-dichloroquinoldithiosulphonate* oxidises to a quinone, and yields a mercaptan, m. p. 215°.

*Benzoylquinolmercaptan*,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{S} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , obtained by mixing benzoquinone and thiobenzoic acid in ethereal solution; m. p. 158–169°; the *tribenzoyl* derivative,  $\text{C}_6\text{H}_3(\text{OBz})_3 \cdot \text{SBz}$ , m. p. 116–118°.

*Quinol xanthate*,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{S} \cdot \text{CS} \cdot \text{OEt}$ , produced by the interaction of benzoquinone and potassium xanthate, is a green, crystalline powder, m. p. 75–79°.

Thio-derivatives of quinol were also obtained by the interaction of benzoquinone with thiocyanic and trithiocarbonic acids.

G. T. M.

**Lupeol.** N. H. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 466—470. Compare Likiernik, *Abstr.*, 1891, 551, 1446; Romburgh, *Abstr.*, 1904, i, 905).—Sack's alstol (*Diss., Göttingen*, 1901) is not a pure substance.

The most probable formula for lupeol is  $C_{31}H_{50}O$ . The benzoate, formed by the action of benzoyl chloride and pyridine on lupeol obtained from djelutung, crystallises in slender, flat needles, m. p. 273—274° (corr.), has  $[\alpha]_D + 60.75^\circ$  in chloroform solution, and on hydrolysis yields lupeol crystallising in long needles, m. p. 215° (corr.). When treated with bromine in a mixture of glacial acetic acid and carbon disulphide, the benzoate yields two *monobromo*-derivatives,  $C_{38}H_{53}O_2Br$ , of which the less soluble in acetone separates from ethyl acetate in stout crystals, m. p. 243°, has  $[\alpha]_D + 44.9^\circ$  in chloroform solution, and on hydrolysis forms benzoic acid and a *bromo-alcohol*. The more readily soluble isomeride crystallises from acetone in leaflets.

The action of bromine on lupeol in carbon disulphide solution leads to the formation of a *monobromo*-derivative,  $C_{31}H_{49}OBr$ , which crystallises in needles, m. p. 185° (corr.), and has  $[\alpha]_D + 3.8^\circ$  in chloroform solution.

Lupeol is oxidised by Kiliani's chromic acid mixture (*Abstr.*, 1902, i, 46), yielding *lupeone*,  $C_{31}H_{48}O$ , which forms rhombo-dipyramidal crystals, m. p. 170° (corr.), has  $[\alpha]_D + 63.1^\circ$  in chloroform solution, and is reduced to lupeol by sodium and alcohol; hence, if lupeone contains an ethylene linking this cannot be in the  $\alpha\beta$ -position to the carbonyl group. The *oxime*,  $C_{31}H_{49}ON$ , crystallises in soft, white needles, m. p. 278.5° (decomp.), and has  $[\alpha]_D + 29.5^\circ$  in chloroform solution. The action of bromine on lupeone in glacial acetic acid solution leads to the formation of hydrogen bromide and a *dibromo*-derivative,  $C_{31}H_{46}OBr_2$ , which crystallises in hard needles, m. p. 254° (decomp.), and has  $[\alpha]_D + 21.4^\circ$  in chloroform solution. The *cyanohydrin*,  $C_{32}H_{49}ON$ , formed by the action of hydrogen cyanide on lupeone in ethereal solution in presence of a trace of ammonia, crystallises in stout needles, m. p. 194° (decomp.), and when treated with 1 mol. of hydrogen chloride and 1 mol. of ethyl alcohol yields a *product*, m. p. 235°.

Neither lupeol nor its acetate is oxidised by potassium permanganate in boiling acetone solution, whilst the benzoate and lupeone in benzene solution at 40° are not acted on by Kiliani's chromic acid mixture; at higher temperatures lupeone forms acid *products* which cannot be crystallised. When oxidised with potassium permanganate in sulphuric acid solution, lupeol yields a mixture of products from which lupeone alone has been isolated; the action of alkaline permanganate on lupeol leads to complete oxidation.

The *product*,  $C_{33}H_{50}O_3$ , obtained by oxidation of lupeol acetate with chromic acid in acetic acid solution, does not redden blue litmus, but can be titrated with alcoholic potassium hydroxide in presence of phenolphthalein, and on hydrolysis yields a *product*,  $C_{31}H_{50}O_3$ , which crystallises in needles, m. p. 263—265°, and behaves towards litmus and phenolphthalein in the same manner as the acetyl derivative. The hydrolysis product forms a *potassium* salt crystallising in needles, and yields a

*diacetyl* derivative,  $C_{35}H_{54}O_5$ , which is formed also directly from the oxidation product.

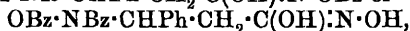
Lupeol and lupeone both give the reaction for unsaturated compounds with Hübl's iodine reagent. G. Y.

**Cholesterol.** VIII. ADOLF WINDAUS (*Ber.*, 1907, 40, 257—261. Compare Abstr., 1906, i, 580).—The oxidation of cholesterol in benzene solution by alkaline potassium permanganate leads to the formation of a crystalline neutral *substance*,  $C_{27}H_{46}O_3$ , m. p.  $236^\circ$ , which does not react with hydroxylamine or phenylhydrazine, yields a *diacetate*,  $C_{31}H_{50}O_5$ , m. p.  $187^\circ$ , and a *dipropionate*,  $C_{35}H_{54}O_5$ , m. p.  $166$ — $167^\circ$ , and by oxidation with chromic and acetic acids is converted into a *diketo*-compound,  $C_{27}H_{42}O_3$ , m. p.  $253^\circ$ ; this is isomeric with Mauthner and Suida's oxysterol (Abstr., 1897, i, 31), and, like the later, yields oxysterolone by treatment with dehydrating agents. This behaviour indicates that the substance,  $C_{27}H_{46}O_3$ , contains three hydroxyl groups; a possible formula is suggested.

C. S.

**Unsaturated Compounds.** IV. Action of Hydroxylamine on Ethyl Cinnamate. THEODOR POSNER (*Ber.*, 1907, 40, 218—230. Compare Abstr., 1904, i, 160; 1905, i, 279; 1906, i, 955; Ley, Abstr., 1898, i, 657; Tingle, Abstr., 1900, i, 544; 1905, i, 930).—The action of hydroxylamine on methyl or ethyl cinnamate in cooled methyl-alcoholic solution is much more complicated than that on cinnamic acid, and leads to the formation of  *$\beta$ -hydroxylaminodihydrocinnamhydroxamoxime hydrate*,  $OH \cdot NH \cdot CHPh \cdot CH_2 \cdot C(NH \cdot OH)_2 \cdot OH$ , which when purified by solution in aqueous ammonia and reprecipitation by evaporation of the ammonia at the ordinary temperature, is obtained as a white, crystalline powder, m. p.  $118$ — $119^\circ$ , or after some days in a vacuum desiccator,  $126^\circ$  (decomp.), and has strong basic but only feeble acid properties; it gives white *precipitates* with lead acetate and mercuric chloride, and with copper sulphate a blue *precipitate*, which on treatment with hydrogen sulphide yields chiefly  *$\beta$ -aminodihydrocinnamic acid* together with a yellow, sparingly soluble *substance*, m. p.  $174^\circ$ , containing only 4.9% of nitrogen. In aqueous solution in contact with air at the ordinary temperature, the hydroxamoxime hydrate is converted partially into 3-phenylisooxazolone, whereas when boiled with ammonia in an open dish on the water-bath it yields  *$\beta$ -hydroxylaminodihydrocinnamic acid* and only traces of 3-phenylisooxazolone. The hydroxamoxime hydrate is converted by boiling water into  *$\beta$ -aminodihydrocinnamic acid* obtained in a 52% yield, or by alcoholic hydrogen chloride at  $0^\circ$  into  *$\beta$ -ethoxylaminodihydrocinnamic acid*, or by the action of sodium nitrite in cooled dilute sulphuric acid solution into  *$\beta$ -dihydroxydihydrocinnamic acid*.

The action of benzoyl chloride on the hydroxamoxime hydrate in pyridine solution leads to the formation of three products: (a) *dibenzhydroxamic acid*; (b) *dibenzoyl- $\beta$ -hydroxylaminodihydrocinnamhydroxamic acid*,  $OBz \cdot NH \cdot CHPh \cdot CH_2 \cdot C(OH) \cdot N \cdot OBz$  or



m. p.  $136$ — $137^\circ$ , which crystallises from alcohol, and (c) a *hexa-*

*benzoyl* derivative,  $\text{OBz}\cdot\text{NBz}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{C}(\text{NBz}\cdot\text{OBz})_2\cdot\text{OH}$ , which crystallises from methyl alcohol in needles, m. p.  $100-101^\circ$ . G. Y.

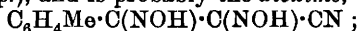
**Resin Acids from Conifers.** VI. ALBERT VESTERBERG (*Ber.*, 1907, 40, 120—123. Compare Abstr., 1906, i, 92; Mach, *ibid.*, 1893, i, 582; 1895, i, 384).—Titrations of abietic acid with standard alcoholic potassium hydroxide, using phenolphthalein as indicator, agree with the formula  $\text{C}_{20}\text{H}_{30}\text{O}_2$  and not with  $\text{C}_{19}\text{H}_{28}\text{O}_2$  (compare Levy, Abstr., 1906, i, 870). When oxidised with sodium hypobromite by Diels and Abderhalden's method (Abstr., 1903, i, 819), a small amount of an acid crystallising in needles, m. p.  $199^\circ$ , was obtained, together with a non-crystalline acid.

*d*-Pimaric acid distils at  $282^\circ/15-20$  mm., and is not racemised during the process. J. J. S.

**Dinitriles and Amyl Nitrite.** JARL LUBLIN (*J. pr. Chem.*, 1906, [ii], 74, 499—531. Compare Abstr., 1904, i, 890; Meyer, Abstr., 1895, i, 582; Euler, Abstr., 1903, i, 298; Euler and Euler, Abstr., 1904, i, 146).—When amyl nitrite is added in excess to *p*-toluacetodinitrile in ethereal solution, a blue coloration and a dark blue to red, sometimes white, precipitate are formed; when boiled for twenty-four hours, the mixture yields (a) the ammonium salt of  $\alpha$ -isonitroso- $\beta$ -nitrosoimino-*p*-tolupropionitrile,  $\text{NO}\cdot\text{N}\cdot\text{C}(\text{C}_7\text{H}_7)\cdot\text{C}(\text{CN})\cdot\text{NONH}_4$ , which crystallises in white needles, m. p.  $156^\circ$  (decomp.), detonates when heated, evolves ammonia with aqueous alkalis, and gives a transient blue coloration with acids; the silver,  $\text{C}_{10}\text{H}_7\text{O}_2\text{N}_4\text{Ag}$ , and barium,  $(\text{C}_{10}\text{H}_7\text{O}_2\text{N}_4)_2\text{Ba}$ , salts of the isonitroso-nitrosoiminonitrile were analysed; and (b) the oxime,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}(\text{CN})\cdot\text{NOH}$ , which is formed also by the action of heat, mineral acids, or acetic acid on the preceding ammonium salt, or of nitrous acid on benzoylacetoneitrile. This separates from benzene in small, slightly yellow crystals, m. p.  $130.5-131^\circ$ , and is hydrolysed only slowly by boiling aqueous sodium hydroxide.

The action of hydroxylamine hydrochloride on the oxime in dilute alcoholic solution leads to the formation of isonitroso-*p*-tolyliso-oxazolone,  $\text{OH}\cdot\text{N}\cdot\text{C}\cdot\text{CO}$   
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}=\text{N}>\text{O}$ , which crystallises in lemon-yellow needles, m. p.  $135.5^\circ$  (decomp.), gives with sodium carbonate solution a stable, with aqueous sodium hydroxide a transient, red coloration, being converted into a substance crystallising in white needles, m. p. about  $95^\circ$  (decomp.).

When treated with hydroxylamine hydrochloride and sodium carbonate in aqueous alcoholic solution, the oxime yields a product which forms white crystals, m. p.  $172^\circ$ , and may have the constitution  $\text{CN}\cdot\text{C}\cdot\text{N}$   
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}\cdot\text{N}>\text{O}$ , whilst if an excess of hydroxylamine is employed in the reaction the product forms white crystals, m. p.  $101-102^\circ$  (decomp.), and is probably the dioxime,



it gives with ferric chloride a red, with hydrogen chloride or amyl nitrite in ethereal solution a blue, coloration, and slowly changes into the preceding substance, m. p.  $172^\circ$ .

The ammonium salt of  $\alpha$ -isonitroso- $\beta$ -nitrosoiminophenylpropionitrile,  $C_9H_9O_2N_3$ , prepared together with isonitrosocyanacetophenone by the action of amyl nitrite on benzacetodinitrile, crystallises in white leaflets, m. p. 152—152.5° (decomp.), detonates when heated, and is identical with the product of the interaction of nitrous acid and benzacetodinitrile (Meyer, *loc. cit.*). The action of hydroxylamine hydrochloride on the oxime leads to the formation of isonitrosophenyl-oxazolone and ammonia.

The ammonium salt of  $\alpha$ -isonitroso- $\beta$ -nitrosoiminobutyronitrile, formed from amyl nitrite and diacetonitrile, crystallises in white needles or leaflets, m. p. 122°; an oxime corresponding with isonitrosocyanacetophenone could not be isolated.

*p*-Tolupropionitrile, acetopropionitrile, and Haller's imino-ether,  $CH_2Bz \cdot C(OEt) : NH$  (Abstr., 1887, 826), do not react with amyl nitrite in ethereal solution.

The oxime,  $C_6H_4Me \cdot C(NOH) \cdot CH_2 \cdot CN$ , prepared by Probst's method (*Diss., Leipzig*, 1894), m. p. 150—151°, is converted by hydrogen chloride in ethereal solution into a chlorinated substance, which evolves ammonia when boiled with aqueous sodium hydroxide, and with ethereal amyl nitrite yields a blue solution, and on evaporation a small amount of a product, m. p. about 205°.

The crystalline substance, m. p. 105—108° (96°, Burns, Abstr., 1893, i, 314), formed by the action of hydroxylamine hydrochloride on diacetonitrile, evolves ammonia when treated successively with hydrogen chloride in ethereal solution and aqueous sodium hydroxide.

The action of ethereal amyl nitrite on phenylisooxazoloneimide (Obrégia, Abstr., 1892, 324) and treatment of the product with aqueous sodium hydroxide leads to the formation of a red substance, 
$$\begin{array}{c} CPh \cdot CH_2 \\ | \\ N \text{---} O > C : N \cdot NO \text{ or } CPh \cdot C(NOH) \\ | \\ N \text{---} O > C : NH \end{array}$$
 m. p. 63° (decomp.), which forms a resin when evaporated with ether. G. Y.

[Dinitriles and Amyl Nitrite.] ERNST VON MEYER (*J. pr. Chem.*, 1906, [ii], 74, 532. Compare preceding abstract).—The product of the action of hydroxylamine on toluacetodinitrile (Probst, *Diss., Leipzig*, 1894), m. p. 151°, is hydrolysed by alcoholic hydrogen chloride, forming *p*-tolyl cyanomethyl ketone, m. p. 106°, hydroxylamine, and traces of ammonia. The statements of Burns on the formation of an oxime from diacetonitrile (Abstr., 1893, i, 314) are confirmed. G. Y.

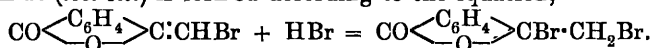
**Acetophenone-*o*-carboxylic Acid.** SIEGMUND GABRIEL (*Ber.*, 1907, 40, 71—83).—Gabriel and Michael found (Abstr., 1878, 229) that, when acetophenone-*o*-carboxylic acid (1 mol.) is acted on by bromine in glacial acetic acid solution at 100°, the monobromo-derivative,  $CO_2H \cdot C_6H_4 \cdot CO \cdot CH_2Br$ , was not obtained, but the compound,  $C_6H_5BrO_2$ , containing 1 mol. of water less than the monobromo-derivative, and having the property of uniting with 1 mol. of bromine, was formed. Gabriel showed subsequently (Abstr., 1884, 1176) that the latter compound was bromomethylenephthalide. The author has now continued the study of the action in question.

$\omega$ -Bromoacetophenone-*o*-carboxylic acid,  $CO_2H \cdot C_6H_4 \cdot CO \cdot CH_2Br$ , pre-

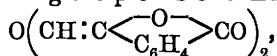


pared by the addition of bromine to a solution of acetophenone-*o*-carboxylic acid in glacial acetic acid on a water-bath and then evaporating the product under diminished pressure at about 60°, separates from chloroform in snow-white, glassy needles or oblong plates, m. p. 127—128°. Its *methyl ester* crystallises in prisms, m. p. 61—62°.

When heated with a solution of hydrogen bromide in glacial acetic acid for one hour at 100° in a sealed tube, *ω*-bromoacetophenone-*o*-carboxylic acid forms bromomethylenephthalide (*loc. cit.*), according to the equation  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Br} - \text{H}_2\text{O} = \text{C}_6\text{H}_4\langle\text{C}(\text{CHBr})\rangle_{\text{CO}}\text{O}$ , if the solution is evaporated on the water-bath. If, however, the solution is allowed to evaporate spontaneously, methylenephthalide dibromide (*loc. cit.*) is formed according to the equation,



*Hydroxymethylenephthalide*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{C}:\text{CH}\cdot\text{OH}$  (or *formyl-phthalide*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{CH}\cdot\text{CHO}$ ), is obtained as snow-white needles, m. p. 147—148°, when *ω*-bromoacetophenone-*o*-carboxylic acid is boiled with water and the solution is allowed to evaporate spontaneously; it is identical with the compound,  $\text{C}_9\text{H}_6\text{O}_3$ , already described by Michael and Gabriel (*loc. cit.*). It forms a yellow solution with alkalis and reduces Fehling's solution in the cold. By the action of a mixture of fuming hydriodic acid and a little phosphonium iodide, it forms the compound,  $\text{C}_{18}\text{H}_{10}\text{O}_5$ , having the probable formula,



m. p. 240° (decomp.); it is an anhydro-compound, being formed according to the equation,  $2\text{C}_9\text{H}_6\text{O}_3 - \text{H}_2\text{O} = \text{C}_{18}\text{H}_{10}\text{O}_5$ .

The presence of a hydroxy-group in hydroxymethylenephthalide is also indicated by its behaviour on esterification with methyl alcohol according to the hydrogen chloride method, when *methoxymethylenephthalide*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{C}:\text{CH}\cdot\text{OMe}$ , is produced; the latter separates from alcohol in needles, m. p. 75°.

That a double linking is present in the molecule of hydroxymethylenephthalide is attested by its behaviour on bromination. When acted on by bromine in chloroform solution, it forms *formylbromophthalide*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{CBr}\cdot\text{CHO}$ , which separates from alcohol in hexagonal plates, m. p. 85—86°.

In certain reactions, however, hydroxymethylenephthalide behaves as if it were an aldehyde. For example, it forms an *oxime*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{CH}\cdot\text{CH}:\text{N}\cdot\text{OH}$ , which crystallises in silky needles, m. p. 147—152°, the *acetyl* derivative of which has m. p. 154—155°.

The *phenylhydrazone*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{CH}\cdot\text{CH}:\text{N}\cdot\text{NHPh}$ , obtained from hydroxymethylenephthalide and phenylhydrazine, forms yellow needles, m. p. 180°.

Similarly, hydrazine hydrate forms the *azine*,  $C_{18}H_{12}O_4N_2$ , which crystallises in yellow needles, and begins to decompose at about  $220^\circ$ .

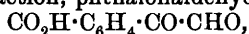
The compound,  $C_{19}H_{13}O_6N$ , obtained by the action of potassium cyanide on  $\omega$ -bromoacetophenone-*o*-carboxylic acid, forms a brown powder, m. p.  $223^\circ$ . It reduces Fehling's solution in the cold.

$\omega$ -Dibromoacetophenone-*o*-carboxylic acid,  $CO_2H \cdot C_6H_4 \cdot CO \cdot CHBr_2$ , prepared by the action of bromine (2 mols.) on a solution of acetophenone-*o*-carboxylic acid in glacial acetic acid, separates from chloroform in tetragonal, colourless plates, m. p.  $131$ – $132^\circ$ . Its *methyl ester* separates from alcohol in hexagonal plates or oblong prisms, m. p.  $112^\circ$ .

By the action of hydroxylamine on  $\omega$ -dibromoacetophenone-*o*-carboxylic acid, both the halogen and the ketonic oxygen of the latter are replaced, with the formation of *phthalonaldehydecaboxylic acid dioxime anhydride*,  $CO \langle \begin{smallmatrix} C_6H_4 \cdot C \cdot CH : N \cdot OH \\ O - N \end{smallmatrix} \rangle$ , which crystallises from glacial acetic acid in silky needles, m. p.  $163^\circ$ .

The behaviour of  $\omega$ -dibromoacetophenone-*o*-carboxylic acid towards phenylhydrazine is analogous, *phthalonaldehydecaboxylic acid osazone anhydride*,  $\begin{smallmatrix} C_6H_4 \cdot C \cdot CH : N_2 \cdot HPh \\ CO - N_2 \cdot Ph \end{smallmatrix}$ , being formed; the latter compound separates from glacial acetic acid in silky needles, m. p.  $228^\circ$ .

When  $\omega$ -dibromoacetophenone-*o*-carboxylic acid is boiled with water, it is converted into phthalidecarboxylic acid,  $CO \langle \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} \rangle CH \cdot CO_2H$ , melting at  $152^\circ$  and identical with the product obtained by Zincke and Schmidt. In this action, phthalonaldehydic acid,



was possibly first formed and then underwent molecular rearrangement into its isomeride.

*Dibromomethylenephthalide*,  $CO \langle \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} \rangle C : CBr_2$ , obtained by the action of concentrated sulphuric acid on  $\omega$ -dibromoacetophenone-*o*-carboxylic acid, separates from alcohol in needles, m. p.  $139$ – $140^\circ$ . Its unsaturated nature is demonstrated by its behaviour towards bromine, when *tetrabromomethylphthalide*,  $CO \langle \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} \rangle CBr \cdot CBr_3$ , is produced; the latter separates from a mixture of benzene and ethyl acetate in glistening pyramids which melt and decompose at  $160$ – $161^\circ$ .  
A. McK.

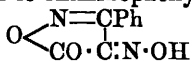
**Catecholcarboxylic Acids.** ANTON PRAXMAREE (*Monatsh.*, 1906, 27, 1199–1209).—Contrary to Miller's statement (*Annalen*, 1883, 220, 113), the action of ammonium carbonate on catechol at  $130$ – $140^\circ$  under pressure leads to the formation of catecholcarboxylic acid only; protocatechuic acid cannot be found in the product. The same result is obtained on heating catechol with glycerol and potassium hydrogen carbonate in a current of carbon dioxide at  $180^\circ$  for twelve to sixteen hours, or at  $210^\circ$  for six to eight hours.

Catecholcarboxylic acid,  $C_7H_6O_4 \cdot \frac{1}{2}H_2O$ , m. p.  $240^\circ$ , decomposes,

evolving carbon dioxide a few degrees above its melting point. The barium,  $(C_7H_5O_4)_2Ba \cdot 4H_2O$  ( $5H_2O$ , Miller, *loc. cit.*), and calcium ( $2\frac{1}{2}H_2O$ ) salts and the ethyl ester, m. p.  $130.5^\circ$  ( $63-64^\circ$ , Schmitt and Hähle, Abstr., 1891, 1366), are described. The methyl ester of the dimethyl ether, m. p.  $57.5^\circ$  ( $47^\circ$ , Fritsch, Abstr., 1898, i, 663), is prepared by the action of methyl iodide and potassium hydroxide on the acid in methyl alcoholic solution. The action of bromine on catecholcarboxylic acid in absence of a solvent leads to the formation of tetrabromocatechol, or in ethereal solution to the formation of this together with *dibromocatecholcarboxylic acid*,  $C_7H_4O_4Br_2$ , which is soluble in water at  $80^\circ$ .

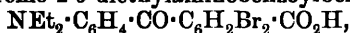
Catecholdicarboxylic acid is formed together with a small amount of catechol by heating the monocarboxylic acid with glycerol, potassium hydrogen carbonate, and a little sodium sulphite in a current of carbon dioxide at  $210^\circ$  for six hours. A product which gives the green coloration of protocathechuic acid with ferric chloride is obtained on heating catechol with sodium hydrogen carbonate and glycerol at a temperature not above  $139^\circ$ . G. Y.

**Ethyl Benzoylglyoxylate.** ANDRÉ WAHL (*Compt. rend.*, 1907, 144, 212—214. Compare Abstr., 1904, i, 556).—*Ethyl benzoylglyoxylate*,  $COPh \cdot CO \cdot CO_2Et$ , prepared by passing nitrous anhydride into a mixture of ethyl benzoylacetate and acetic anhydride dissolved in ether, is an orange-yellow liquid, mobile when freshly prepared and without distinctive odour, b. p.  $150-153^\circ/13$  mm.;  $D_4^{20}$  1.188. It combines with water and alcohol developing much heat, and forming colourless hydrates and alcoholates which do not crystallise. By adding a few drops of piperidine to a molecular mixture of ethyl benzoylglyoxylate and ethyl benzoylacetate, the author has obtained a compound,  $C_{11}H_{12}O_3 \cdot C_{11}H_{10}O_4$ , forming white needles, m. p.  $109-110^\circ$ , and probably identical with that obtained by Sachs and Wolff (Abstr., 1904, i, 876), and having m. p.  $91.5^\circ$ . Ethyl benzoylglyoxylate forms a *monoxime* identical with ethyl *isonitrosobenzoylacetate* and hence having the constitution  $COPh \cdot C(:NOH) \cdot CO_2Et$ ; a dioxime is not formed. Crismer's method gave a small quantity of a crystalline substance which showed the reaction of oximinophenylisooxazolone,

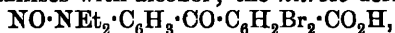


The ester reacts with *o*-phenylenediamine, forming *ethyl 2-phenylquininoxaline-3-carboxylate*, which crystallises in slender, white needles, m. p.  $65-66^\circ$ . It gives a *disemicarbazone*,  $C_{13}H_{16}O_4N_6 \cdot H_2O$ , light yellow needles, m. p.  $185-190^\circ$ , and a *dianilide*,  $C_{23}H_{22}O_3N_2$ , small, yellow needles, m. p.  $127^\circ$ . E. H.

**Condensation Products of Dibromophthalic Acid.** ÉMILE SÉVERIN (*Ann. Sci. Univ. Jassy*, 1907, 4, 141—150).—Most of the work recorded in this paper has been published already (Abstr., 1906, i, 508). 3 : 6-Dibromo-2-*o*-diethylaminobenzoylbenzoic acid,



prepared as already described (*loc. cit.*), furnishes an *ethyl ester*, m. p. 145°, which crystallises with alcohol; the *nitroso-derivative*,



m. p. 155°, crystallises in yellow needles. On reduction of the benzoylbenzoic acid, the corresponding *dibromodiethylaminobenzylbenzoic acid* is produced, which separates from alcohol with difficulty in colourless needles, m. p. 247°, and when warmed with sulphuric acid at 66° furnishes 1-diethylamino-5:8-dibromoanthraquinone, which sublimes in red needles, m. p. 198°.

T. A. H.

**Behaviour of Phenolphthalein towards Highly Concentrated Alkali Hydroxides.** BENJAMIN M. MARGOSCHES (*Zeitsch. angew. Chem.*, 1907, 20, 181—191 and 226—231).—Alkaline solutions containing phenolphthalein may be decolorised by the addition of very concentrated solutions of alkali hydroxides, and to a less extent by the addition of lithium hydroxide. Such solutions recover their pink colour on warming or on dilution; as the colour is, however, not instantaneously restored by dilution, the phenomenon cannot be completely explained by dissociation. The paper contains a very full account of the various theories which have been put forward with regard to the constitution of phenolphthalein and its use as an indicator.

P. H.

**Compounds from Lichens. XVI.** WILHELM ZOPF (*Annalen*, 1907, 352, 1—44. Compare Abstr., 1906, i, 672).—The lichen, *Ramalina subfarinacea*, contains *d*-usnic acid,  $[\alpha]_D^{25} + 492.5^\circ$ , to the extent of  $\frac{1}{3}\%$  and 3 to  $3\frac{1}{2}\%$  of salazinic acid; the product obtained by the action of acetic anhydride on the latter acid has already been described as salazinaric acid (Zopf, Abstr., 1905, i, 789), but is now thought to be the *acetyl* derivative of salazinic acid,  $\text{C}_{21}\text{H}_{16}\text{O}_{11}$ ; its mol. weight was determined cryoscopically in benzene and found to be 455, Hesse's formula for salazinic acid,  $\text{C}_{80}\text{H}_{24}\text{O}_{16}$  (Abstr., 1901, i, 595), cannot therefore be correct.

In addition to *d*-usnic acid ( $[\alpha]_D^{18} + 495.5^\circ$ ), *Ramalina scopulorum* is found to contain a new acid, *scopuloric acid*,  $\text{C}_{19}\text{H}_{16}\text{O}_9$ , which crystallises in white needles, m. p. 260° (decomp.). The *acetyl* derivative,  $\text{C}_{21}\text{H}_{18}\text{O}_{10}$ , crystallises in white needles, m. p. 235—236°. *Ramalina Kullensis* contains about 0.1% of *d*-usnic acid,  $[\alpha]_D^{25} + 461.9^\circ$ , and 2% of *kullensisic acid*,  $\text{C}_{22}\text{H}_{18}\text{O}_{12}$ , a substance not yet met with in any other lichen; it crystallises in white needles and carbonises at 260°.

Only *d*-usnic acid was obtained from *Ramalina minuscula*, whilst *R. Landroënsis* contains in addition to about 0.5% of *d*-usnic acid about 0.1% of *landroënsin*, which crystallises from benzene in small, rhombic plates.

The lichen, *Ramalina obtusata* (*R. minuscula* var. *obtusata*, *R. dilacerata* var. *obtusata*), contains only small quantities of *d*-usnic acid,  $[\alpha]_D^{25} + 474.2^\circ$ , together with two new acids. *Ramalinelllic acid* crystallises from acetone in small needles, m. p. 169°. *Obtusatic acid* crystallises in needles, m. p. 191°.

*Cladonia fimbriata* var. *simplex*, obtained from Daun in Eifel, was found to differ from a *Cladonia fimbriata* var. *simplex*, obtained from the Dortmund-Ems Canal near Münster i. W., in that the first con-

tained fumaroprotocetraric acid together with fimbriatic acid, whereas the latter lichen, besides these two acids also contained atranoric acid; it is therefore probable that they are specifically different. *Fimbriatic acid* crystallises from ether in leaflets, m. p. 98—99°; it reduces potassium permanganate immediately in alkaline solution. The lichen, *Cladonia fimbriata* var. *cornuto-radiata*, contains only fumaroprotocetraric acid. Hesse obtained from this lichen, called wrongly by him *C. fimbriata* var. *chordalis* (compare Abstr., 1901, i, 149), protocetraric acid and not fumaroprotocetraric acid, probably because he employed sodium hydrogen carbonate to extract the acids from the lichen, and thus decomposed the fumaroprotocetraric acid into fumaric and protocetraric acids. Closely related to this latter lichen is *Cladonia pityrea* var. *cladomorpha*, since this also contains only fumaroprotocetraric acid. *Cladonia squamosa* var. *denticollis* contains squamatic acid, but not usnic acid.

*Cladonia silvatica* var. *condensata*, besides *l*-usnic acid,  $[\alpha]_D^{25} - 499.5^\circ$ , contains a substance which, since it is relatively soluble in cold benzene and ether, is not fumaroprotocetraric acid; as the latter acid together with *d*-usnic acid is present in the typical *C. silvatica* (Zopf, Abstr., 1906, i, 673), *C. silvatica* var. *condensata* cannot be regarded as a variety of *C. silvatica*, but must either be regarded as a variety of *C. alpestris* or, better, be named simply *C. condensata*.

*Cladonia verticillata* var. *subcervicornis* contains about 1% of fumaroprotocetraric acid and a small quantity of atranoric acid; there is also present a small amount of a red pigment, *cervicornin*, a red, amorphous substance coloured blue by strong sulphuric acid, and violet to violet-brown by potassium and sodium hydroxides.

*Cladonia chlorophæa* contains fumaroprotocetraric acid together with *chlorophæic acid*, which crystallises in leaflets, m. p. 169° (decomp.).

*Cladonia gracilis* var. *chordalis* contains only fumaroprotocetraric acid; *C. crispata* var. *gracilescens* contains only squamatic acid. The same acid is also present in *C. squamosa* var. *multibrachiata* f. *pseudocrispata* and *C. squamosa* var. *multibrachiata* f. *turfacea*.

*Hypogymnia farinacea* contains about 0.5% of atranoric acid together with about 4.5% of *farinacinic acid*,  $C_{26}H_{32}O_8$ ; this acid crystallises in white needles, m. p. 202—203°; its mol. weight was determined in acetone; it does not taste bitter. When heated with acetic anhydride, a substance, m. p. 156—157°, is obtained. It is possible that this acid is identical with Hesse's physodic acid (Abstr., 1898, i, 679).

W. H. G.

**Derivatives of Methylvanillin [2:4-Dimethoxybenzaldehyde].** FRITZ JULIUSBERG (*Ber.*, 1907, 40, 119—120).—2:4-Dimethoxybenzaldehyde, obtained by methylating vanillin by means of sodium ethoxide and methyl iodide, has m. p. 47°. 2:4-Dimethoxybenzaldehyde-phenylhydrazone,  $C_6H_3(OMe)_2 \cdot CH:N \cdot NPh$ , has m. p. 121°.

1:2-Dimethoxy-4-benzaldoxime,  $C_6H_3(OMe)_2 \cdot CH:N \cdot OH$ , obtained by the action of hydroxylamine on the aldehyde, softens at 87° and has m. p. 90°.

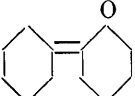
1:2-Dimethoxy-4-benzylamine hydrochloride,  
 $C_6H_3(OMe)_2 \cdot CH_2 \cdot NH_2 \cdot HCl$ ,

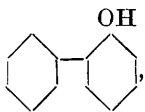
obtained by the reduction of the preceding oxime with sodium amalgam and acetic acid, has m. p. 257—258°. A. McK.

**Influence of Cyclic Linking on Reactivity.** PAVEL PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1907, [ii], 75, 61—64. Compare Abstr., 1900, i, 421; 1901, i, 506; 1903, i, 440; *ibid.*, ii, 719; 1905, i, 355, 742; 1906, ii, 341).—The author replies to Stewart and Baly (*Trans.*, 1906, 89, 489) that the relations which he has observed (*loc. cit.*) to exist between the velocity of reaction and the structure of ketones are completely analogous to those found by Menshutkin in the case of aliphatic and aromatic alcohols and amines in which all possibility of tautomerism is excluded.

The author compares his theoretical views which have been described previously (*loc. cit.*) with those of Menshutkin (*Trans.*, 1906, 89, 1532). G. Y.

**Condensation Products from cycloHexanone.** OTTO WALLACH (*Ber.*, 1907, 40, 70—71. Compare Abstr., 1906, i, 514).—The chloride,  $C_{12}H_{19}OCl$ , obtained by passing a current of dry hydrogen chloride into cyclohexanone, forms colourless crystals, m. p. 41—43°. On rise of temperature, it loses hydrogen chloride and forms cyclo-

hexene-2-cyclohexanone, , which, on reduction, forms the

saturated alcohol, cyclohexyl-2-cyclohexanol, , b. p.

265—270°, m. p. 30—31°. The latter compound, when warmed with hydriodic acid, forms the completely hydrogenated diphenyl, dicyclohexyl,  $C_6H_{11} \cdot C_6H_{11}$ , already described by Borsche and Lange (*Abstr.*, 1905, i, 765).

*Benzylidenecyclohexanone*,  $C_6H_4O \cdot CHPh$ , has m. p. 53°. *Dibenzylidenecyclohexanone*,  $C_{13}H_{14}O$ , has m. p. 116—118°.

By the action of hydroxylamine on monobenzylidenecyclohexanone, a compound of m. p. 104°, crystallising in needles, is obtained.

A. McK.

**Synthesis of Derivatives of cycloHexane.** 3:3-Dimethyl- and 3:3:6-Trimethyl-cyclohexanones. GUSTAV BLANC (*Compt. rend.*, 1907, 144, 143—144. Compare Abstr., 1906, i, 399).—The anhydride,  $CH_2 \begin{smallmatrix} \text{CMe}_2 \cdot CH_2 \cdot CO \\ \text{CH}_2 - CH_2 - CO \end{smallmatrix} O$ , obtained from  $\beta\beta$ -dimethylpimelic acid by the action of acetic anhydride, loses carbon dioxide on slow distillation at the ordinary pressure, and gives the 3:3-dimethylcyclohexanone already described by Léser (*Abstr.*, 1899, i, 743). This compound forms a semicarbazone crystallising in needles, m. p. 203° (Léser gives 198°). On reduction by means of sodium and absolute alcohol it gives the alcohol,  $CH_2 \begin{smallmatrix} \text{CMe}_2 \cdot CH_2 \\ \text{CH}_2 - CH_2 \end{smallmatrix} CH \cdot OH$ , obtained by Crossley and Renouf (*Trans.*, 1905, 87, 1487).

Similarly, slow distillation of  $\beta\beta$ -trimethylpimelic anhydride gives 3:3:6-trimethylcyclohexanone,  $\text{CH}_2\left<\begin{smallmatrix} \text{CMe}_2-\text{CH}_2 \\ \text{CH}_2\cdot\text{CHMe} \end{smallmatrix}\right>\text{CO}$ , a mobile liquid, b. p.  $186^\circ$ , of strong menthone-like odour. The semicarbazone has m. p.  $170^\circ$ . E. H.

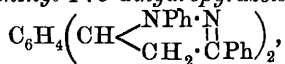
Change of 2-isoNitroso-1-ketohydrindene into Homophthalamic Acid. WALTER PETERS (*Ber.*, 1907, 40, 240—241).—The oxime is unchanged by cold hydrochloric and acetic acids, is oxidised to phthalic acid by nitric acid, and is converted by concentrated sulphuric acid at  $0^\circ$  into Gabriel's homophthalamic acid (*Abstr.*, 1887, 726). C. S.

Condensation of Cinnamyl Chloride with *o*-Cresol. GUSTAV NEURATH (*Monatsh.*, 1906, 27, 1145—1156. Compare Feuerstein and Kostanecki, *Abstr.*, 1898, i, 370; Kostanecki and Tambor, *Abstr.*, 1899, i, 704).—*p*-Hydroxy-*m*-tolyl styryl ketone (4'-hydroxy-3'-methylchalkone),  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$ , prepared by the action of cinnamyl chloride and aluminium chloride on *o*-cresol in nitrobenzene solution, or by heating *o*-cresol with cinnamic acid and zinc chloride at  $200^\circ$ , crystallises from water in reddish-yellow, nacreous needles, m. p.  $137^\circ$  (corr.), and is soluble in aqueous alkalis.

The acetyl derivative,  $\text{C}_{18}\text{H}_{16}\text{O}_3$ , crystallises in needles, m. p.  $72^\circ$  (corr.); the oxime,  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}$ , forms a ruby-red, crystalline mass, m. p.  $49^\circ$  (corr.). The dibromide,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHPhBr}$ , formed by the action of bromine on the unsaturated ketone in ethereal solution, separates in yellowish-red crystals, m. p.  $135^\circ$  (corr.). G. Y.

Condensation of Terephthalaldehyde with Ketones. HANS VON LENDENFELD (*Monatsh.*, 1906, 27, 969—980. Compare Thiele and Winter, *Abstr.*, 1900, i, 500; Thiele and Günther, and Thiele and Falk, *Abstr.*, 1906, i, 750).—The condensation of terephthalaldehyde with ketones in hot alcoholic potassium hydroxide solution leads to the formation of unsaturated ketones, or, in cooled glacial acetic acid solution in presence of hydrogen chloride, to that of the corresponding hydrogen chloride additive products. Aldols are not formed.

Terephthalaldehyde and acetophenone yield a mixture of *p*-aldehydobenzylideneacetophenone,  $\text{COH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$ , which crystallises from methyl alcohol in slightly yellow needles, m. p.  $125^\circ$ , and forms a yellow solution in concentrated sulphuric acid, and terephthalylidenediacetophenone,  $\text{C}_6\text{H}_4[\text{CH}\cdot\text{CH}\cdot\text{COPh}]_2$ , which crystallises from chloroform in yellow, hexagonal plates, m. p.  $200\text{--}201^\circ$ , and is insoluble in methyl alcohol. With phenylhydrazine the latter substance forms *p*-phenylenebis-1:3-diphenyl-4:5-dihydropyrazole,



which crystallises in colourless needles, m. p.  $300^\circ$  (slight decomp.), and gives Knorr's pyrazoline reaction.

The additive product,  $\text{C}_6\text{H}_4[\text{CHCl}\cdot\text{CH}_2\cdot\text{COPh}]_2$ , crystallises from nitrobenzene in colourless needles, m. p.  $194\text{--}195^\circ$ , and at  $160\text{--}170^\circ$

gradually decomposes, yielding terephthalylidenediacetophenone and hydrogen chloride.

The *condensation product* of terephthalaldehyde with phenyl ethyl ketone,  $C_6H_4[CH:CH:CO\cdot C_6H_5]_2$ , crystallises from alcohol in colourless, hexagonal leaflets, m. p.  $162^\circ$ , and reacts with phenylhydrazine, forming a *product* which crystallises from pyridine in yellow needles, sinters at  $245^\circ$ , and is decomposed to a clear liquid at  $254^\circ$ . The hydrogen chloride *additive product*,  $C_6H_4[CHCl\cdot CHMe\cdot CO\cdot C_6H_5]_2$ , crystallises from benzene in long, rhombic plates, decomposing at  $240^\circ$  yielding the unsaturated ketone.

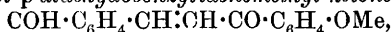
*p-Tolyl p-aldehydobenzylidenemethyl ketone,*



formed from a molecular mixture of terephthalaldehyde and *p*-tolyl methyl ketone, crystallises in small, matted, yellow needles, m. p.  $130^\circ$ . The *phenylhydrazone*,  $C_{23}H_{20}ON_2$ , forms red needles, m. p. about  $224^\circ$ .

The *diketone*,  $C_6H_4[CH:CH\cdot CO\cdot C_7H_7]_2$ , formed from 1 mol. of terephthalaldehyde and 2 mols. of *p*-tolyl methyl ketone, crystallises from alcohol in needles, m. p.  $236$ — $238^\circ$ , gives an orange-red coloration with concentrated sulphuric acid, and reacts with phenylhydrazine in glacial acetic acid solution, forming an amorphous product which gives the pyrazoline reaction. The hydrogen chloride *additive product*,  $C_6H_4[CHCl\cdot CH_2\cdot CO\cdot C_7H_7]_2$ , crystallises in colourless needles, m. p.  $228$ — $230^\circ$ , and yields the unsaturated diketone when heated in a vacuum at  $170^\circ$ .

*p-Methoxyphenol p-aldehydobenzylidenemethyl ketone,*



obtained by the interaction of terephthalaldehyde and anisyl methyl ketone in molecular proportions, crystallises in large, yellow needles, m. p.  $121^\circ$ ; the *phenylhydrazone*,  $C_{23}H_{20}O_2N_2$ , crystallises in reddish-yellow needles, m. p.  $208^\circ$  (decomp.).

The *diketone*,  $C_6H_4[CH:CH\cdot CO\cdot C_6H_4\cdot OMe]_2$ , forms large, yellow leaflets, m. p.  $250^\circ$ , and gives a red coloration with concentrated sulphuric acid. The product formed by the action of hydrogen chloride on terephthalaldehyde and anisyl methyl ketone in glacial acetic acid solution is identical with that obtained by the condensation in presence of alcoholic potassium hydroxide. G. Y.

### Halogen Derivatives of 1:3:4-Triketocyclopentane. III.

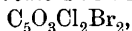
FRANZ HENLE (*Annalen*, 1907, 352, 45—53. Compare Abstr., 1907, i, 144, 161).—Tetrahalogen derivatives of 1:3:4-triketocyclopentane cannot be prepared by the direct bromination or chlorination of chlorotriketocyclopentane; they are, however, obtained by acting on either tribromotriketocyclopentane or chlorodibromotriketocyclopentane with phosphorus pentachloride; phosphorus pentabromide does not react like phosphorus pentachloride; it replaces a hydroxyl group by bromine, so that from tribromotriketocyclopentane, tetrabromodiketocyclopentane is obtained.

Chlorodibromotriketocyclopentane may be prepared by acting on chloro-1:3:4-triketocyclopentane dissolved in thionyl chloride with bromine. When treated with phosphorus pentachloride it gives



*trichlorobromo-1 : 3 : 4-triketocyclopentane*,  $C_5O_3Cl_3Br$ , which crystallises in faintly yellow plates, m. p.  $85^\circ$ .

Tribromo-1 : 3 : 4-triketocyclopentane is converted by phosphorus pentachloride into *dichlorodibromo-1 : 3 : 4-triketocyclopentane*,



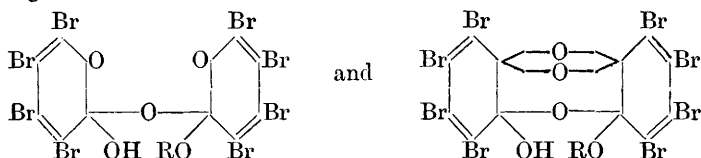
which crystallises in yellow prisms, m. p.  $102^\circ$ . With phosphorus pentabromide, however, *tetrabromo-1 : 3-diketocyclopentene*,  $C_5O_2Br_4$ , is obtained, which crystallises in yellow needles, m. p.  $142^\circ$ .

By heating dichlorodibromo-1 : 3 : 4-triketocyclopentane with phosphorus pentachloride in sealed tubes at  $280-300^\circ$ , octachlorocyclopentene,  $C_5Cl_8$ , is formed, identical with that described by Zincke (Abstr., 1890, 1256).

W. H. G.

**Constitution of the  $\alpha$ - and  $\beta$ -Additive Compounds of Alcohols and Tetrabromo-*o*-benzoquinone.** C. LORING JACKSON and ROBERT D. MACLAURIN (*Amer. Chem. J.*, 1907, 37, 87—106).—Jackson and Porter (Abstr., 1903, i, 266 ; 1904, i, 254) have described two series of additive compounds,  $2C_6Br_4O_2 \cdot R \cdot OH$ , obtained by the combination of tetrabromo-*o*-benzoquinone with alcohols. The  $\alpha$ -compounds are formed by the direct action of alcohols on the quinone at the ordinary temperature, and are converted into the  $\beta$ -compounds by the action of hot dilute sodium hydroxide or by means of acetic anhydride. Further work on these substances has been carried out by Jackson and Carlton (Abstr., 1905, i, 907) and by Jackson and Russe (Abstr., 1906, i, 288).

Further investigation has led to the conclusion that the  $\alpha$ - and  $\beta$ -compounds have respectively the constitutions expressed by the following formulæ :



The reasons for adopting these formulæ in preference to those previously assigned to these compounds are fully discussed and are based chiefly on the facts that the regulated action of acetic anhydride converts the  $\alpha$ -benzyl compound into the  $\beta$ -compound and that the  $\beta$  compounds are remarkably stable. In accordance with these formulæ, the  $\alpha$ - and  $\beta$ -methyl compounds are termed respectively octabromo-1-methoxy-1'-hydroxy-*o*-quino-1-monoxide and octabromo-1-methoxy-1'-hydroxy-*o*-quino-1 : 2 : 2-trioxide.

On adding a considerable quantity of sodium hydroxide solution to hexachloro-*o*-quinocatechol ether,  $C_6Cl_4O_2 \cdot C_6Cl_2O_2$ , an additive compound,  $C_{12}Cl_6O_4 \cdot NaOH$ , separates in purplish-black, short, stout needles. If, however, sodium hydroxide is added drop by drop to a warm mixture of hexachloro-*o*-quinocatechol and water, hexachlorodihydroxycatechol ether and sodium chloroanilate are produced. It is evident that the former product is formed from the tetrachlorocatechol resulting from the decomposition of the hexachloro-*o*-quinocatechol

ether, since on warming tetrachlorocatechol with dilute sodium hydroxide, hexachlorodihydroxycatechol ether is produced.

When hexabromo-*o*-quinocatechol ether is left in contact with dilute sodium hydroxide, sodium bromocanilate is formed.

It has been shown by Jackson and Porter (Abstr., 1904, i, 256) that by the action of heat on tetrabromo-*o*-quinone, bromine is liberated and hexabromo-*o*-quinocatechol ether is produced. It is now found that tetrachloro-*o*-quinone is decomposed similarly by heat with formation of hexachloro-*o*-quinocatechol ether.

The  $\beta$ -methyl compound,  $2C_6Br_4O_2 \cdot CH_3 \cdot OH$ , is more stable towards sodium ethoxide than the  $\alpha$ -compound, but is gradually decomposed with formation of catechol and sodium bromide. By the action of hydroxylamine on the  $\alpha$ -methyl compound, it is converted quantitatively into the  $\beta$ -compound. If the  $\alpha$ -methyl compound is shaken with acetic anhydride for fifteen minutes and then left for several hours, an isomeric  $\gamma$ -compound, m. p.  $225^\circ$ , is produced, which crystallises in yellow plates and is more soluble in organic solvents than the  $\beta$ -compound. By the action of warm acetic acid on the  $\gamma$  compound, there are successively produced a white substance, m. p.  $138-140^\circ$ , a second compound, m. p.  $195^\circ$ , and, finally, hexabromo-*o*-quinocatechol ether. E. G.

**Preparation of 1-Aminoanthraquinone and its *N*-Alkyl or Acyl Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 175024).—When heated with aqueous ammonia or methylamine, anthraquinone- $\alpha$ -sulphonic acid is converted respectively into 1-aminoanthraquinone or 1-methylaminoanthraquinone. With *p*-toluidine this sulphonic acid yields 1-*p*-toluidinoanthraquinone.

G. T. M.

**Preparation of Arylaminoanthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 175069).—The halogenated benzenes interact readily with the aminoanthraquinones in presence of an acid-fixing agent to form arylaminoanthraquinones. Thus *p*-chloronitrobenzene and 1-aminoanthraquinone yield 1-*p*-nitroanilinoanthraquinone, and 1:4-diaminoanthraquinone and *p*-dichlorobenzene give rise to 1:4-di-*p*-chloroanilinoanthraquinone. The colour reactions of these and other arylaminoanthraquinones are tabulated. G. T. M.

**Preparation of Aldehydes of the Anthraquinone Series.** BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 174984).—Although  $\omega\omega$ -dichloromethylanthraquinone does not yield an aldehyde on treatment with alkalis or water at high temperatures, yet it undergoes this change on heating with concentrated sulphuric acid either alone or with addition of boric acid.

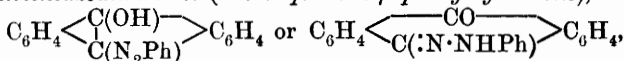
$\beta$ -Anthraquinonealdehyde is obtained in this way from  $\omega$ -dichloro- $\beta$ -methylanthraquinone, or the corresponding bromine compound.

1-Chloro- $\beta$ -anthraquinonealdehyde is produced by the interaction of 1-chloro-2-methylanthraquinone and sulphuric and boric acids at  $130^\circ$ .

4-Bromo-1-hydroxy- $\beta$ -anthraquinonealdehyde is prepared in this way from 4- $\omega\omega$ -tribromo-1-hydroxy-2-methylanthraquinone. G. T. M.

**Meso-derivatives of Anthracene.** FELIX KAUFLEK and W. SUCHANNEK (*Ber.*, 1907, 40, 518—532).—Anthranol and diazobenzene chloride form a substance which may be regarded either as a benzene-azoanthranol from its forming alkali salts, or as an anthraquinone-phenylhydrazone from its colour, its ready decomposition into anthraquinone and phenylhydrazine, and its formation from dibromoanthrone and phenylhydrazine. 9-Aminoanthracene reacts with diazonium salts in a similar manner.

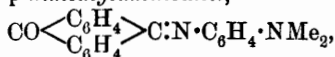
10-Benzeneazoanthranol (*anthraquinone-β-phenylhydrazone*),



m. p. 182—183°, is obtained from the potassium salt of anthranol and diazobenzene chloride in alkaline solution, or from 10-dibromoanthrone and phenylhydrazine; it separates from toluene in red needles, forms a potassium salt which exhibits bluish-red fluorescence in solution, and is converted by boiling alcoholic sulphuric acid into anthraquinone and phenylhydrazine.

10-*p*-Nitrobenzeneazoanthranol, m. p. 238—240°, is prepared in a similar manner to the preceding compound and exhibits similar properties.

*Anthraquinone-10-p-dimethylaminoanil*,



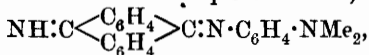
m. p. 138—139°, is obtained from anthranol and *p*-nitrosodimethylaniline; it separates from light petroleum in bluish-black, glistening needles, and by hydrolysis yields anthraquinone and dimethyl-*p*-phenylenediamine.

9-Amino-10-benzeneazoanthracene (*anthraquinoneimidephenylhydrazone*),  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(NH}_2) \diagdown \\ \diagdown \text{C(N}_2\text{Ph)} \diagup \end{array} \text{C}_6\text{H}_4 \text{ or } \text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(:NH)} \diagdown \\ \diagdown \text{C(:N.NHPh)} \diagup \end{array} \text{C}_6\text{H}_4$ , m. p.

182—184°, is obtained in the form of the hydrochloride by the action of diazobenzene chloride on 9-aminoanthracene in cold alcoholic solution; it forms large, brown crystals, and is changed by 3% alcoholic hydrogen chloride into anthraquinone, ammonia, and phenylhydrazine; the *hydrochloride*,  $\text{C}_{20}\text{H}_{15}\text{N}_3\text{HCl}$ , forms red crystals with green reflex.

9-Amino-10-*p*-nitrobenzeneazoanthracene,  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}_4$ , m. p. 239—240°, forms yellowish-brown leaflets.

The *p*-dimethylaminoanil of anthraquinoneimide,



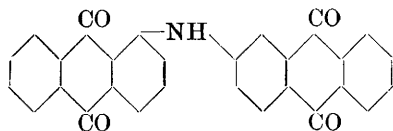
m. p. 118—124°, is obtained from 9-aminoanthracene and *p*-nitrosodimethylaniline in alcoholic solution; it crystallises in black leaflets or prisms, and is converted by 1% acetic acid in alcohol into anthraquinonodimethylaminoanil, and by 1% alcoholic hydrogen chloride into anthraquinone, ammonia, and dimethyl-*p*-phenylenediamine.

Attempts to diazotise 9-aminoanthracene lead to the formation of anthraquinone and a basic substance which appears to be diaminodanthryl,  $\text{C}_{28}\text{H}_{20}\text{N}_2$ ; the best yield is obtained by diazotising with amyl nitrite and sulphuric acid in alcoholic solution. The basic substance is nearly colourless, darkens at 192°, has m. p. 201—202°, yields anthraquinone by oxidation with chromic and acetic acids, and

forms well-defined di-acid salts; the *nitrate*,  $C_{28}H_{20}N_2 \cdot 2HNO_3 \cdot 3H_2O$ , forms colourless needles; the *hydrobromide*,  $C_{28}H_{20}N_2 \cdot 2HBr \cdot 5H_2O$ , forms stout crystals. C. S.

[**Dianthraquinonylamine.**] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 174699).—Halogenated anthraquinones condense with aminoanthraquinones under the influence of metallic salts to form complex secondary amines.

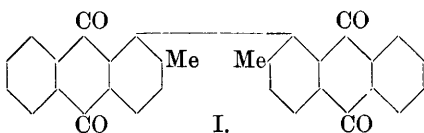
A *dianthraquinonylamine* having the annexed formula is readily prepared by heating together for fifteen hours 2-chloroanthraquinone, 1-aminoanthraquinone, naphthalene, anhydrous sodium acetate, and cupric chloride. The product, which is obtained in well-defined crystals having a



metallic lustre, dissolves in concentrated sulphuric acid to a greenish-blue solution, and may be crystallised from aniline or nitrobenzene.

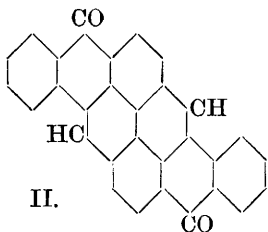
G. T. M.

**Preparation of Anthracene Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 175067).—2:2-Dimethyl-1:1'-dianthraquinonyl



and its derivatives, which are prepared from 1-chloro-2-methylantraquinone and its derivatives by the action of copper powder, are now found to undergo a further condensation in the presence

of dehydrating agents. The substance represented by the formula I loses  $2H_2O$  and becomes converted into the *compound* II, which is insoluble in water, dilute acids, and alkalis, but dissolves in concentrated sulphuric acid to a blue solution, and may be obtained from its solution in nitrobenzene as a brown, crystalline powder.



4:4'-Dichloro-2:2'-dimethyl-1:1'-dianthraquinonyl and 2:4:2':4'-tetramethyl-1:1'-dianthraquinonyl furnish similar condensation products.

G. T. M.

#### The Constituents of Ethereal Oils.

FREDERICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 432—440. Compare this vol.,

i, 11).—I.  $\gamma$ - and  $\alpha$ -Fencholenic acids.—The  $\alpha$ -fencholenic acid obtained from fenchone oxime by the action of dehydrating agents and hydrolysis (Cockburn, *Trans.*, 1899, 75, 501) and that from bromofenchone by the action of alcoholic potassium hydroxide (Czerny, *Abstr.*, 1900, i, 675), are not identical, although their amides and hydrochlorides melt at the same temperature. The acid derived from bromofenchone is called

*γ-fencholenic acid*,  $C_{10}H_{16}O_2$ , and has b. p.  $145-146^\circ/10$  mm.,  $D^{20} 1.0087$ ,  $n_D 1.47838$ ,  $\alpha_D + 52.30'$  (100 mm.). The *ammonium* salt, m. p.  $125^\circ$ , when heated at  $180^\circ$  under pressure, yields the amide, m. p.  $113-114^\circ$ , which does not depress the melting point of the amide from *α*-fencholenic acid. Reduction of the acid with hydrogen iodide and red phosphorus at  $180^\circ$  under pressure gives a mixture of hydrocarbons,  $C_9H_{18}$  or  $C_{10}H_{20}$ , b. p.  $48^\circ/20$  mm.,  $D^{20} 0.7794$ ,  $n_D 1.43155$ , and an acid, b. p.  $280^\circ$  in a vacuum. When heated under pressure at  $160^\circ$  with alcoholic potassium hydroxide, the rotation of *γ*-fencholenic acid falls to  $\alpha_D + 43^\circ$ , or on treatment with acids to  $+41.65^\circ$ ; it also falls when kept for three months, but it never becomes as low as that of *α*-fencholenic acid,  $[\alpha]_D 32.35'$ .

*γ*-Fencholenic acid in benzene solution and water, when treated with ozone and then distilled in a vacuum, gives a monobasic ketonic acid,  $C_8H_{12}O_3$ , in quantitative yield, b. p.  $185-187^\circ/10$  mm.,  $D^{22} 1.121$ ,  $n_D 1.47936$ ,  $\alpha_D + 22.30'$  tube (100 mm.) in 25% alcohol solution. The *semicarbazone*,  $C_9H_{15}O_3N_3$ , m. p.  $190^\circ$ , crystallises from methyl alcohol. When oxidised with alkaline potassium permanganate an acid, b. p.  $210-215^\circ/8$  mm. (decomp.), is obtained. On the other hand, no ketonic acid could be isolated when *α*-fencholenic acid is oxidised by ozone, the product obtained has b. p.  $140-230^\circ/10$  mm., the chief fraction, b. p.  $210-215^\circ$ . This behaviour shows that *α*- and *γ*-fencholenic acids are not identical, but if *γ*-fencholenic acid is treated with acid or alkalis and then oxidised with ozone, not a trace of ketonic acid can be isolated, the product has b. p.  $140-230^\circ/10$  mm.

When shaken with dilute sodium hydroxide for one hundred days, the lactone from *γ*-fencholenic acid of b. p.  $122-123^\circ/9$  mm. and m. p.  $77-78^\circ$  (Czerny, *loc. cit.*) gives *hydroxydihydrofencholenic acid*,  $C_{10}H_{18}O_3$ , m. p.  $105-107^\circ$ , which is monobasic and yields a soluble *silver* and a sparingly soluble *copper* salt. The lactone is regenerated along with an unsaturated acid, b. p.  $143^\circ/10$  mm., probably *α*-fencholenic acid, by treatment with dilute sulphuric acid. This lactone is identical with that obtained from the *α*-acid, as it shows no depression in m. p. when mixed with it, and also on reduction with sodium and alcohol yields the same *glycol*,  $C_{10}H_{22}O_2$ , b. p.  $158-161^\circ/11$  mm., m. p.  $58-60^\circ$ .

The following constants of bromofenchone have been redetermined (compare Czerny, *loc. cit.*, and Balbiano, *Abstr.*, 1901, i, 89), b. p.  $125-130^\circ/10$  mm.,  $D^{22} 1.3005$ ,  $n_D 1.50605$ ,  $\alpha_D + 10-12^\circ$  (100 mm.).

*Constitution of Fenchone*.—Polemical. A reply to Kondakoff (*Abstr.*, 1906, i, 520). A table is also given showing how, by the use of Semmler's formula for fenchone, these compounds are derivable,

that of *γ*-fencholenic acid is 
$$\begin{array}{c} CO_2H \cdot CMe_2 \cdot CH - C \cdot CHMe \\ | \\ CH_2 \cdot CH_2 \end{array} \quad W. R.$$

**Terpineol of Majorana Oil.** OTTO WALLACH and FRIEDRICH BÖDECKER (*Ber.*, 1907, 40, 596-600).—On oxidising the terpineol fraction of majorana oil (compare this vol., i, 65) with permanganate a *ketone* is formed of which the *semicarbazone* melts at  $145-146^\circ$ . The glycerol,  $C_{10}H_{17}(OH)_3$ , is more sparingly soluble in chloroform and crystallises otherwise than the isomeric trioxysterpane; on further

oxidation it gives rise to *acids*,  $C_{10}H_{18}O_6$ , m. p. 205—206° and 188—189°, which form *lactones*, m. p. 63—64° and 72—73° respectively. On shaking the terpineol fraction of majorana oil with sulphuric acid, *cis*-terpinene hydrate, m. p. 117°, and terpinene-terpine, m. p. 137°, are obtained along with mixed crystals of these two substances, m. p. 108° (about). The paper concludes with the discussion of a formula for terpineol.

E. F. A.

**Combination of Glycuronic Acid with Optical Antipodes.** ADOLF MAGNUS-LEVY (*Biochem. Zeitsch.*, 1907, 2, 319—331).—Experiments made on dogs and rabbits indicate that both *d*- and *l*-borneol and *d*- and *l*-camphor readily combine with glycuronic acid, and the animal organism appears to be incapable of differentiating between the stereoisomerides. Inactive methylethylpropylcarbinol as it combines with *d*-glycuronic acid during its passage through the organism is not resolved into active components.

*l*-Camphorglycuronic acid,  $C_{16}H_{24}O_8$ , is most readily isolated from the urine of dogs fed with *l*-camphor by conversion into its *strychnine* salt,  $C_{37}H_{40}O_{10}N_2 \cdot 2H_2O$ , m. p. 189—195° (decomp.). The free acid contains water of crystallisation, and melts between 120° and 130°. When hydrolysed with 10% sulphuric acid, the complex glycuronic acid yields *l*-camphorol,  $C_{10}H_{16}O_2$ , m. p. 207—210° (not sharp),  $[\alpha]_D - 32.93^\circ$ ; its *semicarbazone* melts and decomposes at 235—240°.

*Sodium l-borneolglycuronate*,  $C_{16}H_{25}O_7Na \cdot H_2O$ , has  $[\alpha]_D^{20} - 66.5^\circ$ .

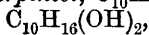
Hydroxycamphorglycuronic acid,  $C_{16}H_{24}O_8 \cdot H_2O$ , obtained from the urine of a dog fed on Manasse's hydroxycamphor (oxaphor), m. p. 212—213°, crystallises from water in glistening plates, m. p. 138°, and the sodium salt has  $[\alpha]_D - 32.7^\circ$ . When hydrolysed it yields hydroxycamphor.

J. J. S.

**Boiling Point and the Nature of Dipentene.** OTTO WALLACH (*Ber.*, 1907, 40, 600—606).—The author had shown previously that whereas dipentene prepared as pure as possible has b. p. 177—178°, *i*-limonene, prepared by mixing *d*- and *l*-limonenes, has b. p. 175—176° (compare Abstr., 1888). Semmler's criticisms (*Ber.*, 1906, 39, 4427) have led him again to purify very carefully dipentene dihydrochloride, heat this with aniline and remove the aniline by steam distillation, the liquor being rendered acid by oxalic acid. The carefully purified dipentene had b. p. 177—178° for the greater part of the distillate, and 10 grams yielded but 8.5 grams of solid tetrabromide, whereas *i*-limonene yielded 10 grams under like conditions. It is considered that dipentene contains another hydrocarbon which cannot be separated from it by distillation, and which, perhaps, represents  $\psi$ -limonene.

E. F. A.

**Terpinenes.** OTTO WALLACH (*Ber.*, 1907, 40, 575—584).—By the interaction of terpinene dihydrochloride and potassium hydroxide (compare this vol., i, 64), a *terpineol*,  $C_{10}H_{17} \cdot OH$ , and a *terpin*,



m. p. 136.5—137.5°, are obtained along with von Baeyer's  $\gamma$ -terpineol (m. p. 69°), and *cis*-terpine (m. p. 117°) and *trans*-terpine (m. p. 156°).

$\gamma$ -Terpineol yields a mixture of *cis*- and *trans*-terpines on shaking with acids as also, though more slowly, when acted on by potassium hydroxide. The terpins obtained above, therefore, probably originate from  $\gamma$ -terpineol. The terpin (m. p.  $137^\circ$ ) is easily obtained by shaking the corresponding terpeneol with sulphuric acid (compare following abstract). It has b. p.  $250^\circ$ , and crystallises in optically inactive characteristic plates.

Terpinene nitrosite when reduced in glacial acetic acid solution, at first at  $0^\circ$  and subsequently at the temperature of the water-bath, yields a considerable quantity of carvenone. A still better yield of carvenone is obtained on reducing under the same conditions terpinenitrolepiperidide (m. p.  $231$ — $232^\circ$ ); whereas the semicarbazone, oxaminoxime, and benzoate of the oxime of the compound obtained all agree with the corresponding carvenone derivatives, the oxime has always a lower m. p.

The paper concludes with a discussion of this reaction and a further consideration of the constitution of terpinene. E. F. A.

**Sabinene and its Relationship to Terpinene.** OTTO WALLACH (*Ber.*, 1907, 40, 585—595).—The paper is largely of a polemical nature, being a reply to Semmler (this vol., i, 145). Attention is again directed to the high value of the molecular refraction of sabinene, due possibly to the presence of a methylene group in a semicyclic ring. The same solid dichloride is formed whether sabinene is treated with hydrogen chloride in acetic acid or in moist ethereal solution; in dry ether no formation of hydrochloride takes place, just as in the case of limonene. In carbon disulphide solution sabinene forms a *monohydrochloride*, b. p.  $87$ — $92^\circ/12$  mm., D  $0.982$ ,  $n_D^{20}$   $1.4824$ , which does not yield a sparingly soluble nitrosate, but forms a *nitrosochloride* decomposed by bases into *nitrolamines*. This monohydrochloride is converted by hydrogen chloride in acetic acid solution into the dichloride.

Sabinene when shaken with sulphuric acid yields a terpin,  $C_{10}H_{18}(OH)_2$ , m. p.  $137^\circ$ , and a terpeneol,  $C_{10}H_{17}\cdot OH$ , b. p.  $209$ — $212^\circ$ , D  $0.9265$ ,  $n_D^{19}$   $1.4785$ , which forms a dichloride,  $C_{10}H_{16} \cdot 2HCl$ , m. p.  $52^\circ$ , and is converted by permanganate into the glycerol already described (this vol., i, 64) from cardamom and majorana oils. The author claims priority over Semmler (*loc. cit.*) on these points. E. F. A.

**Russian Peppermint Oil.** IWAN SCHINDELMEISER (*Chem. Centr.*, 1906, ii, 1764; from *Apoth.-Zeit.*, 21, 927—928).—A sample of peppermint oil from Tambow, which had D $^{19}$   $0.908$ ,  $[\alpha]_D -21.48'$ , and  $n_D$   $1.46108$ , was soluble in 4 parts of 70% and in 0.5 of 95% alcohol. The oil solidified when cooled with sodium chloride and ice for a long time. The aqueous solution of an aldehyde, which distilled at  $115$ — $120^\circ$  when treated with silver oxide, yielded an acid the silver salt of which contained 61% of silver. The oil contained *i*-pinene and more *l*-limonene than *d*-limonene, but neither phellandrene nor menthene was present (compare Andréff and Andres, *Abstr.*, 1892, i, 723). Cineol was separated by means of syrupy phosphoric acid,

and 16.36% of *l*-menthone,  $[\alpha]_D - 23^\circ 4.5'$ , was isolated. The oil yielded 51.22% of a mixture of free *l*- and *d*-menthols, in which the former was present in the greater quantity, and 4.8% of the menthyl esters of acetic and baldrianic acids calculated as acetate. A small quantity of a sesquiterpene was also obtained, but paucity of material prevented identification.

E. W. W.

**$\alpha$ - and  $\beta$ -Amyrins from Bresk.** N. H. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 471. Compare Romburgh and Cohen, *Abstr.*, 1906, 197; Vesterberg, *Abstr.*, 1891, 165).— $\alpha$ -Amyrin, m. p.  $186^\circ$  (corr.), has now been obtained from bresk or djelutung; it has  $[\alpha]_D + 82.6^\circ$  in chloroform, or  $+88.2^\circ$  in benzene solution. The acetate, m. p.  $224$ — $225^\circ$  (corr.), has  $[\alpha]_D + 75.8^\circ$  in chloroform solution; the benzoate, m. p.  $195^\circ$  (corr.); the *cinnamate* crystallises in small, hard needles, m. p.  $178^\circ$  (corr.).

$\beta$ -Amyrin *cinnamate* crystallises from acetone in small needles, m. p.  $241^\circ$  (corr.).

G. Y.

**Solubility of Salicin.** DAVID B. DOTT (*Pharm. J.*, 1907, [iv], 24, 79).—Salicin is soluble to the extent of 1 part in 24 parts of water at  $25^\circ$ .

E. G.

**Elaterin.** FRANZ VON HEMMELMAYR (*Monatsh.*, 1906, 27, 1167—1182. Compare *Abstr.*, 1906, i, 973; Thoms, *Chem. Zeitsch.*, 1906, 923; Pollak, *Abstr.*, 1906, i, 973).—The analytical results obtained by the author and by Berg (*Abstr.*, 1906, i, 596) with elaterin, diacetyl elaterin, bromoelaterin, elaterin diphenylhydrazone, and elateridin are tabulated and found to agree best with the formula,  $C_{24}H_{34}O_6$ , for elaterin, to which in agreement with its properties is now ascribed the extended formula,  $C_{20}H_{29}(CO)_2(OH)_2 \cdot OAc$ . The formula for elateridin derived from this should contain two hydroxyl groups; as, however, elateridin forms only a monoacetyl derivative which is not identical with elaterin, its molecule must undergo some isomeric change during its formation.

The bromo-derivative of elaterin,  $C_{24}H_{33}O_6Br$ , prepared by the action of bromine on elaterin in glacial acetic acid solution, forms a yellow, amorphous powder, m. p.  $112^\circ$ , but decomposes at  $118^\circ$ . The diacetyl derivative,  $C_{24}H_{32}O_6Ac_2$ , m. p.  $124^\circ$ . The diphenylhydrazone,  $C_{36}H_{46}O_4N_4$ , forms a yellow, amorphous mass, commences to sinter at  $158^\circ$ , and decomposes and evolves gas at  $170^\circ$ .

Elateridin,  $C_{22}H_{32}O_5$ , which sinters at  $130^\circ$ , m. p.  $140$ — $150^\circ$ , gives a reddish-brown coloration with alcoholic ferric chloride, and is soluble in aqueous potassium hydroxide only with difficulty. The *monoacetyl* derivative,  $C_{22}H_{31}O_5Ac$ , formed by boiling elateridin with acetic anhydride and sodium acetate, is obtained as a yellow, amorphous mass, sinters at  $130^\circ$ , m. p.  $140$ — $150^\circ$ .

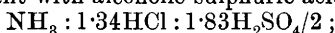
Elateric acid,  $C_{22}H_{32}O_6, \frac{1}{2}H_2O$ , m. p.  $70$ — $80^\circ$ ; the *methyl* ester,  $C_{22}H_{31}O_6Me$ , m. p.  $85$ — $90^\circ$ . When boiled with phenylhydrazine and acetic acid in alcoholic solution, elateric acid forms a resinous compound,  $C_{28}H_{38}O_5N_2$  or  $C_{28}H_{40}O_6N_2$ , which sinters at  $125^\circ$ , m. p. about  $140^\circ$ .



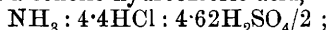
Oxidation of elaterin with chromium trioxide in glacial acetic acid solution leads to the formation of a *product* which sinters at 100°, m. p. 115—120°, and dissolves without change in aqueous potassium hydroxide or carbonate. G. Y.

**Dyeing and Ionisation.** LÉO VIGNON (*Compt. rend.*, 1907, 144, 81—83).—The author has shown previously (this vol., i, 102) that the chemical activity of textile fibres of animal origin towards acids, bases, or salts increases with the dilution, and consequently with the electrolytic dissociation of the solutions employed; in the present paper it is shown that the electrolytic dissociation of dyes, except in the case of picric acid, increases with the dilution of the solution and also with the temperature; the experiments were conducted on solutions of roccellin, orange II, magenta, and picric acid, and the results are tabulated in the original. M. A. W.

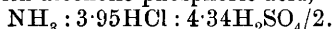
**Process of Dyeing Animal Textile Fibres. III.** P. GELMO and WILHELM SUIDA (*Monatsh.*, 1906, 27, 1193—1198. Compare Abstr., 1905, i, 714; 1906, i, 445).—The experiments described in this paper were performed with the same wool as was employed in the previous series. Samples of the wool were boiled with alcoholic sulphuric, hydrochloric, and phosphoric acids and thoroughly washed; half of each was titrated with *N*/10 sulphuric acid, *N*/10 hydrochloric acid, and *N*/10 ammonia respectively; the remaining half samples were boiled with aqueous ammonium carbonate and then titrated. Ammonia, hydrochloric acid, and sulphuric acid were absorbed in the proportions: after treatment with alcoholic sulphuric acid,



after treatment with alcoholic hydrochloric acid,



or after treatment with alcoholic phosphoric acid,



After the further treatment with ammonium carbonate, these three samples absorbed ammonia, hydrochloric acid, and sulphuric acid in the proportions:  $\text{NH}_3 : 12.5\text{HCl} : 13.4\text{H}_2\text{SO}_4/2$ ;  $\text{NH}_3 : 8\text{HCl} : 8.9\text{H}_2\text{SO}_4/2$ ; and  $\text{NH}_3 : 5.46\text{HCl} : 6.01\text{H}_2\text{SO}_4/2$  respectively. The results of a number of dyeing experiments showed that after treatment with alcoholic acids, wool gives intense shades with acid, but only weak shades with basic, dyes. This effect was least pronounced in the wool treated with phosphoric acid.

A sample of wool treated with hydrogen chloride in absolute alcohol and thoroughly washed with alcohol and water was not dyed by basic dyes, but with acid dyes gave intense shades fast to soaping. Wool treated successively with alcoholic hydrogen chloride and ammonium carbonate was dyed feebly by basic, but intensely by acid, dyes, the shades being removed almost entirely by soaping.

*N*/10 ammonia, *N*/10 hydrochloric acid, and *N*/10 sulphuric acid were absorbed by wool which had been treated with 1% of its weight of sodium nitrite in the proportion  $\text{NH}_3 : 5.9\text{HCl} : 7.1\text{H}_2\text{SO}_4/2$ , or by wool treated with a 1% solution of sodium nitrite in the proportion  $\text{NH}_3 : 2.12\text{HCl} : 2.69\text{H}_2\text{SO}_4/2$ . Wool treated with even traces of

nitrous acid has no affinity for coal-tar dyes, but on exposure to light becomes yellow to intense brownish-orange, depending on the amount of nitrous acid, the shades being rendered more intense by addition of alkali hydroxides.

No difference could be detected in the behaviour in a neutral dye-bath of untreated wool and wool treated with phosphorus trichloride.

G. Y.

**Sulphur Dyes.** HERMANN WICHELHAUS [and, in part, VIEWEG] (*Ber.*, 1907, 40, 126—129).—Many natural, non-nitrogenous colouring matters such as brazilin, hæmatoxylin, maclurin, euxanthone, &c., are transformed into sulphur dyes when heated with sulphur in the absence of air, hydrogen sulphide and to a certain extent sulphur dioxide being evolved. The dyes dissolve in sodium sulphide solution, yielding brown to black tones.

Artificial phenolic dyes of the type of gallacetophenone, aurin, and fluorescein may be transformed into sulphur dyes by a similar process. A stable dye containing 27% of sulphur is formed when fluorescein or a mixture of phthalic anhydride and resorcinol is fused with sulphur at 250—280° for six to eight hours. Similar products may be obtained from di- and tetra-chlorophthalic acids.

J. J. S.

**Oximes of Methylfurfuraldehyde.** K. FROMHERZ and WILHELM MEEGEN (*Ber.*, 1907, 40, 403—406).—When methylfurfuraldehyde is treated with hydroxylamine according to Goldschmidt and Zanoli's method (*Abstr.*, 1892, i, 1433), a product is obtained which is regarded as a mixture of the *syn*- and *anti*-aldoximes. When crystallised from light petroleum it melts at 51—52°, but when repeatedly recrystallised it yields a small amount of pure *syn*-methylfurfuraldoxime,  $C_6H_7O_2N$ , in the form of colourless, glistening needles, m. p. 110°. The same compound may also be obtained by converting the mixture of oximes into the hydrochloride and decomposing this with alkali. The *phenylcarbimide* derivative,  $C_{10}H_{12}O_3N_2$ , exists in two modifications, a yellow, labile form, m. p. 101° (decomp.), and a colourless, stable form, m. p. 106—109°.

The pure *anti*-oxime has not been obtained.

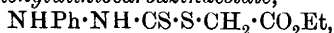
J. J. S.

**Mixed Anhydrides of Tannic and Cinnamic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 173729).—A product containing mono- and di-acetyltannic-cinnamic anhydrides is obtained by heating together at 100° acetic anhydride, tannic acid, and cinnamic acid, and gradually adding phosphorus pentachloride to the mixture. The heating is continued until the product yields neither cinnamic nor tannic acid on treatment with warm water; the mixture is then washed successively with cold and hot water until the filtrate has a neutral reaction. The residue, which is dried at 45°, is soluble in alcohol, and reprecipitated in an amorphous form by water. Although stable in hot water, the mixed anhydrides are hydrolysed by dilute alkalis.

G. T. M.

**Pyrone Hydroperbromides.** ARTHUR HANTZSCH and O. DENSTORFF (*Ber.*, 1907, 40, 241—243. Compare Abstr., 1906, i, 745).—Reply to Feist (Abstr., 1906, i, 974).  
C. S.

**Substituted Rhodanic Acids and their Aldehyde Condensation Products.** V. RUDOLF ANDREASCH (*Monatsh.*, 1906, 27, 1211—1222. Compare Abstr., 1903, i, 855; 1904, i, 444; 1905, i, 930, 933).—The action of ethyl chloroacetate on ammonium phenyldithiocarbazinate (Heller and Bauer, Abstr., 1902, i, 444) leads to the formation of *ethyl phenyldithiocarbazinacetate*,



which crystallises in long needles, m. p. 108—109°, and 3-*anilino-rhodanic acid*,  $\text{NHPh} \cdot \text{N} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CS} \cdot \text{S} \end{smallmatrix}$ . This forms yellow, granular crystals, m. p. 125°, and is less soluble in alcohol than the carbazinate

from which it is formed by heating at 100°, or by boiling with glacial acetic acid and acetic anhydride. The following condensation products of phenylrhodanic acid and aldehydes,  $\text{NHPh} \cdot \text{N} \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CHR} \\ \text{CS} \cdot \text{S} \end{smallmatrix}$ ,

are formed by heating the rhodanic acid or the ethyl carbazinate with the aldehyde and glacial acetic acid.

R = Ph: slender, yellow needles, m. p. 195°; R =  $\cdot\text{C}_6\text{H}_4 \cdot \text{OH}$  (o): yellow, pointed needles, m. p. 170—173°; R =  $\cdot\text{C}_6\text{H}_4 \cdot \text{NMe}_2$  (p): microscopic, scarlet needles, m. p. 219°; R =  $\cdot\text{C}_4\text{OH}_3$ : yellow needles, m. p. 168°.

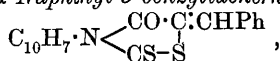
Bargellini's work on the condensation of aldehydes with rhodanic acids (Abstr., 1906, i, 383, 536) is criticised.

The action of ethyl chloroformate on ammonium phenyldithiocarbamate in alcoholic solution leads to the formation of phenylthiocarbamide, carbamide, carbanilide, and a *substance*, m. p. below 100°. Ethyl chlorocarbonate and ammonium phenyldithiocarbamate interact, forming phenyl thiocarbimide, carbon oxysulphide, and ammonium chloride.  
G. Y.

**Substituted Rhodanic Acids and their Aldehyde Condensation Products.** VI. ALOIS WAGNER (*Monatsh.*, 1906, 27, 1233—1244. Compare Abstr., 1903, i, 855; 1904, 444; 1905, i, 930, 933, and preceding abstract).—Andreasch and Zipser having suggested the use of rhodanic acids in the estimation of furfuraldehyde, the author has investigated the suitability of some higher substituted rhodanic acids, but found this to be less than that of phenylrhodanic acid. When pure, the rhodanic acids now described do not condense with aldehydes even in presence of glacial acetic or concentrated sulphuric acid; the condensation products are obtained, however, from the crude ethyl substituted dithiocarbaminacetates formed as intermediate products in the action of ethyl chloroacetate on the substituted dithiocarbamates.

3-*α-Naphthylrhodanic acid*,  $\text{C}_{10}\text{H}_7 \cdot \text{N} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CS} \cdot \text{S} \end{smallmatrix}$ , prepared together with *s-di-α-naphthylcarbamide* by the action at 100° of ethyl chloro-

acetate on ammonium  $\alpha$ -naphthylthiocarbamate obtained from  $\alpha$ -naphthylamine, carbon disulphide, and concentrated aqueous ammonia, crystallises in colourless, tetragonal leaflets, m. p. 167—168°. *Ethyl  $\alpha$ -naphthylthiocarbaminacetate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is formed if the action of ethyl chloroacetate on ammonium  $\alpha$ -naphthylthiocarbamate takes place below 100°; it crystallises in large, white needles, m. p. 81°. *3- $\alpha$ -Naphthyl-5-benzylidenetherhodanic acid*,



crystallises in long, yellow needles, m. p. 159°. The *furfurylidene* derivative is obtained as an oil.

The corresponding  $\beta$ -naphthyl and *p*-ethoxyphenyl compounds were prepared in the same manner.

*3- $\beta$ -Naphthylrhodanic acid*,  $\text{C}_{13}\text{H}_9\text{ONS}_2$ , formed together with *s*-di- $\beta$ -naphthylthiocarbamide, crystallises in microscopic, brown, pointed needles, m. p. 180—190°. *Ethyl  $\beta$ -naphthylthiocarbaminacetate*,  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{NS}_2$ , crystallises in needles, m. p. 83°. *3- $\beta$ -Naphthyl-5-benzylidenetherhodanic acid*,  $\text{C}_{20}\text{H}_{13}\text{ONS}_2$ , crystallises in microscopic, yellow leaflets, m. p. 202°. *3- $\beta$ -Naphthyl-5-furfurylidenetherhodanic acid*,  $\text{C}_{10}\text{H}_7\cdot\text{N} \begin{array}{c} \text{CO}\cdot\text{C}\cdot\text{CH}\cdot\text{C}_4\text{H}_3\text{O} \\ \diagup \quad \diagdown \\ \text{CS-S} \end{array}$ , crystallises in slender, yellow needles, m. p. 208°.

*3-p-Ethoxyphenylrhodanic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CS-S} \end{array}$ , crystallises in long, yellowish-white needles, m. p. 180—188°. The *5-benzylidene* derivative,  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{NS}_2$ , forms long, sulphur-yellow needles, m. p. 212—214°. The *5-furfurylidene* derivative,  $\text{C}_{14}\text{H}_{13}\text{O}_3\text{NS}_2$ , crystallises in long, chrome-yellow needles, m. p. 197°. G. Y.

**Derivatives of Hordenine.** EUGÈNE LÉGER (*Compt. rend.*, 1907, 144, 208—210. Compare Abstr., 1906, i, 204, 761; this vol., i, 151).—The following derivatives of hordenine acting (1) as a tertiary amine, (2) as a phenol, and (3) as both amine and phenol are described. The *normal tartrate*,  $(\text{C}_{10}\text{H}_{15}\text{ON})_2\cdot\text{C}_4\text{H}_6\text{O}_6$ , anhydrous needles; the *hydrogen tartrate*,  $\text{C}_{10}\text{H}_{15}\text{ON}\cdot\text{C}_4\text{H}_6\text{O}_6$ , anhydrous needles; *hordenine methochloride*,  $(\text{C}_{10}\text{H}_{15}\text{ON})\cdot\text{MeCl}$ , anhydrous needles; *hordenine ethochloride*,

$\text{C}_{10}\text{H}_{15}\text{ON}\cdot\text{EtCl}$ , anhydrous needles; *hordenine ethobromide*,  $\text{C}_{10}\text{H}_{15}\text{ON}\cdot\text{EtBr}$ , square plates; *hordenine ethiodide*,  $\text{C}_{10}\text{H}_{15}\text{ON}\cdot\text{EtI}$ , anhydrous, prismatic needles; *benzoylhordenine hydrochloride*,  $\text{C}_{10}\text{H}_{14}\text{BzON}\cdot\text{HCl}$ , anhydrous needles; *benzoylhordenine hydrobromide*,  $\text{C}_{10}\text{H}_{14}\text{BzON}\cdot\text{HBr}$ , brilliant, rectangular lamellæ; *cinnamoylhordenine*, long slender, needles, m. p. 55·8° (corr.) (partial decomp.), but forming stable salts which crystallise easily; *cinnamoylhordenine hydrochloride*,

$\text{C}_{10}\text{H}_{14}(\text{C}_8\text{H}_7\text{O})\text{ON}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , prismatic needles; *anisoylhordenine hydrochloride*,  $\text{C}_{10}\text{H}_{14}(\text{C}_8\text{H}_7\text{O}_2)\text{ON}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , large, efflorescent plates. *Methylhordenine methiodide*,

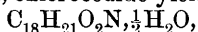
$\text{OMe}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{NMe}_3\text{I}$ , slender, white, felted needles containing  $1\frac{1}{2}\text{H}_2\text{O}$ .

E. H.

**Preparation of Acetyl Derivatives of Morphine Bases.**

KNOLL & Co. (D.R.-P. 175068).—By treating morphine bases with sulphoacetic acid or a mixture of acetic anhydride and sulphuric acid, a series of new acetyl derivatives has been obtained. *Triacetylmorphine*, m. p. 206—208°; *diacetylcodeine*, m. p. 145—146°, and *dibenzoylacetylmorphine* (from dibenzoylmorphine), m. p. 166—168°, are described. G. T. M.

**Behaviour of Chlorocodide on Reduction.** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, 40, 376—377. Compare Göhlich, *Abstr.*, 1894, i, 431; Vongerichten and Müller, *Abstr.*, 1903, i, 571).—On reduction with sodium and ethyl or amyl alcohol, or with tin or zinc dust and hydrochloric acid, chlorocodide yields *deoxycodeine*,



which crystallises in shining leaflets, loses  $\frac{1}{2}\text{H}_2\text{O}$  above 100°, m. p. about 126° (decomp.) when quickly heated; the anhydrous substance is vitreous. It forms crystalline salts; the *hydrochloride* separates from alcohol in prisms, m. p. about 165° (decomp.). G. Y.

**Melting Point of Cotarnine.** DAVID B. DOTT (*Pharm. J.*, 1907, [iv], 24, 78—79).—Freshly prepared cotarnine, purified by crystallisation from benzene, has m. p. 125° (decomp.). When the crystalline base is heated on the water-bath, it loses weight equivalent to more than 1 mol.  $\text{H}_2\text{O}$  and then melts at 100°. It is therefore considered that the m. p. of cotarnine is of little value as a test for purity. E. G.

**Preparation of Cotarnine Phthalates.** KNOLL & Co. (D. R.-P. 175079).—*Cotarnine phthalate*, m. p. 102—105°, is obtained by mixing 237 parts of cotarnine and 83 parts of phthalic acid in aqueous or methyl alcoholic solution, and concentrating under reduced pressure. *Cotarnine hydrogen phthalate*, produced by mixing alcoholic solution of sodium hydrogen phthalate and cotarnine hydrochloride, is obtained from the solution, after removing sodium chloride, in well-defined, yellow crystals, m. p. 115°. The normal salt when recrystallised from alcohol tends to decompose into the acid salt and free base.

G. T. M.

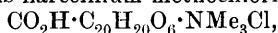
**Narceine.** MARTIN FREUND [and BESCHKE] (*Ber.*, 1907, 40, 194—204. Compare Freund and Frankforter, *Abstr.*, 1894, i, 58).—The author has repeated the alkylation of narceine by the action of methyl and ethyl iodides on sodium narceine, and confirms Tambach and Jäger's statement that the alcohol used as solvent is without influence on the nature of the product (*Abstr.*, 1906, i, 879); contrary, however, to these authors' view it is found that the product of methylation, m. p. 208—209°, is the narceinium methiodide methyl ester,  $\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}(\text{OMe})(\langle \text{O} \rangle \text{CH}_2) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_3\text{I}$ , and not methylnarceinium methiodide, whilst similarly the product of ethylation, (+  $\text{H}_2\text{O}$ ), m. p. 141° or, (+  $\text{C}_2\text{H}_6\text{O}$ ), m. p. 181, is narceinium ethiodide ethyl ester,  $\text{CO}_2\text{Et} \cdot \text{C}_{20}\text{H}_{20}\text{O}_6 \cdot \text{NMe}_2\text{EtI}$ , and not ethylnar-

ceinium ethiodide. The formulæ given by Tambach and Jäger for the remainder of their products of narceine must be altered in the same sense.

Narceinium methiodide, formed by heating narceine with methyl iodide at  $100^{\circ}$ , and described previously as a resin (Freund and Frankforter, *loc. cit.*), crystallises from water in needles, m. p.  $207^{\circ}$ , and when boiled with aqueous alkalis yields trimethylamine and narceonic acid, m. p.  $217^{\circ}$  ( $208^{\circ}$ , *loc. cit.*).

The product formed by heating narceine with methyl sulphate and alcohol (Tambach and Jäger) is narceinium hydrogen methosulphate,  $C_{23}H_{27}O_8N \cdot MeHSO_4$ , which is decomposed by water, forming narceine.

The action of 1 mol. of methyl sulphate on sodium narceine leads to the formation of the sodium salt of methylnarceinium methosulphate,  $CO_2Na \cdot C_{20}H_{20}O_6 \cdot NMe_3 \cdot SO_4Me$ , which on treatment with hydrochloric acid yields narceinium methochloride,



m. p.  $243^{\circ}$ ; this is converted by potassium iodide into the methiodide, m. p.  $207^{\circ}$ .

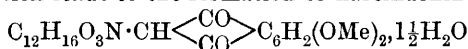
The product, m. p.  $184-186^{\circ}$ , of the action of 2 mols. of methyl sulphate on sodium narceine is the *additive* compound of methyl sulphate and narceine methyl ester; it is converted by potassium iodide into the methyl ester of narceinium methiodide which is insoluble in aqueous alkalis.

Ethyl sulphate (1 mol.) and sodium narceine yield sodium narceinium ethosulphate, which on treatment with hydrochloric acid forms narceinium ethochloride,  $CO_2H \cdot C_{20}H_{20}O_6 \cdot NMe_2EtCl$ , m. p.  $231^{\circ}$ ; this is converted by boiling aqueous alkalis into narceonic acid. The base, m. p.  $175-177^{\circ}$ , obtained from the ethochloride, is probably

the betaine,  $C_{20}H_{20}O_6 \cdot \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ NMe_2Et \end{matrix} O$ . The ethochloride is converted by alcoholic hydrogen chloride into narceinium ethochloride ethyl ester,  $CO_2Et \cdot C_{20}H_{20}O_6 \cdot NMe_2EtCl$ , m. p.  $218-219^{\circ}$ , which is formed also by the action of silver chloride on the ethyl ester of narceinium ethiodide; this yields narceonic acid when boiled with aqueous alkalis.

The product (m. p.  $191-193^{\circ}$ : Tambach and Jäger, *loc. cit.*) of the action of ethyl iodide on narceine ethyl ester is narceinium ethiodide ethyl ester, m. p.  $181^{\circ}$  when recrystallised from alcohol.

The action of sodium methoxide on narceine ethyl ester in methyl alcoholic solution leads to the formation of narceindonine,



which is formed also, together with narceine, by the action of sodium methoxide on *aponarceine* (compare Freund and Michaels, *Abstr.*, 1895, i, 630; Eibner, *Abstr.*, 1906, i, 588); it crystallises in red plates, m. p.  $168-169^{\circ}$ , loses  $1\frac{1}{2}H_2O$  at  $110^{\circ}$ , and then has m. p.  $174^{\circ}$ .

Tambach and Jäger's *aponarceine* is considered to be probably the lactone,  $C_{12}H_{16}O_3N \cdot CH : C \begin{matrix} O \\ \diagup \quad \diagdown \\ C_6H_2(OMe)_2 \end{matrix} CO$ . G. Y.

**Preparation of Narceine and Homonarceine Derivatives.** KNOLL & Co. (D.R.-P. 174380).—The alkali derivatives of narceine

and homonarceine, or the corresponding compounds with the alkali earth metals, when treated with methyl or ethyl sulphate give rise to new alkyl derivatives of these bases in which the carboxyl group is still unesterified.

Narceine dissolved in *N*-sodium hydroxide and treated with methyl sulphate furnishes a base the salt of which crystallises from alcohol, m. p. 242°. This compound when esterified with alcoholic hydrogen-chloride, yields an ester *hydrochloride*, m. p. 214—216°; *platini-chloride*, m. p. 220°.

Narceine and ethyl sulphate give rise to a similar base: *hydrochloride*, m. p. 231°; *hydrochloride of ethyl ester*, m. p. 219°.

The base from homonarceine and methyl sulphate has the following derivatives: *hydrochloride*, m. p. 231—232°; *platinichloride*, m. p. 181—182°; *hydrochloride of ethyl ester*, m. p. 212—214°. Homonarceine and ethyl sulphate give a similar ethyl derivative: *hydrochloride*, m. p. 211°. G. T. M.

### Tertiary and Quaternary Bases from Piperidine. II.

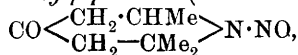
SEIGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1907, 40, 424—427. Compare *Abstr.*, 1906, i, 881; Gabriel and Stelzner, 1896, i, 702; Hörlein and Kneisel, 1906, i, 458).—1- $\gamma$ -Hydroxypropylpiperidine,  $C_5H_{10}N \cdot [CH_2]_3 \cdot CH_2 \cdot OH$ , obtained by heating 2 parts of trimethylenechlorohydrin with 4 parts of piperidine for one hour at the temperature of the water-bath and then liberating the base with potassium hydroxide, is a colourless oil, b. p. 225—228°/759 mm. The base is precipitated from its aqueous solution by potassium hydroxide. The *hydrochloride* is precipitated from alcoholic solution by acetone as a crystalline, hygroscopic powder, m. p. 151°; the *aurichloride* forms golden-yellow, hexagonal plates, m. p. 69—70°. When heated with hydrochloric acid at 150°, the base is converted into 1- $\gamma$ -chloropropylpiperidine.

By repeated fractionation of the portion distilling at 200—300°, obtained in the interaction of the quaternary salt and potassium hydroxide (*loc. cit.*), an oil, b. p. 224—227°, was isolated and identified as 1- $\gamma$ -hydroxypropylpiperidine. The chief product of this interaction, dipiperidinopropyl ether, is formed either by the condensation of the 1- $\gamma$ -chloropropylpiperidine and  $\gamma$ -hydroxy base, or by dehydration of the base.

1- $\delta$ -Chlorobutylpiperidine *hydrochloride*,  $C_5H_{10}N \cdot [CH_2]_4Cl \cdot HCl$ , crystallises from acetone in colourless needles, m. p. 167°. W. R.

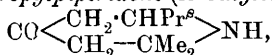
**Nitroso-derivatives of Cyclic Acetone Bases.** MORITZ KOHN and FRANZ WENZEL (*Monatsh.*, 1906, 27, 981—986. Compare Heintz, this *Journal*, 1877, ii, 428; Fischer, *Abstr.*, 1884, 1290; Antrick, *Abstr.*, 1885, 502).—Nitroso-derivatives have been obtained from vinylidiacetonamine, isobutylidenediacetonamine, and benzylidenediacetonamine by the action of potassium nitrite on the hydrochloride of the base in aqueous solution.

1-Nitroso-2 : 2 : 6-trimethylpiperidone (*nitrosovinylidiacetonamine*),



crystallises from dilute methyl alcohol in light yellow, rhombic plates,  $[a:b:c=0.9878:1.0932:1]$  or  $a:b:c=0.6585:0.7288:1]$ , m. p. 58—59°.

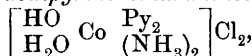
2:2-Dimethyl-6 isopropylpiperidone (isobutylidenediacetonamine),



prepared by boiling isobutaldehyde with diacetonamine oxalate in alcoholic solution, is obtained as a slightly yellow oil, b. p. 115°/22 mm. The *aurichloride*,  $\text{C}_{10}\text{H}_{19}\text{ON} \cdot \text{HAuCl}_4$ , was analysed. The *nitroso-derivative*,  $\text{C}_{10}\text{H}_{18}\text{ON} \cdot \text{NO}$ , crystallises in light spears, m. p. 51—52°.

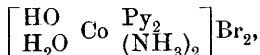
1-Nitroso-6-phenyl-2:2-dimethylpiperidone (nitrosobenzylidenediacetonamine),  $\text{CO} < \begin{array}{c} \text{CH}_2 \cdot \text{CHPh} \\ \text{CH}_2 - \text{CMe}_2 \end{array} > \text{N} \cdot \text{NO}$ , forms large, yellow, rhombic crystals,  $[a:b:c=0.6465:0.7286:1]$ , m. p. 66—68°. G. Y.

**Hydroxo-aquodipyridinediammincobalt and Diaquodipyridinediammincobalt Salts.** ALFRED WERNER (*Ber.*, 1907, 40, 468—479).—*Hydroxo-aquodipyridinediammincobaltichloride*,



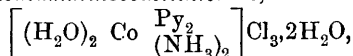
obtained by the addition of dichlorodiaquodiammincobaltichloride,  $\left[ \text{Cl}_2 \text{ Co} \begin{array}{c} (\text{OH})_2 \\ (\text{NH}_3)_2 \end{array} \right] \text{Cl}$ , to a mixture of potassium chloride, water, and pyridine at 0°, separates as a pink, crystalline deposit with a nacreous lustre. Its aqueous solution is brownish-red, gives a feebly alkaline reaction with litmus, and quickly decomposes, the odour of pyridine becoming perceptible. When potassium bromide, potassium thiocyanate, &c. are added to a freshly-prepared solution, the corresponding hydroxo-aquo-salts are precipitated.

*Hydroxo-aquodipyridinediammincobaltibromide*,



is a violet-red, microcrystalline salt. It may also be obtained by the addition of potassium bromide to diaquodipyridinediammincobaltichloride by the treatment of the diaquo-bromide with water or by the precipitation of the aqueous solution with a little hydrobromic acid and by washing the diaquo-bromide with alcohol. The *nitrate* crystallises in bluish, pale-red needles; the *thiocyanate* forms violet-brown needles. The *dithionate* forms reddish-brown leaflets with a metallic lustre.

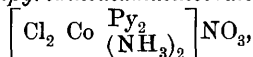
*Diaquodipyridinediammincobaltichloride*,



obtained by the action of concentrated hydrochloric acid on hydroxo-aquodipyridinediammincobaltichloride, forms a grey, crystalline powder, and may be obtained also as ruby-red crystals or as greenish-grey or yellowish-brown prisms. When heated at 60°, it is converted into the *compound*,  $\left[ \text{Cl}_2 \text{ Co} \begin{array}{c} \text{Py}_2 \\ (\text{NH}_3)_2 \end{array} \right] \text{Cl}$ , which is a chocolate-coloured powder; its solution in water is brownish-red and gives an acid reaction.

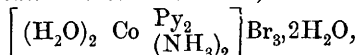


When an aqueous solution of diaquodipyridinediammincobaltichloride is heated with concentrated hydrochloric acid, chlorine is evolved. When, however, concentrated hydrochloric acid is added to the solid salt, *dichlorodipyridinediammincobaltionitrate*,



separates in dark green leaflets.

*Diaquodipyridinediammincobaltibromide*,



obtained by the action of concentrated hydrobromic acid on hydroxo-aquodipyridinediammincobaltichloride, forms yellowish-brown leaflets. Its aqueous solution is brownish-red and shows an acid reaction.

The *sulphate*,  $\left[ (\text{H}_2\text{O})_2 \text{ Co } \begin{smallmatrix} \text{Py}_2 \\ (\text{NH}_3)_2 \end{smallmatrix} \right]_2 (\text{SO}_4)_3, 2\text{H}_2\text{SO}_4$ , separates in brownish-violet leaflets. Its aqueous solution is red and shows an acid reaction.

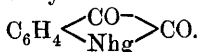
The *nitrate*,  $\left[ (\text{H}_2\text{O})_2 \text{ Co } \begin{smallmatrix} \text{Py}_2 \\ (\text{NH}_3)_2 \end{smallmatrix} \right] (\text{NO}_3)_3, 2\text{H}_2\text{O}$ , forms red crystals. The *dithionate*,  $\left[ (\text{H}_2\text{O})_2 \text{ Co } \begin{smallmatrix} \text{Py}_2 \\ (\text{NH}_3)_2 \end{smallmatrix} \right]_2 (\text{S}_2\text{O}_6)_3, 2\text{H}_2\text{O}$ , is a brown, crystalline powder.

A. McK.

### Mercury Salts of Isatin and of 1:3-Diketohydrindene.

WALTER PETERS (*Ber.*, 1907, 40, 235—240).—The author's aim is the preparation of *N*- and of *O*-metallic derivatives of isatin and of *C*' and *O*-derivatives of 1:3-diketohydrindene (compare Hantzsch, *Abstr.*, 1902, i, 662).

*Mercurysisatin*, obtained in 95% yield by decomposing a boiling alcoholic solution of isatin with concentrated aqueous mercuric acetate, is a dark red, glistening substance which dissolves in alkalis to a yellow solution; consequently it has the constitution

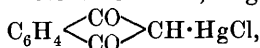


When an aqueous solution is treated with potassium hydroxide and subsequently neutralised, a precipitate of *o*-mercuriaminobenzoylformic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{CO}_2\text{H} \\ \text{Nhg} \end{smallmatrix}$ , is obtained in glistening, white or grey

leaflets containing  $2\text{H}_2\text{O}$  which is lost at  $100^\circ$ , the substance turning red; at higher temperatures isatin is formed. An attempt to prepare the potassium salt of the preceding acid by passing carbon dioxide into an alkaline solution of mercury isatin, resulted in the formation of the substance,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} - \text{CO} \\ \text{NH} \cdot \text{Hg} \end{smallmatrix} \text{O}.$

*O*-metallic derivatives of isatin have not been prepared.

When an aqueous or alcoholic solution of sodio-1:3-diketohydrindene is treated with excess of mercuric chloride, a light yellow substance,



is obtained which is changed by sodium carbonate into a white hydroxide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{CH} \cdot \text{Hg} \cdot \text{OH}.$

C. S.

**Indolinones.** KARL BRUNNER (*Monatsh.*, 1906, 27, 1183—1192. Compare Abstr., 1897, i, 100; 1898, i, 90; 1905, i, 468; Schwarz, Abstr., 1903, i, 853).—A list is given of the indolinones which have been prepared by heating hydrazides with calcium oxide, and two new members of the group are described.

iso*Butyryl-o-tolylhydrazide*,  $C_7H_7 \cdot NH \cdot NH \cdot CO \cdot CHMe_2$ , formed by heating *o*-tolylhydrazine with isobutyric acid at 130°, crystallises in leaflets, m. p. 93°, and when heated with calcium oxide at 190—200° is converted into 3:3:7-trimethylindoline-2-one,  $C_6H_3Me \begin{smallmatrix} <CMe_2> \\ NH \end{smallmatrix} CO$ , which crystallises in colourless, rhombic leaflets, m. p. 150°, b. p. 285—295°, is soluble in concentrated mineral acids or aqueous alkalis, and gives a transient, intense, carmine-red coloration with manganese dioxide or potassium dichromate in concentrated sulphuric acid solution; the *silver* derivative,  $C_{11}H_{12}ONAg$ , forms microscopic prisms. The *bromo*-derivative,  $C_{11}H_{12}ONBr$ , formed by the action of hydrobromic acid on the indolinone, crystallises in rectangular leaflets, m. p. 179—180°.

iso*Butyryl-p-tolylhydrazide*, prepared from isobutyric acid and *p*-tolylhydrazine, crystallises in white leaflets, m. p. 147—148°, and when heated with calcium oxide at 220—240° yields 3:3:5-trimethylindoline-2-one,  $C_{11}H_{13}ON$ ; this crystallises from dilute alcohol in leaflets, m. p. 144—145°, or in needles, m. p. 140° when rapidly heated, when slowly heated, m. p. 144—145°. It dissolves in hot concentrated sodium hydroxide and deposits the *sodium* derivative in long needles on cooling; the *silver* derivative,  $C_{11}H_{12}ONAg$ , is gelatinous. The *bromo*-derivative,  $C_{11}H_{12}ONBr$ , crystallises in long prisms, m. p. 214°. G. Y.

**A New Indolinol.** GUIDO JENISCH (*Monatsh.*, 1906, 27, 1223—1232).—Brunner (Abstr., 1898, i, 384, 682; 1900, i, 360) has shown that indolinium bases having an alkyl group in the position 2, lose water, forming 2-methyleneindolines, but that the  $\psi$ -ammonium base or indolinol is obtained if position 2 is occupied by hydrogen. This is now found to be the case with 2-arylindolinium bases.

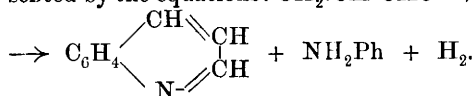
2-Phenyl-1:3:3-trimethyl-2-indolinol,  $C_6H_4 \begin{smallmatrix} <CMe_2> \\ NMe \end{smallmatrix} CPh \cdot OH$ , is formed by the successive action of alcoholic stannous chloride and potassium hydroxide on the condensation product of phenyl isopropyl ketone and *as*-phenylmethylhydrazine, or by the action of magnesium phenyl bromide on 1:3:3-trimethylindolinone in ethereal-benzene solution; it crystallises in almost colourless leaflets, m. p. 101—102°, and dissolves readily in dilute mineral acids, forming solutions which slowly became red on exposure to air. The *ferrichloride*,

$C_{17}H_{18}NCl, FeCl_3$ , forms yellowish-green crystals; the *platinichloride*,  $(C_{17}H_{18}NCl)_2PtCl_4$ , m. p. 216—216.5°; the *picrate*,  $C_{23}H_{22}O_8N_4$ , m. p. 139—140°. The  $\psi$ -base remains unchanged when boiled with concentrated hydrochloric acid or heated with zinc chloride at 120°, but is oxidised by alcoholic potassium permanganate, and with hydrobromic acid in hydrochloric acid solution yields a crystalline product, m. p. 191°. G. Y.

**Mechanism of the Synthesis of Quinoline Derivatives.** LOUIS J. SIMON (*Compt. rend.*, 1907, **144**, 138—140. Compare Abstr., 1906, i, 887, 888).—A theoretical paper discussing possible mechanisms of the synthesis of quinoline derivatives. E. H.

**$\beta$ -Chloroethyl Ketones and Alkyl Vinyl Ketones. Method of Synthesising 4-Alkylquinolines.** EDMOND E. BLAISE and M. MAIRE (*Compt. rend.*, 1907, **144**, 93—95. Compare Abstr., 1906, i, 142).—4-Alkylquinolines can be readily prepared by heating 1 mol. of a  $\beta$ -chloroethyl ketone with 2 mols. of aniline in alcoholic solution on a water-bath, in this case the aniline hydrochloride, which is one of the products of the reactions, serves to effect the formation of a cyclic compound from the open chain compound first formed, and in fact  $\beta$ -anilinoethyl ethyl ketone yields the corresponding quinoline when heated with aniline hydrochloride. 4-Ethylquinoline, b. p.  $134^{\circ}/9$  mm., yields cinchoninic acid on oxidation and differs from the compound described by Reher (Abstr., 1887, 279), which was probably impure; 4-n-propylquinoline has b. p.  $159^{\circ}/16$  mm.

In view of the fact that phenolic amines form compounds with vinyl ketones owing to the presence of the ethylenic linking in the ketone, the authors suggest that Skraup's quinoline synthesis may be represented by the equations:  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO} \rightarrow \text{NHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}$ ,



M. A. W.

**Alkylation of Pyridones.** HANS MEYER (*Monatsh.*, 1906, **27**, 987—996. Compare Abstr., 1906, i, 108, 604).—The action of diazomethane on kynurine in ethereal solution in presence of a small quantity of methyl alcohol leads to the formation of 4-methoxyquinoline together with a small amount of the  $\psi$ -methyl ether. The hydrochloride of 4-methoxyquinoline crystallises in long, colourless needles, m. p.  $164$ — $166^{\circ}$  (decomp.). Kynurine aurichloride forms slender, lemon-yellow needles, m. p.  $217^{\circ}$  (decomp.).

4-Methoxy-2-methylquinoline, formed by the action of diazomethane on 2-methylkynurine, crystallises in white needles, m. p.  $62^{\circ}$  ( $82^{\circ}$ , Conrad and Limpach, Abstr., 1877, 679).

3-Phenyl-6-methylkynurine,  $\text{C}_6\text{H}_5\text{Me} \begin{array}{c} \text{C}(\text{OH})\cdot\text{CPh} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{CH} \end{array}$ , is prepared by the action of *p*-toluidine in presence of alcohol at the laboratory temperature on ethyl formylphenylacetate, obtained by treating ethyl phenylacetate with ethyl formate and sodium in ethereal solution, and heating the resulting ethyl  $\alpha$ -phenyl- $\beta$ -*p*-toluidinoacrylate at  $300^{\circ}$ . It crystallises from alcohol in long, white, glistening needles, m. p.  $315^{\circ}$ . When treated with a large excess of diazomethane it yields only a small amount of the *O*-methyl ether,  $\text{C}_9\text{H}_4\text{NPhMe}\cdot\text{OMe}$ , which separates from methyl alcohol in needles, m. p.  $117^{\circ}$ .

4-Methoxy-2-methyl- and 4-methoxy-3-phenyl-6-methylquinoline yield methyl iodide readily and quantitatively when heated with hydriodic acid; the corresponding 4-ethoxyquinolines have been

prepared and their behaviour in this respect compared (see Goldschmidt, this vol., i, 30).

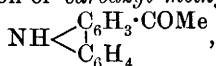
4-Ethoxy-2-methylquinoline,  $C_6H_4 \begin{smallmatrix} \text{C(OEt):CH} \\ \text{N} = \text{CMe} \end{smallmatrix}$ , m. p. 40–41°, b. p. 290°, prepared by heating 4-chloro-2-methylquinoline (Conrad and Limpach, *loc. cit.*) with sodium ethoxide and absolute alcohol under pressure at 130°, reacts only slowly with hydriodic acid, and, when treated according to the Herzig-Meyer method of estimating *N*-alkyl groups, yields about 40% of the theoretical amount of silver iodide.

4-Chloro-3-phenyl-6-methylquinoline,  $C_6H_3Me \begin{smallmatrix} \text{C(OEt):CPh} \\ \text{N} = \text{CH} \end{smallmatrix}$ , prepared by the action of phosphorus pentachloride and oxychloride on the hydroxyquinoline, crystallises in white needles, m. p. 94°, and when heated with sodium ethoxide and absolute alcohol at 100° is converted into the *O*-ethyl ether; this is obtained as an oil, and yields ethyl iodide quantitatively when heated with hydriodic acid.

G. Y.

**New Carbazoles.** WALTHER BORSCHKE and M. FEISE (*Ber.*, 1907, 40, 378–386).—This investigation, undertaken with the object of preparing homologues of carbazole by the Friedel-Craft reaction, has led to the formation of carbazyl methyl ketones and by oxidation of these to that of carbazolecarboxylic acids. The position assumed by the acetyl- and carboxyl-groups respectively has not been determined. Attempts to do so were unsuccessful in consequence of the stability of 3-methylcarbazole (Delétra and Ullmann, *Abstr.*, 1904, i, 270) towards oxidising agents. Two new formations of 3-methylcarbazole are described.

Diacetylcarbazole,  $N\text{Ac} \begin{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{COMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix}$ , formed by the action of acetyl bromide and aluminium chloride on 9-acetylcarbazole in anhydrous carbon disulphide solution, is obtained as a brown, crystalline precipitate, m. p. 104°. The *oxime*,  $C_{16}H_{14}O_2N_2$ , crystallises from alcohol or ethyl acetate in white, nodular aggregates, m. p. 172°. Hydrolysis of the diacetyl compound with boiling alcoholic sulphuric acid leads to the formation of *carbazyl methyl ketone*,



which crystallises from alcohol or toluene in white leaflets, m. p. 227°; the *semicarbazone* crystallises in colourless scales, m. p. above 360°; the *oxime*,  $C_{14}H_{12}ON_2$ , forms glistening, colourless leaflets, m. p. 253°.

Cinnamoylcarbazole,  $NH \begin{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh} \\ \text{C}_6\text{H}_4 \end{smallmatrix}$ , prepared by the action of benzaldehyde and sodium ethoxide on the methyl ketone in alcoholic solution, crystallises in small, yellow needles, m. p. 282°.

Carbazolecarboxylic acid,  $NH \begin{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CO}_2H \\ \text{C}_6\text{H}_4 \end{smallmatrix}$ , formed by heating the methyl ketone with fused potassium hydroxide, crystallises in slender,

colourless needles, m. p. 320—322°; the *ethyl* ester,  $C_{15}H_{13}O_2N$ , forms colourless leaflets, m. p. 184°.

2'-Nitro-4-methyldiphenylamine (Jacobson and Lischke, Abstr., 1899, i, 276) is prepared by hydrolysis with concentrated hydrochloric acid in a sealed tube at 130—140° of *p*-toluidine 3-nitro-4-*p*-toluidino-benzenesulphonate formed by boiling *p*-toluidine 4-chloro-3-nitro-benzenesulphonate with *p*-toluidine.

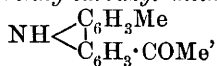
The benzoyl derivative of *p*-tolyl-*o*-phenylenediamine,  $C_{20}H_{18}ON_2$ , crystallises in colourless needles, m. p. 143—144°.

1-*p*-Tolyl-1 : 2 : 3-benzotriazole,  $N \begin{smallmatrix} \nwarrow N(C_7H_7) \\ \nearrow \end{smallmatrix} > C_6H_4$ , formed by the action of sodium nitrite on *p*-tolyl-*o*-phenylenediamine in hydrochloric acid solution, crystallises in colourless needles, m. p. 84—85°, and on distillation yields 3-methylcarbazole.

The *hydrochloride* of 2-amino-4-methyldiphenylamine, formed by the action of bromobenzene on nitrotoluidine in nitrobenzene solution and reduction of the resulting product, crystallises in colourless needles, m. p. 200—201°; the *base*,  $NHPh \cdot C_6H_3Me \cdot NH_2$ , crystallises in glistening needles, m. p. 140°. The *benzoyl* derivative,  $C_{20}H_{18}ON_2$ , crystallises from alcohol in colourless needles, m. p. 161°.

1-Phenyl-5-methyl-1 : 2 : 3-benzotriazole,  $N \begin{smallmatrix} \nwarrow NPh \\ \nearrow \end{smallmatrix} > C_6H_3Me$ , prepared by the action of nitrous acid on the preceding base, crystallises from a mixture of benzene and light petroleum in small, glistening prisms, m. p. 117°, and on distillation yields 3-methylcarbazole.

9-Acetyl-3-methylcarbazole,  $NAc \begin{smallmatrix} \nwarrow C_6H_3Me \\ \nearrow C_6H_4 \end{smallmatrix}$ , prepared by heating 3-methylcarbazole with acetic anhydride at 220—240°, is obtained as an oil which reacts with acetyl bromide and aluminium chloride, forming 9-acetyl-3-methylcarbazyl methyl ketone,  $NAc \begin{smallmatrix} \nwarrow C_6H_3Me \\ \nearrow C_6H_3 \cdot COMe \end{smallmatrix}$ ; this crystallises in yellow needles, m. p. 131°, and on hydrolysis with sulphuric acid yields 3-methylcarbazyl methyl ketone,



which crystallises in white nodules, m. p. about 200°.

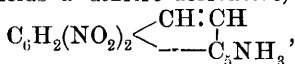
3-Methylcarbazolecarboxylic acid,  $NH \begin{smallmatrix} \nwarrow C_6H_3Me \\ \nearrow C_6H_3 \cdot CO_2H \end{smallmatrix}$ , formed by fusing 9-acetyl-3-methylcarbazyl methyl ketone with potassium hydroxide, crystallises in colourless scales, which darken above 220°, m. p. 265°. G. Y.

**Estimation of Loosely Combined Methylene Groups.** EMIL VOTOČEK and VIKTOR VESELY (*Ber.*, 1907, 40, 410—414).—Methylene derivatives which contain the methylene group attached to oxygen of aliphatic compounds or those containing the methylene groups attached to nitrogen readily react with a glacial acetic acid solution of carbazole in the presence of hydrochloric or sulphuric acid, yielding insoluble products. It is claimed that the compound, m. p. 202—203°, obtained by Morgan (*Trans.*, 1898, 73, 550) by the action

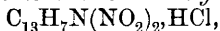
of formaldehyde on  $\beta$ -naphthylamine cannot have the constitution suggested, as it does not react with carbazole. The product obtained by the action of formaldehyde on carbazole has the composition  $C_{20}H_{20}ON_2$ .

Carbazole and dimethylene gluconic acid yields a crystalline product,  $C_{25}H_{18}N_2$  m. p., above  $280^\circ$ . J. J. S.

**Nitro-derivatives of  $\beta$ -Naphthaquinoline.** HANS HEPNER (*Monatsh.*, 1906, 27, 1045—1068. Compare Haid, Abstr., 1906, i, 605; Claus and Bessler, Abstr., 1898, i, 331).—On nitration at  $70$ – $80^\circ$  by Claus and Kramer's method (Abstr., 1885, 908),  $\beta$ -naphthaquinoline yields a dinitro-derivative,



which forms microscopic needles, m. p.  $249^\circ$ ; when recrystallised from concentrated hydrochloric acid it forms a *hydrochloride*,

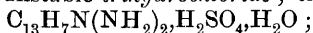


which crystallises in prismatic needles, m. p.  $249^\circ$ , evolving hydrogen chloride, and decomposes on treatment with water.

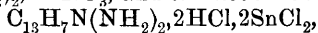
Nitration of  $\beta$ -naphthaquinoline at the laboratory temperature leads to the formation of a mononitro-derivative, m. p.  $173^\circ$ , which is identical with Claus and Bessler's compound (*loc. cit.*).

**Diamino- $\beta$ -naphthaquinoline**,  $C_6H_2(NH_2)_2 \begin{array}{l} \text{CH:CH} \\ \text{---} \text{C}_5\text{NH}_3 \end{array}$ , prepared

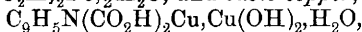
reduction of the dinitro-compound with stannous chloride and hydrochloric acid, crystallises in yellow, microscopic needles, m. p.  $249^\circ$ ; the *hydrochloride*,  $C_{13}H_7N(NH_2)_2 \cdot 2HCl$ , forms dark red needles, remains unchanged at  $300^\circ$ , but at higher temperatures decomposes without melting, and when recrystallised from concentrated hydrochloric acid forms an unstable *trihydrochloride*; the *sulphate*,



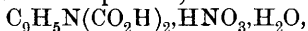
*nitrate*,  $C_{13}H_7N(NH_2)_2 \cdot 2HNO_3$ , and *stannoehloride*,



are described. On oxidation with potassium permanganate or chromic acid in sulphuric acid solution, the base yields *quinoline-5:6-dicarboxylic acid*,  $C_9H_5N(CO_2H)_2 \cdot H_2O$ , which crystallises in almost colourless, rhombic leaflets, sinters at  $233^\circ$ , m. p.  $238$ – $241^\circ$  (decomp.), and is stable towards oxidising agents. A number of salts are described; the *lead*,  $C_9H_5N(CO_2H)_2 \cdot Pb \cdot \frac{1}{2}H_2O$ , and *basic copper*,



salts were analysed. The *hydrochloride*,  $C_9H_5N(CO_2H)_2 \cdot HCl$ , forms strongly refracting, colourless prisms; the *nitrate*,



crystallises in needles, m. p.  $208$ – $210^\circ$  (decomp.); the *platinichloride*,  $[C_9H_5N(CO_2H)_2]_2 \cdot H_2PtCl_6$ , forms yellow needles and gradually decomposes when heated. G. Y.

**Constitution of *o*-Tolidine.** GUSTAV SCHULTZ, GEORG ROHDE, and F. VICARI (*Annalen*, 1907, 352, 111–131. Compare Abstr., 1904, i, 532).—Proof is given that *o*-tolidine is 4:4'-diamino-3:3'-

dimethyldiphenyl. *Sodium bisdiazoo-o-ditolylsulphonate* is obtained by adding sodium sulphite to a cold diazotised solution of *o*-tolidine in sulphuric acid; it crystallises in white needles which when heated decompose without melting.

This substance when reduced by stannous chloride and hydrochloric acid is converted into *o-tolidinedihydrazine hydrochloride*, which crystallises in yellow needles; the *free base* is obtained as a greyish-white precipitate by decomposing the hydrochloride with sodium carbonate or sulphite; it could not be obtained in a crystalline form; by warming it with an alcoholic solution of benzaldehyde, a yellow substance is obtained; with acetone a grey substance is obtained. By distilling a mixture of *o-tolidinedihydrazine* with copper acetate, 3 : 3'-dimethyldiphenyl,  $C_{14}H_{14}$ , is obtained; it is a colourless oil, b. p.  $286-287^{\circ}/713$  mm., which solidifies at  $-16^{\circ}$  to a white, crystalline mass, m. p.  $+5-7^{\circ}$ . The same compound is obtained by the action of sodium on *m*-iodotoluene in ether, therefore in *o*-tolidine the methyl groups occupy the 3 : 3'-positions.

3 : 3'-Dimethyldiphenyl is converted by a mixture of nitric and sulphuric acids into 4 : 4'-dinitro-3 : 3'-dimethyldiphenyl,  $C_{14}H_{12}O_4N_2$ , which crystallises in faintly yellow needles, m. p.  $228^{\circ}$ . When reduced with sodium sulphide it is converted into 4-nitro-4'-amino-3 : 3'-dimethyldiphenyl which crystallises in yellow needles, m. p.  $142-143^{\circ}$ ; *o*-tolidine is obtained from the latter compound by reduction with tin and hydrochloric acid in alcoholic solution.

That in *o*-tolidine the amino-groups occupy the 4 : 4'-positions is shown by the fact that the same dichlorodiphenyldicarboxylic acid is obtained both from *o*-tolidine and from benzidinedicarboxylic acid. In the latter substance the 4 : 4'-positions of the amino-groups has been definitely proved.

Dichloro-3 : 3'-dimethyldiphenyl, obtained by Sandmeyer's reaction from *o*-tolidine, may be oxidised to dichlorodiphenyldicarboxylic acid; the acid has m. p.  $323-324^{\circ}$  and its methyl ester, m. p.  $134^{\circ}$ . When heated above  $324^{\circ}$ , carbon dioxide is evolved and 4 : 4'-dichlorodiphenyl is formed.

W. H. G.

**Hydroxy-derivatives of Malachite-Green.** EMIL VOTOČEK and J. JELÍNEK (*Ber.*, 1907, 40, 406-410. Compare Noeltig and Gerlinger, *Abstr.*, 1906, i, 610).—*o-Methoxy-leucomalachite-green*,  $C_{24}H_{28}ON_2$ , obtained from anisaldehyde and dimethylaniline, crystallises from alcohol in colourless prisms, m. p.  $106^{\circ}$ , and when oxidised yields a green dye with a red fluorescence. The corresponding *ethoxy*-derivative melts at  $125^{\circ}$  and also yields a green dye. The *leuco-base*,  $C_{24}H_{26}O_2N_2$ , from piperonal and dimethylaniline melts at  $109-110^{\circ}$  and yields a bluish-green dye. Anisole and tetramethyldiaminobenzhydrol yield a *leuco-base*,  $C_{24}H_{28}ON_2$ , m. p.  $155^{\circ}$ , which is oxidised to a blue dye. It dyes cotton mordanted with tannin a greenish-blue, but this changes to violet on the addition of alkalis. The corresponding *leuco-base* from phenetole melts at  $165^{\circ}$  and yields a dye which gives a blue colour on mordanted cotton. The addition of alkali produces a violet colour. Guaiacol and tetramethyldiaminobenzhydrol yield a *leuco-base* which forms pale rose-coloured crystals, m. p.

134—135°. The corresponding dye is blue.  $\beta$ -Naphthol and tetramethyldiaminobenzhydrol yield a leuco-base which could not be isolated in a crystalline form. The corresponding dye is pure blue in colour. The *acetyl* derivative of the leuco-base,  $C_{29}H_{30}O_2N_2$ , melts at 136° and yields a green dye. J. J. S.

**3-Phenyl-1-methyl-5-pyrazolone.** AUGUST MICHAELIS (*Annalen*, 1907, 352, 152—217).—Although 1-phenyl-3-methyl-5-pyrazolone and its derivatives have been studied extensively, the isomeric 3-phenyl-1-methyl-5-pyrazolone had not been investigated to any extent. The two isomerides, although different physically, are very similar chemically, differing chiefly in their behaviour towards benzaldehyde, with which substance 1-phenyl-3-methyl-5-pyrazolone alone gives a crystalline benzylidene derivative. From 3-phenyl-1-methyl-5-pyrazolone an anti-pyrene has been prepared which the author calls *isopantipyrene*, the isomeride previously known by this name being called 3-antipyrene; all three isomeric antipyrenes behave similarly physiologically, the 3-antipyrene being the most poisonous.

[With WILHELM RASSMANN.]—By heating 3-phenyl-5-pyrazolone, dissolved in benzene, with phosphorus oxychloride in sealed tubes at 190—200°, 5-chloro-3-phenylpyrazole is formed; it crystallises in white needles, m. p. 142°, but sublimes below this temperature, and distils undecomposed at 295°/760 mm.; soluble both in strong acids and dilute alkalis; the *silver* salt,  $C_9H_6N_2ClAg$ , and *hydrochloride*,  $C_9H_7N_2Cl \cdot HCl$ , m. p. 131°, decomposed by water into its components, have been prepared. 5-Chloro-3-phenylpyrazole when heated with phosphorus pentachloride in sealed tubes at 120° is converted into 4:5-dichloro-3-phenylpyrazole, m. p. 95—96°, whilst with bromine in acetic acid solution it gives 5-chloro-4-bromo-3-phenylpyrazole, which crystallises in white needles, m. p. 90°.

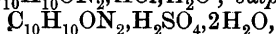
4-Benzeneazo-5-chloro-3-phenylpyrazole,  $NH \begin{matrix} \swarrow CCl:C:N:N \cdot Ph \\ \searrow N=CPh \end{matrix}$ , cannot

be directly obtained from 5-chloro-3-phenylpyrazole; it is prepared by acting on 4-benzeneazo-3-phenyl-5-pyrazolone with phosphorus oxychloride and crystallises in red needles, m. p. 192°; the chlorine atom cannot be replaced by hydrogen, as is possible with other benzeneazochloropyrazoles. By acting on 5-chloro-3-phenylpyrazole with a mixture of nitric and sulphuric acids, 5-chloro-3-nitrophenylpyrazole is obtained; it crystallises in yellowish-green needles, m. p. 180°; that the nitro-group is present in the phenyl radicle is shown by the fact that on brominating this compound, 5-chloro-4-bromo-3-nitrophenylpyrazole, yellow needles, m. p. 130°, is formed, the same compound being obtained by nitrating 5-chloro-4-bromo-3-phenylpyrazole.

[With HUGO DORN.]—A better yield of 3-phenyl-1-methyl-5-pyrazolone is obtained from 3-phenyl-5-pyrazolone by using methyl sulphate instead of methyl iodide (compare von Rothenburg, *Abstr.*, 1895, i, 686); that the compound has the formula assigned to it is supported by the fact that it is obtained by the condensation of methylhydrazine with ethyl benzoylacetate; further, since its *isonitroso*-derivative is red, it



is undoubtedly a 5-pyrazolone, the nitroso-derivatives of 3-pyrazolones being green. The following salts have been obtained in a crystalline form: *hydrochloride*,  $C_{10}H_{10}ON_2 \cdot HCl \cdot H_2O$ ; *sulphate*,



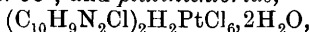
and *nitrate*,  $C_{10}H_{10}ON_2 \cdot HNO_3 \cdot H_2O$ . On treatment with nitrous acid, 3-phenyl-1-methyl-5-pyrazolone is converted into 4-isonitroso-3-phenyl-

1-methyl-5-pyrazolone,  $NMe \begin{array}{c} \text{N}=\text{CPh} \\ \diagup \quad \diagdown \\ \text{CO}-\text{C} \cdot \text{N} \cdot \text{OH} \end{array}$ , crystallising in orange leaflets, m. p.  $162^\circ$ ; it dissolves in alkalis and gives the Liebermann's reaction.

4-Benzeneazo-3-phenyl-1-methyl-5-pyrazolone is produced by the interaction of 3-phenyl-1-methyl-5-pyrazolone with diazobenzene chloride; it forms orange needles, m. p.  $158^\circ$ ; when heated with phosphorus oxychloride in sealed tubes at  $120^\circ$  it is converted into 4-benzeneazo-5-chloro-1-methyl-3-phenylpyrazole, which forms yellow needles, m. p.  $94^\circ$ ; the chlorine cannot be replaced by hydrogen by the action of tin and hydrochloric acid. When 3-phenyl-1-methyl-5-pyrazolone is heated with phosphorus oxychloride at  $160^\circ$  it is converted into 5-chloro-3-phenyl-1-methylpyrazole, which is obtained also by heating 5-chloro-3-phenylpyrazole with methyl iodide in sealed tubes at  $100^\circ$ ; it crystallises in white leaflets, m. p.  $62^\circ$ . When heated with excess of methyl iodide for several days, the *methiodide*,

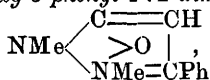
$NMe \begin{array}{c} \text{NMeI} \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{CCl}=\text{CH} \end{array}$ , forming colourless needles, m. p.  $167^\circ$ , is obtained

together with a *periodide*,  $C_{11}H_{12}N_2ClI_4$ , which forms dark reddish-violet leaflets, m. p.  $105^\circ$ ; the periodide is also formed by adding iodine to the methyl iodide derivative; the *hydrochloride*,  $C_{10}H_9N_2Cl \cdot HCl$ , m. p.  $95^\circ$ , and *platinichloride*,

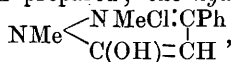


m. p.  $193^\circ$ , were prepared. An isomeric 3-chloro-5-phenyl-1-methylpyrazole is obtained either by methylating 5-chloro-3-phenylpyrazole in alcoholic solution or by eliminating methyl chloride from anti-pyrene chloride by the action of phosphorus oxychloride; it crystallises in white needles, m. p.  $76^\circ$ . When heated with potassium hydrogen sulphide, the methyl iodide derivatives of either of these isomerides give the same thiopyrene, and with alkalis they yield the same anti-pyrene. The formula given to the compound has not been definitely proved. When heated with phosphorus pentachloride in sealed tubes at  $140^\circ$ , or treated in acetic acid solution with bromine, 5-chloro-3-phenyl-1-methylpyrazole is converted respectively into 4:5-dichloro-3-phenyl-1-methylpyrazole, which forms transparent crystals, m. p.  $25.5^\circ$ , b. p.  $317^\circ/760$  mm., and 5-chloro-4-bromo-3-phenyl-1-methylpyrazole, white needles, m. p.  $65^\circ$ . A *perbromide*,  $C_{10}H_8N_2ClBr_3$ , is obtained by adding excess of bromine to a solution of 5-chloro-3-phenyl-1-methylpyrazole in light petroleum; it is a yellow powder, m. p.  $103^\circ$ , and is converted by sodium hydroxide into the preceding compound, m. p.  $65^\circ$ . Iodine in the presence of iodic acid converts 5-chloro-3-phenyl-1-methylpyrazole into 5-chloro-4-iodo-3-phenyl-1-methylpyrazole, white needles, m. p.  $105^\circ$ .

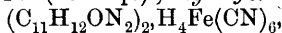
*isoAntipyrine* (2 : 5-oxy-3-phenyl-1 : 2-dimethylpyrazole),



may be prepared, either by heating 3-phenyl-1-methyl-5-pyrazolone (1 mol.) with methyl iodide (1 mol.) in a sealed tube at  $100^\circ$  or from 3-phenyl-5-pyrazolone by heating with methyl iodide; it forms white crystals, which soften at  $98^\circ$  and completely liquefy at  $108^\circ$ , and differs from Knorr's antipyrine in that it is hygroscopic and gives with mercuric chloride a precipitate which dissolves only with great difficulty on heating, whereas with antipyrine the precipitate dissolves immediately on warming slightly. The following salts of *isoantipyrine* have been prepared; the *hydrochloride*,



white needles, m. p.  $207^\circ$ ; *hydroiodide*,  $\text{C}_{11}\text{H}_{12}\text{ON}_2\text{HI} \cdot \text{H}_2\text{O}$ , crystalline powder, m. p.  $100\text{--}118^\circ$  (decomp.); *hydroferrocyanide*,

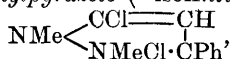


yellowish-white powder; *hydroferricyanide*, yellow needles, m. p.  $122^\circ$  (decomp.); *picrate*,  $\text{C}_{11}\text{H}_{12}\text{ON}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , yellow needles, m. p.  $142^\circ$ .

When *isoantipyrine* is treated with bromine in chloroform, a *perbromide*, m. p.  $187^\circ$  (decomp.), is formed; the latter on treatment with water gives rise to 4-bromo*isoantipyrine*, crystallising in white leaflets, m. p.  $179^\circ$ ; by the action of nitrous acid, *isoantipyrine* is converted into 4-nitroso-*isoantipyrine*, which crystallises in emerald-green leaflets, m. p.  $215^\circ$  (decomp.); it is decomposed by warm sodium hydroxide; its *hydrochloride*,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3 \cdot \text{HCl}$ , crystallises in orange needles, m. p.  $162^\circ$ ; by treating *isoantipyrine* in strong hydrochloric acid with an excess of sodium nitrite it is converted into 4-nitro*isoantipyrine*, crystallising in yellow prisms, m. p.  $143^\circ$  (decomp.).

4 : 4'-Benzylidenedi-*isoantipyrine*,  $\text{CHPh}(\text{C}_3\text{N}_2\text{PhMe}_2\text{O})_2$ , is produced by the condensation of *isoantipyrine* (2 mols.) with benzaldehyde (1 mol.) in the presence of a little strong hydrochloric acid; it crystallises in white leaflets containing  $2\text{H}_2\text{O}$ ; m. p.  $70^\circ$  when hydrated or  $213^\circ$  when anhydrous, it gives no coloration with ferric chloride.

5-Chloro-3-phenyl-1-methylpyrazole ("isoAntipyrine chloride"),

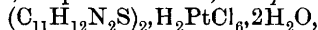


obtained by the action of phosphorus oxychloride on *isoantipyrine*, is a white, hygroscopic powder containing, when precipitated from alcoholic solution by ether,  $2\text{H}_2\text{O}$ , m. p.  $70^\circ$ , or when anhydrous, m. p.  $130^\circ$ ; it gives a faint red coloration with ferric chloride, and when heated decomposes into 3-chloro-5-phenyl-1-methylpyrazole and methyl chloride; when treated with picric acid in alcoholic solution, the 2-chlorine atom is replaced, the compound formed,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Cl} \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$ , crystallises in yellow leaflets, m. p.  $155^\circ$ ; the same chlorine atom of *isoantipyrine* chloride may be replaced by iodine by treatment with potassium iodide; the *platinichloride*,  $(\text{C}_{10}\text{H}_9\text{N}_2\text{CH}_2\text{Cl})_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ , m. p.  $214^\circ$ ; and *mercurichloride*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Cl}_2 \cdot \text{HgCl}_2$ , m. p.  $136^\circ$ , are crystalline.

*isoThiopyrine*,  $\text{NMe} \begin{array}{l} \diagup \text{C} = \text{CH} \\ \diagdown \text{S} \quad | \\ \text{NMe} : \text{CPh} \end{array}$ , is obtained by treating "*isoanti*-

pyrine chloride" with potassium hydrogen sulphide; it crystallises in long needles, m. p.  $178^\circ$ , and is coloured yellow by sulphurous acid; on one occasion an *isomeride*, m. p.  $162^\circ$ , of similar properties was obtained, but could not again be prepared. The *hydrochloride*,

$\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}\cdot\text{HCl}$ , crystallises in needles, m. p.  $155-162^\circ$ ; the *platinichloride*,

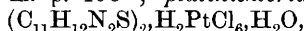


is a red powder, m. p.  $231^\circ$ ; *mercurichloride*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}\cdot\text{HgCl}_2$ , a white, crystalline powder, m. p.  $224^\circ$ ; *hydroiodide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}\cdot\text{HI}$ , forms monoclinic crystals, m. p.  $131^\circ$ ; the *methiodide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}\cdot\text{MeI}\cdot\text{H}_2\text{O}$ , crystallises in needles, m. p.  $102.5^\circ$ .

*isoThiopyrine trioxide*,  $\begin{array}{c} \text{NMe} \\ | \\ \text{C} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{NMe} \\ | \quad | \\ \text{CH} \quad \text{CPh} \end{array}$ , prepared by heating "*isoanti*-

pyrine chloride" with a solution of sodium sulphite, forms fan-shaped crystals, m. p.  $291^\circ$ .

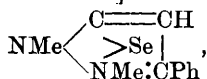
$\psi$ -*isoThiopyrine* (5-methylthiol-3-phenyl-1-methylpyrazole) is obtained by distilling the methyl iodide derivative of *isothiopyrine*; it is a colourless liquid, b. p.  $184^\circ/10$  mm., and combines with methyl iodide at  $100^\circ$ , forming the compound from which it is prepared; its *hydrochloride*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , forms white needles, m. p.  $106^\circ$ , or when anhydrous, m. p.  $158^\circ$ ; *platinichloride*,



yellow needles, m. p.  $204^\circ$ ; *hydroiodide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}\cdot\text{HI}\cdot\text{H}_2\text{O}$ , m. p.  $174^\circ$ . When  $\psi$ -*isothiopyrine* is acted on by nitrous acid, 4-nitroso- $\psi$ -*isothiopyrine* is formed; it crystallises in green needles, m. p.  $137^\circ$ . The isomeric  $\psi$ -*thiopyrine* gives under the same conditions 4-nitroso- $\psi$ -

*thiopyrine*,  $\text{NPh} \begin{array}{l} \diagup \text{N} = \text{CMe} \\ \diagdown \text{C}(\text{SMe}) : \text{C} \cdot \text{NO} \end{array}$ , which forms dark green leaflets, m. p.  $96^\circ$ .

[With THOMAS VON DER HAGEN.]—*isoSelenopyrine*,



is formed by the interaction of "*isoanti*pyrine chloride" with potassium hydrogen selenide; it crystallises in white needles, m. p.  $198^\circ$ , and gives no coloration with ferric chloride, but with sulphurous acid a temporary yellow coloration is produced; it does not readily form salts with acids, crystallising unchanged from hydrochloric acid; the *platinichloride* is a brown powder which commences to decompose at  $150^\circ$  and does not melt at  $300^\circ$ ; the *mercurichloride* is a white powder, m. p.  $200^\circ$

(decomp.); the *methiodide*,  $\text{NMe} \begin{array}{l} \diagup \text{NMeI} = \text{CPh} \\ \diagdown \text{C}(\text{SeMe}) : \text{CH} \end{array}$ , crystallises with  $8\text{H}_2\text{O}$ , m. p.  $152^\circ$ ; the corresponding *ethiodide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Se}\cdot\text{EtI}$ , forms anhydrous crystals, m. p.  $118^\circ$ .

*Dichloroisoselenopyrine*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Cl}_2\text{Se}$ , is formed by passing chlorine

into a chloroform solution of *isoselenopyrine*; it is a light yellow powder, m. p.  $163^{\circ}$  (decomp.). By the action of bromine, *isoselenopyrine tetrabromide*,  $C_{11}H_{12}N_2Br_4Se$ , is obtained in golden-brown needles, m. p.  $108^{\circ}$ ; when repeatedly evaporated with water it is converted into *isoselenopyrine dibromide*,  $C_{11}H_{12}N_2Br_2Se_2$ , which forms golden-yellow needles, m. p.  $215^{\circ}$ , and on treatment with sodium carbonate is converted into *isoselenopyrine*.

*iso-ψ-Selenopyrine* (5-methylselenol-3-phenyl-1-methylpyrazole) is formed by the combination of methyl iodide with *isoselenopyrine* in ether; it is a light yellow liquid, b. p.  $196-197^{\circ}/15$  mm.; it combines with chlorine to form a *dichloride*, a yellowish-green powder, m. p.  $161^{\circ}$ ; the *dibromide*, m. p.  $177^{\circ}$ , when heated with a solution of sodium carbonate is converted into 4-bromoiso-ψ-selenopyrine, m. p.  $129^{\circ}$ ; the *hydrochloride* of iso-ψ-selenopyrine,  $C_{11}H_{12}N_2Se, HCl$ , forms white needles, m. p.  $106^{\circ}$ ; the *platinichloride*,  $(C_{11}H_{12}N_2Se)_2, H_2PtCl_6$ , is a reddish-brown powder, and does not melt at  $300^{\circ}$ . On treatment with nitrous acid, iso-ψ-selenopyrine gives 4-nitrosoiso-ψ-thiopyrine, which crystallises in green needles, m. p.  $136^{\circ}$ .

[With HANS WREDE].—By the reduction of 4-isonitroso-3-phenyl-1-methyl-5-pyrazolone with zinc dust in acetic acid solution, 4-amino-3-phenyl-1-methyl-5-pyrazolone is produced; it cannot be obtained in the free state since it at once oxidises to isorubazonic acid; its *hydrochloride* forms white needles, m. p.  $175^{\circ}$  (decomp.). The base condenses readily

with aldehydes; the *benzylidene* derivative,  $NMe \begin{matrix} N=CPh \\ | \\ CO \cdot CH \cdot N : CHPh \end{matrix}$ , crystallises in yellow needles, m. p.  $227^{\circ}$ ; the *o-hydroxybenzylidene* derivative,  $C_{10}H_9ON_2 \cdot N : CH \cdot C_6H_4 \cdot OH$ , crystallises in faintly yellow prisms, decomposing at  $230^{\circ}$ ; the *p-methoxybenzylidene* derivative crystallises in yellow needles, m. p.  $220^{\circ}$  (decomp.), and the *p-nitrobenzylidene* derivative commences to decompose at  $250^{\circ}$ ; *furfurylidene* and *cinnamylidene* derivatives melt at  $180^{\circ}$  and  $152^{\circ}$  respectively.

*isoRubazonic acid*,  $NMe \begin{matrix} C(OH) : C \cdot N : C \cdot CO \\ | \\ N = CPh \quad CPh : N \end{matrix} NMe$ , is obtained

by the oxidation of 4-amino-3-phenyl-1-methyl-5-pyrazolone with ferric chloride; it crystallises in dark red needles, m. p.  $188^{\circ}$ ; it forms violet-coloured salts with alkalis; treatment with phenylhydrazine gives benzeneazo-3-phenyl-1-methyl-5-pyrazolone.

4-Aminoisoantipyrine,  $C_{11}H_{13}ON_3$ , is obtained by the reduction of 4-nitrosoisoantipyrine with zinc dust and acetic acid or stannous chloride and hydrochloric acid; it forms large, white, stable crystals, m. p.  $109^{\circ}$ ; the *hydrochloride*,  $C_{11}H_{13}ON_3, HCl$ , crystallises in white needles, m. p.  $210^{\circ}$ ; the *stannochloride*,  $(C_{11}H_{13}ON_3)_2, SnCl_2$ , forms thick, white crystals which are decomposed by hydrochloric acid when concentrated with the precipitation of 4-aminoisoantipyrine hydrochloride; the *sulphate*,  $C_{11}H_{13}ON_3, H_2SO_4$ , m. p.  $205^{\circ}$ , and *picrate*,

$C_{11}H_{13}ON_3, C_6H_2(NO_2)_3 \cdot OH$ , yellow prisms decomposing at  $165^{\circ}$  were also prepared. *Aminoisoantipyrine mucobromate*,  $C_{11}H_{13}ON_3, C_4H_2O_3Br_2$ , is a yellow powder, m. p.  $115^{\circ}$ , obtained by mixing together solutions of its components.

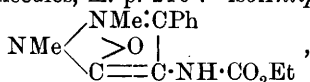
The following condensation products of 4-aminoisoantipyrine with various aldehydes and ketones were prepared.

*Benzylideneaminoisoantipyrine*,  $\text{NMe} \begin{array}{l} \text{NMe} \cdot \text{CPh} \\ \text{>O} \mid \\ \text{C} = \text{C} \cdot \text{N} : \text{CH} \cdot \text{Ph} \end{array}$ , crystallises

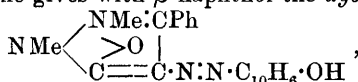
in yellow prisms, m. p.  $151^\circ$ ; *o*-hydroxybenzylideneaminoisoantipyrine, yellow needles, m. p.  $173^\circ$ ; *p*-methoxybenzylideneaminoisoantipyrine, yellow needles, m. p.  $177^\circ$ ; *p*-nitrobenzylidene derivative, m. p.  $155^\circ$ ; *cinnamylidene* derivative, colourless prisms, m. p.  $151^\circ$ ; *ethyl acetate* derivative, colourless crystals, m. p.  $141^\circ$ , and *acetophenone* derivative, colourless prisms, m. p.  $167^\circ$ .

*Formylaminoisoantipyrine*,  $\text{C}_{11}\text{H}_{11}\text{ON}_2 \cdot \text{NH} \cdot \text{COH}$ , crystallises in colourless, rhombic plates, m. p.  $209^\circ$ ; *acetyl*aminoisoantipyrine forms colourless prisms, m. p.  $233^\circ$ ; *benzoyl*aminoisoantipyrine crystallises in colourless crystals, m. p.  $234^\circ$ ; a dibenzoyl derivative could not be prepared. *Benzenesulphonylaminoisoantipyrine*,  $\text{C}_{11}\text{H}_{11}\text{ON}_2 \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$ , crystallises in needles, m. p.  $245^\circ$ .

*s*-*Di*-isoantipyrinylthiocarbamide,  $\text{CS}(\text{NH} \cdot \text{C}_3\text{N}_2\text{Me}_3\text{PhO})_2$ , obtained by heating aminoisoantipyrine in alcoholic solution with carbon disulphide, crystallises in white prisms, m. p.  $225^\circ$ . By heating 4-aminoisoantipyrine with phenylthiocarbimide in alcoholic solution, *phenyl*-isoantipyrinylthiocarbamide,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{11}\text{H}_{11}\text{ON}_2$ , is obtained, crystallising in white needles, m. p.  $210^\circ$ . *isoAntipyrilurethane*,



forms colourless crystals, m. p.  $190^\circ$ . Although the diazo-derivatives of pyrazoles and pyrazolones are stable, no diazo-derivative of aminoisoantipyrine could be isolated; however, a freshly-diazotised solution of aminoisoantipyrine gives with  $\beta$ -naphthol the *dye*,

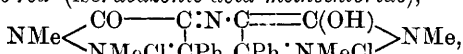


a red, crystalline substance dissolving in concentrated sulphuric acid with a violet colour.

*Dimethylaminoisoantipyrine* (*isopyramidone*),  $\text{NMe} \begin{array}{l} \text{NMe} \cdot \text{CPh} \\ \text{>O} \mid \\ \text{C} = \text{C} \cdot \text{NMe}_2 \end{array}$ , is

prepared by acting on aminoantipyrine with either methyl iodide or methyl sulphate; it forms monoclinic crystals, m. p.  $118^\circ$ ; the *picrate*,  $\text{C}_{13}\text{H}_{17}\text{ON}_3 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ , crystallises in yellow leaflets, m. p.  $166^\circ$ ; the *methiodide* forms colourless needles, m. p.  $197^\circ$ . *Diethylaminoisoantipyrine*, obtained by acting on aminoisoantipyrine with ethyl sulphate, is a colourless oil. By heating aminoisoantipyrine with ethylene bromide at  $140^\circ$ , both *di*-isoantipyrinediethylenediamine,  $\text{C}_4\text{H}_8\text{N}_2(\text{C}_{11}\text{H}_{11}\text{ON}_2)_2$ , white crystals, m. p.  $300^\circ$ , and *di*-isoantipyrine-ethylenediamine,  $\text{C}_2\text{H}_4\text{N}_2(\text{C}_{11}\text{H}_{11}\text{ON}_2)_2$ , white needles, m. p.  $132^\circ$ , are obtained; the *picrate* of the latter crystallises in yellow needles, m. p.  $148^\circ$ .

*isoAntipyrine-red* (*isorubazonic acid methochloride*),

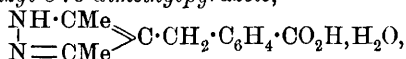


is formed by the oxidation of aminoisoantipyrine in aqueous solution



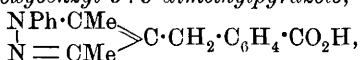
The action of hydroxylamine hydrochloride and sodium acetate on acetylacetone- $\gamma$ -benzyl-*o*-carboxylic acid in aqueous acetic acid solution leads to the formation of 4-*o*-carboxybenzyl-3 : 5-dimethyliso-oxazole,  $\begin{smallmatrix} \text{N}:\text{CMe} \\ | \\ \text{O}:\text{CMe} \end{smallmatrix} \gg \text{C} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , which separates in white crystals, m. p. 117—118°.

4-*o*-Carboxybenzyl-3 : 5-dimethylpyrazole,



prepared by boiling acetylacetonebenzyl-*o*-carboxylic acid with semi-carbazide acetate in alcoholic or with hydrazine in glacial acetic acid solution, crystallises in needles, loses  $\text{H}_2\text{O}$  at 100—110°; m. p. 180°.

1-Phenyl-4-*o*-carboxybenzyl-3 : 5-dimethylpyrazole,



formed from phenylhydrazine and acetylacetonebenzyl-*o*-carboxylic acid, separates from alcohol in transparent crystals, m. p. 217—218°.

G. Y.

**Preparation of 5 : 5-Dialkylbarbituric Acids.** EMANUEL MERCK (D. R.-P. 174178).—When heated with concentrated acids (sulphuric, hydrochloric, benzenesulphonic, and naphthalenetrisulphonic acids) the dialkylmalonuramides yield 5 : 5-dialkylbarbituric acids. In this way diethylmalonuramide when heated with excess of concentrated sulphuric acid at 100—110° gives rise to 5 : 5-diethylbarbituric acid.

G. T. M.

**Preparation of 2-Imino-4 : 6-dioxy-mono- and di-5-alkyl-pyrimidines.** CHEMISCHE FABRIK AUF AKTIEN (vorm. E. Schering) (D. R.-P. 174940).—Although barbituric acid is not readily alkylated in alkaline or dilute alcoholic solutions, yet 2-imino-4 : 6-dioxypyrimidine (malonylguanidine) furnishes a good yield of alkyl derivatives. The interaction of 1 mol. of ethyl iodide in presence of potassium hydroxide gives rise to 2-imino-4 : 6-dioxy-5-ethylpyrimidine, whilst 2-imino-4 : 6-dioxy-5 : 5-diethylpyrimidine is formed when 2 mols. of alkyl iodide are employed. The yield of the latter product is, however, improved by alkylating in two stages.

G. T. M.

**Indoleaminopropionic Acid and its Halogen Derivatives. The Tryptophan Reaction.** CARL NEUBERG and NIKOLAUS POWOWSKY (*Biochem. Zeitsch.*, 1907, 2, 357—382. Compare Hopkins and Cole, *Abstr.*, 1901, i, 310).—Pure tryptophan (indoleaminopropionic acid) may be obtained somewhat more readily from fibrin than from casein by Hopkins and Cole's method. From 600 grams of dried material 8 grams of tryptophan were obtained. It is a convenience to combine the preparation of tyrosine with that of tryptophan.

The reddish-violet coloration obtained by the addition of chlorine or bromine water to tryptophan attains a maximum when the amount of

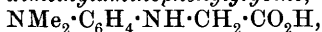
halogen is equivalent to 4 atoms per gram-mol. of tryptophan. When concentrated solutions are used, red, amorphous precipitates of monohalogen derivatives,  $C_{11}H_{11}O_2N_2Br$  and  $C_{11}H_{11}O_2N_2Cl$ , are obtained. The compounds dissolve in amyl alcohol or ether, yielding reddish-violet solutions, and both decompose at about  $280^\circ$ . Excess of halogen converts the red compounds into yellow *perhaloids*,  $C_{11}H_{11}O_2N_2Br_3$  and  $C_{11}H_{11}O_2N_2Cl_3$ , which contain two of the three halogen atoms only loosely combined.

The contradictory results obtained by previous authorities are due to their having worked with mixtures of the yellow and red compounds. No trace of sulphur is contained in the pure coloured substances. The nitrogen in tryptophan and its derivatives may be estimated by Kjeldahl's process. J. J. S.

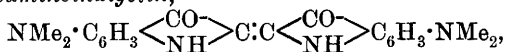
**Preparation of Quinazoline from *o*-Nitrobenzaldehyde.** J. D. RIEDEL (D. R.-P. 174941. Compare Abstr., 1904, i, 1060; 1905, i, 944).—The following operations afford a ready means of preparing quinazoline, a substance hitherto obtained only with some difficulty.

*o*-Nitrobenzylidenediformamide,  $NO_2 \cdot C_6H_4 \cdot CH(NH \cdot CHO)_2$ , produced by passing hydrogen chloride into a mixture of *o*-nitrobenzaldehyde (1 part) and formamide (2 parts) at  $40-50^\circ$ , is soluble in hot water and alcohol, but insoluble in ether; stellar aggregates of prisms, m. p.  $177-178^\circ$ . Quinazoline is obtained from this diformamide by reducing it with zinc dust and dilute acetic acid. G. T. M.

**Di-*p*-dimethylaminoindigotin.** MARTIN FREUND and ADOLF WIRSING (*Ber.*, 1907, 40, 204—206).—*p*-Dimethylaminophenylglycinitrile,  $NMe_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CN$ , prepared by the action of hydrogen cyanide and formaldehyde on dimethyl-*p*-phenylenediamine in alcoholic solution at  $100^\circ$  under pressure, crystallises in colourless needles, m. p.  $80-81^\circ$ , and is hydrolysed by boiling aqueous potassium hydroxide forming *p*-dimethylaminophenylglycine,



m. p.  $182-183^\circ$ ; the potassium salt,  $C_{10}H_{13}O_2N_2K$ , crystallises in glistening scales, commences to decompose at  $280^\circ$ , and is melted at  $308^\circ$ . When added to fused sodamide, the potassium salt forms di-*p*-dimethylaminoindigotin,

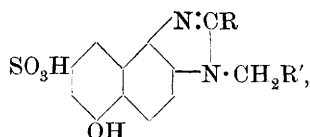


which separates from water as a green, flocculent substance, does not melt or sublime when heated, forms bluish-green solutions in organic solvents, or blue solutions in dilute hydrochloric or concentrated sulphuric acid, dyes wool green in acetic acid solution or in presence of sodium hydrogen sulphite, and forms sparingly double salts with zinc, mercuric, and platinic chlorides. G. Y.

**Preparation of 5-Hydroxynaphthaminobenzaldehyde-7-sulphonic Acid.** LEOPOLD CASSELLA & Co. (D.R.-P. 175023. Compare Abstr., 1906, i, 989).—Hydroxynaphthaminobenzaldehyde-



sulphonic acids having the general formula

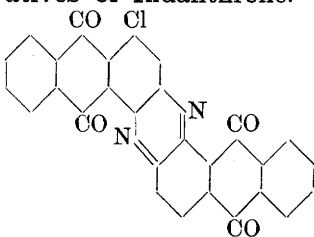


where R and R' are dissimilar radicles, may be prepared by condensing 1 : 2-diamino-5-hydroxynaphthalene-7-sulphonic acid with the bisulphite compound of an aldehyde, whereby an intermediate product is obtained which can then be further condensed with a molecule of a second aldehyde.

The bisulphite compound of *m*-aminobenzaldehyde was condensed with the sulphonic acid and the intermediate product condensed with the bisulphite compound of benzaldehyde. The final product is a yellow, amorphous substance, sparingly soluble in alcohol or water, and having both acidic and weak basic properties. It combines with diazo-compounds and is readily diazotised, giving an insoluble diazo-derivative which is reddened by alkalis.

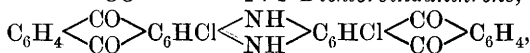
G. T. M.

**Indanthrene and Flavanthrene. III. The Halogen Derivatives of Indanthrene.** ROLAND SCHOLL, HANS BERBLINGER, and



JOHANNES MANSFIELD (*Ber.*, 1907, 40, 320—325. Compare *Abstr.*, 1904, i, 110).—4-*Chloroanthraquinonazine*, prepared by the oxidation of 4-chloroindanthrene with nitric acid, D 1·285, on the water-bath, has a greenish-yellow colour somewhat darker than anthraquinonazine.

4 : 4'-*Dichloroindanthrene*,



is obtained as a blue powder when the monochloro-derivative is heated for three hours at 180° with hydrochloric acid.

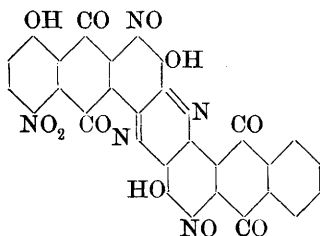
4-*Bromoindanthrene*,  $\text{C}_{28}\text{H}_{18}\text{O}_4\text{N}_2\text{Br}$ , prepared by heating anthraquinonazine with hydrobromic acid, D 1·47, for two hours at 150° in a closed tube, crystallises from quinoline in slender blue needles with a copper-red reflex. It is oxidised to 4-*bromoanthraquinonazine*,  $\text{C}_{28}\text{H}_{11}\text{O}_4\text{N}_2\text{Br}$ , by nitric acid, D 1·285. It is greenish-yellow and dissolves more easily in concentrated sulphuric acid than the parent azine. 4-4'-*Dibromoindanthrene*,  $\text{C}_{28}\text{H}_{12}\text{O}_4\text{N}_2\text{Br}_2$ , prepared similarly to the dichloro-derivative, is blue and has not been obtained quite pure. 4 : 4'-*Dibromoanthraquinonazine* 3 : 4-*dibromide*,  $\text{C}_{28}\text{H}_{10}\text{O}_4\text{N}_2\text{Br}_4$ , is prepared by heating indanthrene with bromine in a sealed tube at 100° for six hours. The dark green base is converted into 3 : 4 : 4'-*tribromoindanthrene*,  $\text{C}_{28}\text{H}_{11}\text{O}_4\text{N}_2\text{Br}_3$ , by boiling quinoline, and crystallises in slender blue needles.

W. R.

**Indanthrene and Flavanthrene. IV. Action of Nitric Acid on Indanthrene.** ROLAND SCHOLL and JOHANNES MANSFIELD (*Ber.*, 1907, 40, 326—329).—Boiling dilute nitric acid, D 1·24, oxidises indanthrene to anthraquinonazine, but when boiling acid is employed, a

nitrodinitrosotrihydroxy- or tetranitrotetrahydroxyanthraquinonazine is obtained according to the conditions.

*Nitrodinitrosotrihydroxyanthraquinonazine*,  $C_{28}H_9O_{11}N_5$ , obtained by boiling 1 part of indanthrene with 12 to 15 parts of nitric acid, D 1.4, for twelve hours, is a yellow, crystalline powder when crystallised from concentrated nitric acid or nitrobenzene; it dissolves in sulphuric acid with a yellowish-red colour. The *sodium* salt is black. The compound is of the nature of a nitro- or nitroso-phenol, as it dissolves in aqueous sodium carbonate; no nitro- or nitroso-group is attached to an azine nitrogen atom, as boiling phenol is without action.

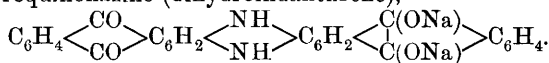


The constitution provisionally assigned is as here given. On reduction with excess of dilute sodium hydrogen sulphide at 70–80°, *triaminotrihydroxyindanthrene*,  $C_{28}H_{17}O_7N_3$ , is obtained, and crystallises from nitrobenzene in violet-black needles; the *hydrochloride* is yellow, and the base is sparingly soluble in hot dilute sodium hydroxide.

*Tetranitrotetrahydroxyanthraquinonazine*,  $C_{28}H_9O_{16}N_6$ , is obtained by boiling indanthrene in a mixture of fuming nitric acid, D 1.5, and sulphuric acid, and yields, on reduction with sodium hydrogen sulphide, *tetra-aminotetrahydroxyindanthrene*,  $C_{28}H_{18}O_8N_6$ .

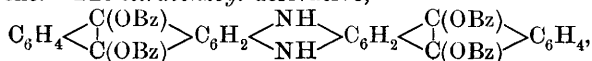
Nitrodinitrosotrihydroxyanthraquinonazine dyes cotton substantively a wine red, but the two amino-compounds are of no technical value as dyes for vegetable fibres. W. R.

**Indanthrene and Flavanthrene. V. Reduction Products of Indanthrene.** ROLAND SCHOLL, WILHELM STEINKOPF, and A. KABACZNIK (*Ber.*, 1907, 40, 390–394. Compare Abstr., 1904, i, 109, 110, and preceding abstracts).—The blue substance formed by reduction of indanthrene by means of sodium hydrogen sulphite in aqueous sodium hydroxide solution, and termed commercially “indanthrene S,” is the *disodium* derivative of *N*-dihydro-1:2:1':2'-anthraquinone-anthrahydroquinonazine (dihydroindanthrene),



When treated with benzoyl chloride and sodium hydroxide it yields a *dibenzoyl* derivative,  $C_6H_4 \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} C_6H_2 \begin{array}{c} \diagup NH \diagdown \\ \diagdown NH \diagup \end{array} C_6H_2 \begin{array}{c} \diagup C(OBz) \diagdown \\ \diagdown C(OBz) \diagup \end{array} C_6H_4$ , which is obtained as an insoluble, blue, crystalline powder.

The yellowish-brown substance formed by reduction of indanthrene by means of sodium hydrogen sulphite and zinc dust is the *tetra-sodium* derivative of tetrahydroindanthrene; it cannot be isolated in consequence of the ease with which it is oxidised, yielding finally indanthrene. The *tetrabenzoyl* derivative,



formed by the action of benzoyl chloride and sodium hydroxide on the reduction product, is obtained as a brownish-yellow, microcrystalline powder, m. p. above  $300^{\circ}$ , which dissolves in chloroform, benzene,  $\psi$ -cumene, or ethyl benzoate, forming a solution with green fluorescence. G. Y.

**Indanthrene and Flavanthrene. VI. Action of Quinoline and Acyl Chlorides on Indanthrene.** ROLAND SCHOLL and HANS BERBLINGER (*Ber.*, 1907, 40, 395—400. Compare preceding abstracts).—The action of benzoyl chloride on indanthrene in boiling quinoline solution leads to the formation of the tetrabenzoyl derivative of tetrahydroindanthrene, which, when heated, yields a sublimate of benzoic acid and dissolves in alcoholic potassium hydroxide, forming a blue solution depositing indanthrene on dilution and exposure to air. It is oxidised by concentrated nitric acid, yielding the *nitrate* of tetrabenzoylanthrahydroquinonazine, which forms an indigo-blue solution and is hydrolysed on heating with the acid, forming a soluble, brown anthraquinonazine. When boiled with quinoline, the tetrabenzoyltetrahydroindanthrene is converted slowly into anthranonazine.

*Tetra-acetyl-N-dihydroanthrahydroquinonazine* is formed slowly by boiling indanthrene with acetyl chloride and quinoline in glacial acetic acid solution; it crystallises in microscopic, brownish-yellow needles, dissolves in organic solvents, forming reddish-yellow solutions with green fluorescence, and is converted into dihydroindanthrene by the action of alcoholic potassium hydroxide. On prolonged boiling with quinoline, it yields anthranonazine, which is formed more rapidly by the action of acetyl chloride on indanthrene in boiling quinoline solution in the absence of acetic acid.

The formation of *O*-acyl derivatives of a reduced indanthrene instead of substitution of the imine hydrogen atoms must result from increased stability of these when in proximity to carbonyl groups (compare Abstr., 1904, i, 109), as is the case with the hydroxyl-hydrogen of the aldol of diacetyl (von Pechmann, Abstr., 1895, i, 647). The reducing action of acid anhydrides or acyl chlorides on quinones and similar substances has been observed in other cases; thus, methylene-blue is converted into the acetyl derivative of the leuco-compound when heated with acetic anhydride and sodium acetate, a reaction which takes place also with thiazine and oxazine dyes (compare Japp and Graham, *Trans.*, 1881, 39, 174). G. Y.

**Action of Hydrogen Sulphide on Rosaniline and Phenylated Rosanilines.** RUDOLF LAMBRECHT (*Ber.*, 1907, 40, 247—255. Compare Abstr., 1905, i, 243).—The action of hydrogen sulphide on rosanilines is explicable on the assumption of the intermediate formation of a hydrosulphide,  $:C_6H_4:NH_2 \cdot SH$ ; attempts to isolate such a compound, however, lead to the formation of a quinonoid oxidation product of unknown constitution.

In acid or neutral alcoholic solution, hydrogen sulphide reduces *p*-rosaniline to the leucaniline; excess of ammonium hydrosulphide produces *triaminotriphenylcarbothiol*,  $C_{19}H_{19}N_3S$ . The carbothiol forms colourless solutions in mineral acids, but loses hydrogen sulphide in

alcohol-acetic acid solution. It dissolves in alcohol to an intensely magenta coloured solution, by the evaporation of which a quinonoid substance is obtained; a similar greenish-red glistening substance is formed when the carbothiol is heated at  $140^{\circ}$ .

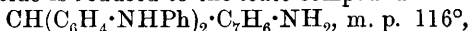
*Triaminotritolylcarbothiol*,  $C_{22}H_{25}N_3S$ , obtained from new magenta in a similar manner to the preceding compound, yields the carbinol base by treatment with alkalis, and in alcoholic solution is converted into quinonoid products.

*p*-Rosaniline-blue (Kalle & Co.), treated with hydrogen sulphide in alcoholic solution, yields triphenyl-*p*-leucaniline, m. p.  $182^{\circ}$ , whereas excess of ammonium hydrosulphide produces the carbinol base,



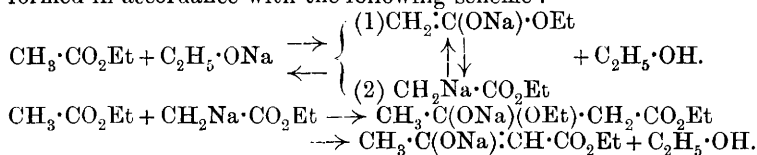
Diphenylamine-blue is an impure triphenyl-*p*-rosaniline, since by treatment with alcoholic hydrogen sulphide it yields impure triphenyl-*p*-leucaniline, m. p.  $178^{\circ}$ .

Rosaniline-blue is reduced to the *leuco*-compound



by alcoholic hydrogen sulphide, and yields the carbinol base by treatment with excess of ammonium hydrosulphide. C. S.

**Urazoles. VIII. Sale of Tautomeric Compounds.** SALOMON F. ACREE (*Amer. Chem. J.*, 1907, 37, 71—85).—This paper deals with the behaviour of the metallic salts of tautomeric acids. The relations between the concentration of solutions of such salts and the equilibrium constants are discussed. It is considered that all syntheses analogous to the ethyl acetoacetate synthesis depend on the reactions of tautomeric salts. Thus, in the formation of ethyl acetoacetate from ethyl acetate and sodium ethoxide, a sodium salt of ethyl acetate is formed, which exists in two tautomeric forms. The sodium salt (2) reacts vigorously with the ethyl acetate present, and ethyl acetoacetate is formed in accordance with the following scheme:



It is well known that when the silver salts of certain amides are treated with alkyl halides at the ordinary temperature, oxygen ethers are formed principally, whilst the potassium salts at higher temperatures yield chiefly the nitrogen compounds. The theories which have been advanced by Comstock, Wheeler, Nef, and Michael to account for such reactions are discussed and shown to be inadequate. In place of these the following hypothesis is brought forward. "A salt of a tautomeric compound reacts with an alkyl halide or other reagent and forms two compounds, because the tautomeric salt is really a mixture of two tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions. This reaction may, in certain cases, be complicated by the simultaneous rearrangement of one of the reaction products into the other or into some other product."

This theory is supported by the results of experiments which have been carried out with a view of ascertaining the conditions of equilibrium which exist in solutions of salts of 1-phenyl-4-methylurazole. When a salt of this urazole is heated with ethyl iodide in solution in dilute alcohol, ether, or benzene, a mixture of 3-ethoxy-1-phenyl-4-methylurazole,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OEt} \\ \text{CO}-\text{NMe} \end{smallmatrix}$ , and 1-phenyl-4-methyl-2-ethylurazole,  $\text{NPh} \begin{smallmatrix} \text{NEt}\cdot\text{CO} \\ \text{CO}-\text{NMe} \end{smallmatrix}$ , is produced. The proportions in which these two compounds are formed varies with the salt employed. Thus, in dilute alcohol (40%), 90% of the *N*-ethyl and 10% of the *O*-ethyl derivatives are produced. In the same solvent, the barium salt gives 93.5% of the former and 6.5% of the latter, whilst the sodium salt yields 58.7% of the *O*-compound and 41.3% of the *N*-compound. The silver salt in ether gives 35% of the *N*-ethyl and 65% of the *O*-ethyl derivatives. The determination of these ratios at 22°, 60°, and 90° shows that each is nearly constant, or the two side reactions have approximately the same temperature coefficient. Neither of the two derivatives undergoes rearrangement into the other under any of the conditions studied. The proportions in which the two compounds are produced vary not only with the salt and the solvent employed, but also with the particular alkyl halide used; thus, whilst in dilute alcohol (40%) at 60°, the potassium salt reacts with ethyl iodide in one hour to the extent of 30.35%, and 90% of the product consists of the *N*-ethyl derivative; the same salt reacts with ethyl bromide under the same conditions to the extent of 22.5%, and the *N*-ethyl derivative forms 87.7% of the product.

E. G.

**Triazoles.** MAX BUSCH (*J. pr. Chem.*, 1906, [ii], 74, 533—549. Compare Abstr., 1906, i, 115).—An attempt to prepare acylendaiminotriazoles by the action of formic acid on benzoylaminodiphenylguanidines failed, as the action leads to the formation of the colourless, feebly basic 5-aminotriazoles formed previously by heating the acylaminoguanidines (Busch and Bauer, Abstr., 1900, i, 414).

*Triazoles from benzoylaminodiphenylguanidines.*—[With HERM. BRANDT.]—The action of carbodiphenylimide on benzhydrazide in benzene solution at 50° leads to the formation of benzoylaminodiphenylguanidine and 5-anilino-1:2-diphenyl-1:2:3-triazole, which are separated by conversion of the slightly acid guanidine into its soluble *sodium* salt. When oxidised with alcoholic ferric chloride, benzoylaminodiphenylguanidine yields a blue product which is probably the azo-compound,  $\text{NHPh}\cdot\text{C}(\text{NPh})\cdot\text{N}\cdot\text{NBz}$ .

The anilinotriazole, which is the chief product of the action of carbodiphenylimide on benzhydrazide in boiling benzene solution, is formed also by heating benzoylaminodiphenylguanidine with formic acid in a sealed tube at 170°; it yields only traces of aniline and benzoic acid when heated with concentrated hydrochloric acid under pressure at 200°.

The following tolyl compounds are prepared in the same manner.

*Benzoylaminodi-o-tolylguanidine*,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}(\text{N}\cdot\text{C}_7\text{H}_7)\cdot\text{NH}\cdot\text{NHBz}$ ,

crystallises from alcohol in nodular aggregates, m. p.  $151^{\circ}$ , intumescing, and, when heated above its melting point, forms water and 5-o-toluidino-2-phenyl-1-o-tolyltriazole,  $\begin{array}{c} \text{N} \cdot \text{C}(\text{NHC}_7\text{H}_7) \\ \text{N} = \text{CPh} \end{array} > \text{N} \cdot \text{C}_7\text{H}_7$ , which is obtained as a white, crystalline powder, m. p.  $142^{\circ}$ .

*Benzoylamino-di-p-tolylguanidine*,  $\text{C}_{22}\text{H}_{22}\text{ON}_4$ , forms yellow, transparent prisms, m. p.  $190^{\circ}$ , intumescing.

5-p-Toluidino-2-phenyl-1-p-tolyltriazole,  $\text{C}_{22}\text{H}_{20}\text{N}_4$ , crystallises in glistening spears, m. p.  $196^{\circ}$ .

The action of carbodiphenylimide on semicarbazide leads to the formation of ammonia, carbon dioxide, hydrazodicarboxylamide, triphenylguanazole, and triphenylguanidine.

*endoIminotriazoles*.—[With HERM. BRANDT.]—*p-Bromoanilinodi-phenylguanidine*,  $\text{NHPh} \cdot \text{C}(\text{NPh}) \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$ , prepared from *p*-bromophenyldiazine and carbodiphenylimide, is obtained as a white, crystalline powder, m. p.  $141^{\circ}$ . When boiled with formaldehyde in alcoholic solution, it forms 3-anilino-4-phenyl-1-p-bromophenyl-4:5-dihydro-1:2:4-triazole,  $\begin{array}{c} \text{N} \cdot \text{C}(\text{NHPh}) \\ \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{CH}_2 \end{array} > \text{NPh}$ , which crystallises in sheaves of needles, m. p.  $119^{\circ}$ , and on successive treatment with sodium nitrite and nitric acid in glacial acetic acid solution yields the sparingly soluble *nitrate* of 4-phenyl-1-p-bromophenyl-3:5-endo-anilo-4:5-dihydro-1:2:4-triazole,  $\text{C}_{20}\text{H}_{15}\text{N}_4\text{Br} \cdot \text{HNO}_3$ , crystallising in

slender needles; the free base (*bromonitron*),  $\begin{array}{c} \text{N} = \text{C} \\ \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{CH} \end{array} \begin{array}{c} \text{NPh} \\ \text{NPh} \end{array} > \text{NPh}$ , crystallises in stout, glistening needles, m. p.  $223^{\circ}$  (decomp.); the *nitrate* is slightly more, the *hydrochloride* and *sulphate* less, soluble than the corresponding nitron salts.

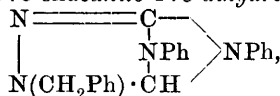
$\alpha$ -Naphthylaminodiphenylguanidine,  $\text{C}_{23}\text{H}_{20}\text{N}_4$ , prepared from  $\alpha$ -naphthylhydrazine and carbodiphenylimide, crystallises from benzene in colourless leaflets containing benzene of crystallisation, m. p.  $143^{\circ}$ , and is oxidised by mercuric oxide in alcoholic solution, yielding the *azo*-compound,  $\text{NHPh} \cdot \text{C}(\text{NPh}) \cdot \text{N} \cdot \text{N} \cdot \text{C}_{10}\text{H}_7$ , which forms deep bluish-violet, glistening needles, m. p.  $148^{\circ}$ . When heated with formic acid at  $180^{\circ}$ , the aminoguanidine yields 4-phenyl-1- $\alpha$ -naphthyl-3:5-endoanilo-4:5-dihydro-1:2:4-triazole, which crystallises in yellow leaflets, m. p.  $212^{\circ}$ ; the *nitrate*,  $\text{C}_{24}\text{H}_{19}\text{O}_3\text{N}_5$ , forms a microcrystalline powder, m. p.  $219^{\circ}$ , and is much more easily soluble than nitron *nitrate*.

$\beta$ -Naphthylaminodiphenylguanidine crystallises in needles, m. p.  $152^{\circ}$ ; the *azo*-derivative forms dark violet, glistening prisms, m. p.  $172^{\circ}$ , and dissolves in alcohol, forming a red solution which gradually becomes colourless in consequence of the formation of chloronaphthyl-diphenylaminoguanidine (compare Abstr., 1906, i, 465). *Phenyl- $\beta$ -naphthylendoanilodihydrotriazole* crystallises in light yellow leaflets, m. p.  $205^{\circ}$  (decomp.); the *nitrate* crystallises in slender needles, m. p.  $238^{\circ}$ , and is only slightly less insoluble than nitron *nitrate*; the *hydrochloride* and *sulphate* are also only sparingly soluble.

4:5-Diphenyl-1-benzyl-3:5-endoanilo-4:5-dihydro-1:2:4-triazole,

$$\begin{array}{c} \text{N}=\text{C} \\ | \quad \quad | \\ \text{N}(\text{CH}_2\text{Ph}) \cdot \text{CPh} \end{array} \rangle \text{NPh, formed by the action of benzoyl chloride on benzylaminodiphenylguanidine, crystallises from alcohol in slender, yellow needles, m. p. 186°; the nitrate, } \text{C}_{27}\text{H}_{22}\text{N}_4\cdot\text{HNO}_3, \text{ crystallises in needles, m. p. 239°}, \text{ and is comparatively soluble in water.}$$

4-Phenyl-1-benzyl-3:5-endoanilo-4:5-dihydro-1:2:4-triazole,



is obtained by heating benzylaminodiphenylguanidine with formaldehyde in alcoholic solution, and oxidising the resulting dihydrotriazole with sodium nitrite in glacial acetic acid; it forms yellow crystals, m. p. 129°; the nitrate is only sparingly soluble in water.

*Action of Carbodi-imides on 4-Phenylsemicarbazide.*—[With GUSTAV BLUME.]—The action of carbodiphenylimide on 4-phenylsemicarbazide in benzene solution leads to the formation of 1-diphenylguanyl-4-phenylsemicarbazide [phenylcarbamyldiphenylguanidine],



which crystallises in slender, white needles, m. p. 171° (decomp.), and is soluble in dilute mineral acids or acetic acid; the product of its decomposition when heated is 3-anilino-4-phenyl-5-triazolone (Abstr., 1902, i, 574).

*Di-o-tolylguanyl-4-phenylsemicarbazide*,  $\text{C}_{22}\text{H}_{23}\text{ON}_5$ , formed from di-o-tolylcarbimide and 4-phenylsemicarbazide, crystallises in white needles, m. p. 164°, decomposing with formation of aniline and 3-o-toluidino-4-

o-tolyl-5-triazolone,  $\begin{array}{c} \text{N}:\text{C}(\text{NHC}_7\text{H}_7) \\ | \quad \quad | \\ \text{NH} \text{---} \text{CO} \end{array} \rangle \text{N} \cdot \text{C}_7\text{H}_7$ , which crystallises from alcohol in colourless prisms, m. p. 183°, and has feeble, basic, and acid properties. G. Y.

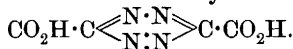
### Behaviour of the Group N·C·N towards Acylating Agents.

II. GUSTAV HELLER (Ber., 1907, 40, 114—119. Compare Abstr., 1904, i, 942).—The author has studied the behaviour on benzylation of tetrazole as a type of a cyclic compound containing the group N·C·N and containing more than two nitrogen atoms.

When a mixture of equal amounts of ethyl alcohol and concentrated sulphuric acid is slowly added to a mixture of ethyl formazylcarboxylate, ethyl alcohol, and amyl nitrite, ethyl diphenyltetrazoliumcarboxylate ethosulphate,  $\text{C}_{18}\text{H}_{20}\text{O}_6\text{N}_4\text{S}$ , separates as glistening needles, m. p. 214—215° (decomp.). When a mixture of dilute nitric acid and potassium permanganate is added to its aqueous solution heated to 75°, it is oxidised to tetrazole.

When tetrazole in pyridine solution is acted on by benzoyl chloride, it forms, in addition to a dark yellow, non-crystalline substance, dibenzoylcarbamide, m. p. 210°. Tetrazole alone, however, is acted on by benzoyl chloride, when heated at 100°, with evolution of nitrogen and formation of dibenzoylhydrazine, which separates from alcohol in fine needles, m. p. 237°. Dibenzoylhydrazine is also formed by the interaction of benzoyl chloride and 1:2:4-triazole. A. McK.

**1:2:4:5-Tetrazine.** THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, 40, 84—88. Compare Curtius, *Abstr.*, 1889, 369; Hantzsch and Lehmann, *Abstr.*, 1901, i, 132; Curtius, Darapsky, and Müller, *Abstr.*, 1906, i, 939; this vol., i, 21).—The authors had previously shown that the acid formerly described by Curtius, and by Hantzsch and Lehmann, as bisazoxyacetic acid is in reality 1:2:4:5-tetrazine-3:6-carboxylic acid,



It is now shown that when this acid is heated, the product obtained is not bisazoxymethane as described by Hantzsch and Lehmann, but is free from oxygen and is 1:2:4:5-tetrazine.

When 1:2:4:5-tetrazine-3:6-carboxylic acid is heated with dry sand at about 160°, a purple vapour is evolved which condenses as red crystals. By heating the latter with barium oxide, 1:2:4:5-tetrazine,

$\text{CH}\begin{smallmatrix} \text{N}\cdot\text{N} \\ \text{N}:\text{N} \end{smallmatrix}\text{CH}$ , is obtained as glistening, purple pyramids, m. p. 99°.

(The bisazoxymethane of Hantzsch and Lehmann is described as having m. p. 75°.) The absorption spectra of its vapour and of its solutions were examined. Its solutions in water, alcohol, and in other solvents are bright red, and may be boiled for some time without undergoing decomposition.

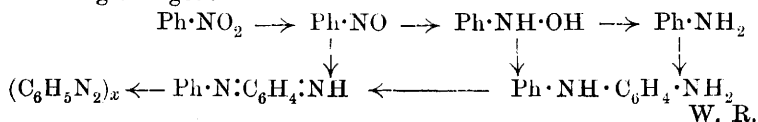
When 1:2:4:5-tetrazine is dissolved in concentrated hydrochloric acid, the solution is at first deep red, but nitrogen is soon evolved and the solution becomes colourless.

When hydrogen sulphide is passed into a solution of 1:2:4:5-tetrazine in water or in benzene, the dark red colour gradually disappears and sulphur is deposited; the red colour is restored when dilute acetic acid and sodium nitrite are added. When the tetrazine is reduced it forms a dihydro-derivative, which is readily reoxidised to the tetrazine.

A. McK.

**Emeraldine.** W. NOVER (*Ber.*, 1907, 40, 288—297).—A new green electrolytic reduction product of nitrobenzene is formed in small quantities at a nickel gauze cathode when the cathode electrolyte is either a 50% solution of sodium hydrogen sulphate or a hydrofluosilicic acid solution of D 1·3. Its constitution was determined by preparing it either by oxidising *p*-aminodiphenylamine with ferric chloride or nitrosobenzene, or by shaking  $\beta$ -phenylhydroxylamine with sodium hydrogen sulphate. It is also prepared by the polymerisation of phenyl-quininedi-imide with acids (compare Caro, *Chem. Zeit.*, 1896, 21, 840). By treatment of the green salt so obtained with sodium hydroxide and crystallisation from a mixture of light petroleum and xylene, emeraldine,  $(\text{C}_6\text{H}_5\text{N}_2)_x$ , is obtained as a blue, amorphous substance giving a carmine-red coloration with concentrated sulphuric acid.

The formation of emeraldine in the cell is supposed to be due to the following changes:



W. R.



**Preparation of *o*-Hydroxyazo-derivatives.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 175827).—Diazotised *o*-aminophenol and its derivatives, containing neither nitro, nor sulphonic groups, do not readily couple with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid in the presence of aqueous alkali hydroxides. When, however, the coupling is effected in the presence of milk of lime the reaction proceeds smoothly, and a good yield of the pure product is obtained. The disulphonic acid is employed in the form of its disodium salt, and the calcium hydroxide emulsion and the diazo-solution are added successively. The mixture is left for some hours in order that the condensation may be completed, and the azo-derivative is freed from the calcium hydroxide by means of acid and then salted out in the usual way. The patent contains a table giving the properties of the azo-dyes prepared by this method from seventeen derivatives of *o*-aminophenol.  
G. T. M.

**Hyposulphites. IV. Action of Sodium Hyposulphite on Diazo-Salts.** EUGÈNE GRANDMOUGIN (*Ber.*, 1907, 40, 422—423. Compare Abstr., 1906, i, 716, 967; this vol., i, 166).—When a solution of diazobenzene sulphate or chloride is added to a cold well-stirred suspension of sodium hyposulphite in water, a mixture of diazobenzeneimide and benzenesulphonphenylhydrazide (m. p. 164·5°, not 148—150°; compare W. Königs, Abstr., 1877, 219) is precipitated; sodium phenylhydrazine- $\beta$ -sulphonate, the chief product of the reaction, is obtained from the mother liquor. Phenol and a small quantity of phenyl disulphide are formed when warm hyposulphite solution is used.  
W. R.

[The Orientation of Sulphonated Chlorotoluene-azo- $\beta$ -naphthols and their Lake-forming Properties.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 175378 and 175396).—6-Chloro-*p*-toluidine-3-sulphonic acid furnishes a sparingly soluble diazo-derivative which, when coupled with  $\beta$ -naphthol, yields an azo-dye forming very sparingly soluble calcium, barium, aluminium, and lead salts. These salts have a brilliant scarlet hue, which is affected neither by acids nor alkalis, and is very fast to light. The following isomerides : 5-chloro-*p*-toluidine-3-sulphonic, 4-chloro-*o*-toluidine-5-sulphonic, and 5-chloro-*o*-toluidine-3-sulphonic acids give coloured salts, which, on account of their great solubility in water and their sensitiveness to scouring agents, cannot be employed as lakes.

The following bases : 4-chloro-*m*-nitroaniline, 6-nitro-4-*m*-xylidine and 2 : 5-dichloro-*p*-toluidine, when diazotised and combined with  $\beta$ -naphthol-3 : 6-disulphonic acid, yield azo-dyes giving insoluble dark red barium salts suitable for lakes. This property is found to be generally true of all derivatives of aniline which contain two substituent groups or atoms in positions adjacent to one another. The patent contains a table of bases which have been examined from this standpoint.

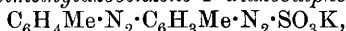
G. T. M.

**Coloured Hydrazinesulphonic Acids.** JULIUS TROGER and GEORG PUTTKAMMER (*Ber.*, 1907, 40, 206—212. Compare Abstr., 1904, i, 118; 1906, i, 120, 993, 994; Farbenfabriken vorm. F. Bayer

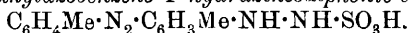
& Co., D.R.-P. 163447).—The red azobenzene-*p*-hydrazinesulphonic acid,  $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{SO}_3\text{H}$ , prepared previously by passing a current of sulphur dioxide through a cooled solution of diazobenzene sulphate, has now been synthesised (*a*) by the action of diazotised *p*-aminoazobenzene on potassium sulphite in cooled aqueous potassium carbonate solution and reduction of the resulting stable potassium azobenzenediazosulphonate,  $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SO}_3\text{K}$ , by means of ammonium sulphide, and (*b*) by passing a current of sulphur dioxide into an aqueous solution of diazotised *p*-aminoazobenzene.

2:3'-Dimethylazobenzene-4-hydrazinesulphonic acid has been prepared in the same manner from 4-amino-2:3'-dimethylazobenzene by diazotisation, conversion into potassium 2:3'-dimethylazobenzene-4-diazosulphonate, and reduction of this with ammonium sulphide. The resulting hydrazinesulphonic acid forms a *p*-toluidine salt, m. p.  $154^\circ$ , which is identical with that obtained from the product of the action of sulphur dioxide on diazotised *m*-toluidine.

*Potassium 2:3'-dimethylazobenzene-4'-diazosulphonate*,



prepared by the action of potassium sulphite on diazotised 4'-amino-2:3-dimethylazobenzene, is obtained as an orange-red precipitate, and when reduced with aqueous ammonium sulphide yields the reddish-brown 2:3'-dimethylazobenzene-4'-hydrazinesulphonic acid,



This forms yellow *alkali* and *ammonium* salts, reduces ammoniacal silver solution, and when heated with aromatic aldehydes in sulphuric acid and alcohol gives a bluish-violet coloration.

The coloured hydrazinesulphonic acids condense with ketones in alcoholic-sulphuric or glacial acetic acid solution, forming coloured *sulphates* from which ammonia liberates the crystalline *hydrazones*.

G. Y.

[An Azopyrazolone Derivative.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 175290).—*m*-Xylidine-*o*-sulphonic acid, when diazotised and coupled with phenylpyrazolonesulphocarboxylic acid, yields an azosulphocarboxylic acid which surpasses tartrazine in its tinctorial properties and in fastness to light. The new acid is precipitated from alkaline solutions by mineral acids and sodium chloride.

G. T. M.

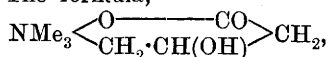
**Extractives of Muscle. VI. Identity of Ignotine and Carnosine.** WLADIMIR GULEWITSCH (*Zeitsch. physiol. Chem.*, 1906, 50, 204—208).—Kutscher's ignotine (*Zeitsch. Nahr. Genussm.*, 1905, 10, 528) is identical with carnosine (Abstr., 1900, i, 516); both melt and decompose at  $241\text{--}245^\circ$ .

J. J. S.

**Extractives of Muscle. VII. Compounds of Carnitine.** R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1907, 50, 361—373. Compare Abstr., 1905, i, 726).—Carnitine yields two double salts with mercuric chloride. The one,  $\text{C}_7\text{H}_{15}\text{O}_3\text{N}\cdot 2\text{HgCl}_2$ , m. p.  $196\text{--}197^\circ$ , is formed when alcoholic solutions of the base or its carbonate and of mercuric chloride are mixed; it crystallises well and is sparingly soluble in water. The other,  $\text{C}_7\text{H}_{15}\text{O}_3\text{N}\cdot\text{HCl}\cdot 6\text{HgCl}_2$ , is obtained from solutions con-

taining an excess of hydrochloric acid, usually as an oil which slowly crystallises; it is more readily soluble than the other mercurichloride, from which it can be separated by fractional crystallisation. The compound with 2 mols. of mercuric chloride can be made use of for the isolation of carnitine.

*Carnitine phosphotungstate* crystallises in fan-shaped aggregates of needles. The *hydrochloride* is very hygroscopic and is laevorotatory. The *aurichloride*,  $C_7H_{16}O_3N, AuCl_4$ , crystallises in pale-yellow needles and orange-coloured needles and prisms, m. p. 150. The *nitrate* is also very hygroscopic. The formula,



is suggested for the base.

J. J. S.

**Caseinokyryne. III.** MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1906, 50, 163—173. Compare Abstr., 1905, i, 104).—Further examination has shown that the specimens of caseinokyryne previously obtained were pure. The fact that Skraup and Witt's preparations (Abstr., 1906, i, 916) were not pure is due to the fact that they did not follow the details of the author's method of purification.

The carbamino-reaction (Abstr., 1905, ii, 332; 1906, i, 144) has been employed in the case of caseinokyryne and the ratio  $CO_2/N$  found to be  $1/2.25$ . For the products of hydrolysis the ratio is  $1/1.5$ .

J. J. S.

**Light Absorption of Hæmoglobin.** HANS ARON and FRANZ MÜLLER (*Zeitsch. physiol. Chem.*, 1907, 50, 443—444).—Polemical against R. von Zeynek (this vol., i, 167).

W. D. H.

**The Gradual Hydrolysis of the Oxyhæmoglobin of the Horse.** HUGO KIRBACH (*Zeitsch. physiol. Chem.*, 1906, 50, 129—162. Compare Siegfried, Abstr., 1905, i, 104).—A basic complex *globinokyryne*, analogous to Siegfried's caseinokyryne, has been isolated from the products obtained by the hydrolysis of pure recrystallised horse's oxyhæmoglobin with 12% sulphuric acid at  $37-40^\circ$ . It may be precipitated by means of phosphotungstic acid and purified by conversion into the sulphate; the yield of crude sulphate varying from 50 to 60 grams per 10 litres of blood. Neither phosphotungstate nor sulphate could be obtained in a crystalline form. The base and its sulphate dissolve readily in water and the base is insoluble in ether and practically insoluble in alcohol; it gives the biuret, but not Millon's, reaction. The sulphate is optically inactive and gives the Congo-reaction. The mean analytical data obtained from several pure specimens are C, 34.26; H, 5.89; N, 15.08; S, 10.95, and O, 33.73%. When hydrolysed with 33.3% sulphuric acid the sulphate yields histidine, arginine, lysine, and glutamic acid. Of the total nitrogen in the hydrolytic products, the proportions due to the bases and to the amino-acids have been determined and also the proportions due to each product of hydrolysis. The results agree with the view that the nitrogen in the kyryne is distributed between 2 mols. of histidine, 1 of arginine, 2 of lysine, and 4 of glutamic acid.

J. J. S.

**Preparation and Analysis of Nucleic Acids. XII. Nucleic Acid from the Spermatozoa of the Shad. (Alosa).** PHÆBUS A. LEVENE and JOHN A. MANDEL (*Zeitsch. physiol. Chem.*, 1906, 50, 1—10. Compare Abstr., 1906, i, 125, 468; this vol., i, 168).—The nucleic acid from the spermatozoa of the shad contains C, 36.27; H, 5.00; N, 15.96, and P, 8.11%. In the estimation of purine bases, much smaller yields of guanine are obtained when the copper nucleate is hydrolysed instead of the free acid. The purine bases isolated were adenine, guanine, thymine; and, in addition, cytosine and lævulic acid were obtained. J. J. S.

**Nucleic Acids from the Thymus.** IVAR BANG (*Zeitsch. physiol. Chem.*, 1907, 50, 442).—Polemical against Steudel (Abstr., 1904, i, 837; 1905, i, 398; 1906, i, 125; this vol., i, 168). W. D. H.

**Peptones from Albumins. II. Peptones Derived from Blood Albumin and Precipitated by Potassium Mercury Iodide.** HENRY S. RAPER (*Beitr. Chem. Physiol. Path.*, 1907, 9, 168—182. Compare Stookey, Abstr., 1906, i, 327).—The potassium mercury iodide peptone precipitate, obtained after blood albumin had been fermented with pepsin and sulphuric acid for six weeks, was extracted with water in which some two-thirds dissolved *B*, the residue *A* dissolved completely in 5% ammonium carbonate solution. A portion of *B* dissolved in alcohol, *Ba*, but a considerable amount was insoluble, *Bβ*. The phenylcarbimide derivative from fraction *A* was prepared and resolved into three separate fractions by conversion of the carbimide into its sodium salt and precipitating this with carbon dioxide and extracting with hot alcohol. The fraction *Aa* was insoluble in alcohol, *Ab* separated out at 0°, and *Ac* was obtained on removal of the alcohol. The m.p.'s are respectively 203—205°, 178—180°, and 169—170°. From *p*-bromophenylcarbimide a bromo-derivative corresponding with fraction *Ab* was prepared. The percentage composition agrees with the formula  $C_{64}H_{89}O_{18}N_{16}Br_3$ , m. p. 184—185°. The bromo-derivative corresponding with the fraction *Ac* has the composition  $C_{34}H_{46}O_9N_8Br_2$ , m. p. 173—175°.

The phenylcarbimide derivative *Ac*, when hydrolysed with concentrated sulphuric acid, yields lysine, proline, leucine, tyrosine, aniline, ammonia, glutamic acid, a base, m. p. 231—233°, and a product, m. p. 110—112°, and soluble in ether.

From fraction *B* two phenylcarbimide derivatives were obtained. The one *Ba* is soluble in 10% alcohol and has m. p. 167—169°. None of the compounds could be obtained in a crystalline form.

J. J. S.

**Protamines and Histones.** ALBRECHT KOSSEL and H. PRINGLE (*Zeitsch. physiol. Chem.*, 1906, 49, 301—321. Compare Abstr., 1905, ii, 467).—The simplest protamines are those of the salmine group (salmine, clupeine, scombrine); 8/9ths of the nitrogen present is in the form of arginine, the remaining 1/9th as monoamino-acids; alanine, serine, aminovaleric acid, and proline. Two or more of these mono-acids may be present. As arginine contains 4 atoms of nitrogen, it follows that 1 molecule of monoamino-acid is present to

every 2 molecules of arginine, and such protamines are therefore diarginyl compounds. Reasons are given for believing that the linkage is symmetrical, thus:  $aab'$ ,  $aab''$ ,  $aab'''$ , where  $a$  is arginyl and  $b'$ ,  $b''$ ,  $b'''$  monoamino-groups. The protones obtained as the first cleavage products from these protamines also contain 8/9ths of their nitrogen in the form of arginine. Diarginylalanine will have the molecular weight, 401, diarginylserine, 417, diarginylproline, 427, and diarginylaminovaleric acid, 429. The boiling point and freezing point methods of determination gave the molecular weight of the protones as from 419 to 423. It therefore appears that the protones are mixtures of the diarginyl compounds just enumerated. By the action of nitrous acids on this mixture, ornithine is split off, from which it is argued that the symmetric arrangement is probably  $b a a$  rather than  $a a b$  or  $a b a$ . It is only by considering such simple cases that the study of more complex proteids becomes possible. In histones, arginine is again the most abundant cleavage product (24% to 26% of the total nitrogen), and lysine comes next (7% to 8%). From various histones the substance called histopeptone was prepared by peptic digestion; this yields the same proportion of arginine, but it appears to be a chemical unit, not a mixture as the protones are. The method of obtaining this substance by the silver-baryta method is given. Globin is not regarded as a histone.

W. D. H.

**Histopeptone.** T. KRASNOSSELSKY (*Zeitsch. physiol. Chem.*, 1906, 49, 322—323).—Attempts to obtain histopeptone (see preceding abstract) from various vegetable proteids failed. It was, however, obtained by Kossel's method from various animal organs, namely, from the testes of the cod and the spleen. The percentage of nitrogen in the former preparation was 19.5, in the latter 19.7. Kossel found it to be 19.9 in the histopeptone prepared from thymus. Histopeptone was also obtained from liver, lymph glands, intestinal mucous membrane, and red marrow. The most abundant yield was from the spleen, the least from the liver.

W. D. H.

**Action of Ultra-violet Light on Invertase.** A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, ii, 1512; from *Arch. klin. Med.*, 87, 373—388. Compare Abstr., 1906, ii, 917).—Comparative experiments are recorded on the amount of destruction of invertase by ultra-violet light in atmospheres containing oxygen, and in the presence of gases free from oxygen, in the presence and absence of materials such as sulphites which absorb oxygen; in the presence and absence of fluorescent materials, &c. The destruction which occurs in the absence of oxygen, as, for instance, in atmospheres of hydrogen or nitrogen, is less than when oxygen is present, but is not due to the presence of traces of oxygen. The presence of oxygen is not a condition for the biological action of light.

W. D. H.

**Lactic Acid Fermentation.** REGINALD O. HERZOG (*Zeitsch. physiol. Chem.*, 1906, 49, 482—483).—Polemical against Buchner and Meisenheimer (Abstr., 1906, i, 919).

W. D. H.

**A Case of Specific Adsorption of Enzymes.** SVEN G. HEDIN (*Bio-chem. J.*, 1907, 2, 112—116).—The  $\alpha$ - and  $\beta$ -proteases in ox-spleen

are adsorbed in the same proportions by charcoal; kieselguhr adsorbs the former, but probably not the latter at all. W. D. H.

**Influence of Temperature on the Work of the Proteolytic Enzyme and the Zymase in Killed Yeast Cells.** ANNA PETRUSCHEWSKY (*Zeitsch. physiol. Chem.*, 1907, 50, 251—262).—The experiments recorded confirm the statement that the proteolytic ferment (endotryptase) separated from yeast cells destroys zymase, and the destruction of the latter is the more complete, the more energetic the action of the former is. Zymase is not yet obtainable in a pure condition, and therefore observations on the physicochemical laws that regulate its action are not possible. The harmful action of it on endotryptase can be lessened by working at low temperatures or by the addition of strong solutions of sugar. W. D. H.

**Extraction by Caseinogen of Trypsin Adsorbed by Charcoal.** SVEN G. HEDIN (*Bio-chem J.*, 1907, 2, 81—88).—A solution of caseinogen in 0.2% sodium carbonate solution extracts trypsin which has been adsorbed by charcoal. Usually in less than thirty minutes at 20° the extraction comes to an end; the final amount extracted rises with the temperature, and with the amount of caseinogen used up to a certain limit, beyond which the amount extracted is independent of the amount of caseinogen. The amount of water present makes no difference. The results support the view that proteids combine with trypsin before they are broken up by it. W. D. H.

**Behaviour of Peroxydase towards Iodine.** ALEXIS BACH (*Ber.*, 1907, 40, 230—235. Compare Abstr., 1904, ii, 310).—As the oxidising action of hydrogen peroxide on hydriodic acid, aromatic amines, and phenols is increased by the presence of peroxydase from horse-raddish roots or other vegetable sources, according to the theory of specific ferment action, the peroxydase should consist of at least three enzymes. All attempts, however, either by fractional precipitation, by means of alcohol or acetone, or by destroying part of the peroxydase by means of iodine, to obtain a peroxydase incapable of increasing the activity of hydrogen peroxide towards all three classes of substances, have been unsuccessful.

The effect of iodine on the influence of peroxydase on the oxidation of phenols by hydrogen peroxide has been studied quantitatively in the case of pyrogallol. With peroxydase extract the maximum formation of purpurogallin increases to a certain extent with the amount of iodine present, diminishing on addition of larger quantities of iodine; this points to the presence of the zymogen the conversion of which into the active peroxydase is accelerated by addition of iodine. Precipitated peroxydase, on the other hand, does not contain zymogen, since its influence on the oxidation of pyrogallol by hydrogen peroxide is not increased by addition of iodine. G. Y.

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## Organic Chemistry.

**Melting Points and Boiling Points of Aliphatic and Aromatic Hydrocarbons.** GUSTAVE HINRICHS (*Compt. rend.*, 1907, 144, 431).—The author states that the anomalies in the melting points of fatty and aromatic hydrocarbons to which Tsakalotos has drawn attention (this vol., i, 105) have already been studied by him (*Abstr.*, 1891, 1330, 1441; 1892, 260; 1906, i, 723). E. H.

**Artificial Naphtha.** K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 878—880, 880—881).—Artificial naphtha was obtained by Sabatier and Senderens' method, by passing a mixture of hydrogen and acetylene over nickel shavings at 300°; the yield is very poor, a large quantity of resin being formed. The naphtha itself is a mixture resembling the decomposition products of natural naphtha, and contains a large proportion of unsaturated substances as well as some products of oxidation. The iodine numbers (*A*) and the coefficients of acidity (*B*) of various fractions are as follows:

	(1) For decomposition products.		(2) Artificial naphtha.	
	<i>A.</i>	<i>B.</i>	<i>A.</i>	<i>B.</i>
Up to 150°.....	129	0.5	237	14.05
150—200 .....	112	1.8	189	2.81
200—270 .....	66	1.5	124	6.1

Thus the higher the boiling point of a fraction of artificial naphtha, the less oxygen does it contain; this fact is also in accordance with the results of analysis, which shows that the residue, boiling above 270°, consists mainly of hydrocarbons and is very similar to the heavy naphtha residues and resins. All this leads to the conclusion that during the experiment various complex processes of condensation and polymerisation occur and it is probable that the complex nature of natural naphtha is also due to such reactions. Z. K.

**Octanes from Rock-oil.** FELIX B. AHRENS (*Ber.*, 1907, 40, 848—852).—A number of derivatives have been prepared from an oil,  $C_{10}H_{18}$ , b. p. 121—122°,  $D^{25}_4$  0.7245, obtained from rock-oil after removal of the toluene by nitration; it solidifies to a paraffin wax-like mass in liquid air. The action of chlorine on the oil leads to the formation of mono-, di-, and tri-chloro-derivatives. The *monochloro*-product,  $C_{10}H_{17}Cl$ , is a colourless oil, b. p. 164—166°. The *dichloro*-product,  $C_8H_{16}Cl_2$ , is a yellow oil, b. p. 122—124°/49 mm. The *product* obtained by the action of bromine on the oil decomposes on distillation.

The action of nitric acid,  $D$  1.075, on the oil leads to the formation of (*a*) hydroxy- $\beta$ -methylglutaric acid; (*b*) a white, crystalline acid,  $C_7H_{12}O_7$ , m. p. 184°, and (*c*) two *nitro-octanes*.

The *tert.-nitro-octane*,  $C_8H_{17}\cdot NO_2$ , is a colourless liquid, b. p. 113—114°/36 mm.,  $D^{25}_4$  0.9671, and on reduction with tin and hydro-

chloric acid yields the *tert*-*octylamine*,  $C_8H_{17}\cdot NH_2$ . This is a colourless liquid, b. p. 155—156°,  $D^{25}_D$  0·8051, which has a sharp odour. The *platinichloride*,  $(C_8H_{19}N)_2H_2PtCl_6$ , decomposes above 200°; the *aurichloride*,  $C_8H_{15}N_2HAuCl_4$ , long needles, m. p. 77—79°; the *picrate*,  $C_8H_{19}N\cdot C_6H_3O_7N_3$ , m. p. 138°. A small amount of a *picrate*, m. p. 200°, was obtained also.

The *sec*-*nitro-octane* is an almost colourless liquid, b. p. 114—115°/30 mm.,  $D^{19}_D$  0·9342. The *sec*-*base* obtained on reduction of this forms two *picrates*. The *picrate* crystallising from benzene in slender needles, m. p. 108°, yields colourless *sec*-*octylamine*, b. p. 164—166°,  $D^{12}_D$  0·801, which forms a *platinichloride* decomposing above 200°, and an *aurichloride*, m. p. 41—42°. The *picrate* crystallising in yellow needles, m. p. 82—83°, yields *sec*-*octylamine*, b. p. 163—164°,  $D^{25}_D$  0·788; this forms a *platinichloride* crystallising in leaflets or needles and decomposing above 200°, and an *aurichloride*, yellow leaflets, m. p. 42—43°. G. Y.

**Action of Nitrous Acid on *iso*Butylene.** K. W. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 955—958).—The author has shown previously (*Bull. Moscow Inst. Rural Economy*, 1899, 5, 248) that the action of nitrogen peroxide on *isobutylene* yields a liquid giving *isobutylenediamine* on reduction, and a colourless, crystalline compound,  $C_4H_8O_4N_2$ , m. p. 104°, which could not be reduced.

The action of an ethereal solution of nitrous acid (rather less than 1 mol.  $N_2O_3$ ) on a cooled ethereal solution of *isobutylene* yields: (1) a small quantity of a *nitrosite*,  $C_4H_8O_3N_2$ , m. p. 80—80·2°, which crystallises in colourless, shining plates and dissolves sparingly in most of the ordinary solvents, forming blue solutions; (2) a large proportion of a blue *liquid*, of which the crystalline compound is probably a polymeride. Both compounds yield *isobutylenediamine* on reduction with tin and hydrochloric acid.

The reducibility of the *nitrosite* depends on the presence of the grouping  $CH_2\cdot C$  (compare Demjanoff, *Abstr.*, 1899, i, 845; Schmidt, *Abstr.*, 1903, i, 597). T. H. P.

**Electrolytic Preparation of Chloroform.** P. TRECHZINSKY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 734—741).—Chloroform has been prepared by the electrolysis of calcium chloride in the presence of ethyl alcohol. Judging by the yield of chloroform, the reaction most probably proceeds in the following stages:  $CH_3\cdot CH_2\cdot OH + Cl_2 \rightarrow CH_3\cdot CHO + CH_3\cdot CHO + 3Cl_2 \rightarrow CCl_3\cdot CHO + 2CCl_3\cdot CHO + Ca(OH)_2 = 2CHCl_2 + Ca(HCO_3)_2$ . This is further confirmed by the fact that when the yield of chloroform is small, the escaping gas has an odour of acetaldehyde, acetic acid, and ethyl acetate. The concentration of the calcium chloride must lie between 40 and 70 grams per 100 c.c. of water, the alcohol must be in the proportion of 5—10 c.c. per 450 c.c. of calcium chloride solution, and the temperature must lie between 49° and 73°. The voltage employed has no effect providing it is above 2·2 and the best strength of current is 8 amperes. With slight modifications potassium or sodium chloride can replace calcium chloride.

Z. K.



**Action of Dilute Nitric Acid on Haloid Compounds. III.** MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 607—612. Compare Abstr., 1904, i, 495, 657).—The action of dilute nitric acid on isobutyl chloride yields: (1) *α-chloro-β-nitro-β-methylpropane* (tertiary chloronitroisobutane),  $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{NO}_2$ , b. p. 181—183°,  $D_0^{20}$  1.1960,  $D_0^{25}$  1.1822,  $n_D^{20}$  1.44461; reduction with tin and hydrochloric acid gives a mixture of bases including *α-chloro-β-amino-β-methylpropane*,  $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{NH}_2$ , b. p. 120—130°,  $D_0^{25}$  0.9464,  $n_D^{25}$  1.42705; (2) a mixture of primary and secondary chloronitroisobutanes.

With isobutyl bromide, dilute nitric acid gives *α-bromo-β-nitro-β-methylpropane*,  $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{NO}_2$ , b. p. 110—115°/60 mm.,  $D_0^{25}$  1.5545,  $n_D^{25}$  1.47838, and other products not yet identified.

On heating isoamyl chloride with nitric acid ( $D$  1.075) in a sealed tube at 125°, it yields *α-chloro-γ-nitro-γ-methylbutane*,

$\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NO}_2$ ,  
b. p. 203—204°/735 mm.,  $D_0^{20}$  1.1739,  $D_0^{25}$  1.1576,  $n_D^{25}$  1.45412, which gives a mixture of bases when reduced with tin and hydrochloric acid.  
T. H. P.

**Transformation of the Primary Saturated Alcohols into the Corresponding Monobasic Acids.** H. FOURNIER (*Compt. rend.*, 1907, **144**, 331—333).—Under conditions employed by previous authors, the oxidation of primary saturated alcohols by means of alkaline potassium permanganate gives very little of the corresponding monobasic acid. The author shows that if the alcohol is dissolved in a 10% solution of potash and treated gradually with a 3% solution of potassium permanganate in quantity sufficient to give 2 atoms of oxygen for each molecule of alcohol, the mixture being kept cold, the potassium salt of the corresponding monobasic acid is formed, and the latter may be liberated, after removal of manganese dioxide by filtration, by adding sulphuric acid very slowly. In this way isoamyl alcohol,  $\delta$ -methylamyl alcohol,  $\epsilon$ -methylhexyl alcohol, *n*-butyl alcohol, isobutyl alcohol, and propyl alcohol, on oxidation, give yields of the corresponding monobasic acids varying from 70—75% of the theory. Ethyl alcohol gives only a 50% yield of acetic acid.

E. H.

**Certain Molecular Compounds of Calcium Chloride.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1010—1036. Compare Abstr., 1906, i, 131, 132).—The alcoholates of calcium chloride are readily obtained by dissolving anhydrous calcium chloride in dehydrated alcohols. Heat is developed and, when the solution cools, the alcoholate is deposited in crystals.

The melting point diagram of the system  $\text{CaCl}_2\cdot\text{MeOH}$  consists of three intersecting curves: (1) the solubility curve of the compound  $\text{CaCl}_2\cdot 4\text{MeOH}$  reaching to 55°; (2) the solubility curve of the compound  $\text{CaCl}_2\cdot 3\text{MeOH}$  extending from 55° to 178°, the m. p. of the compound, and (3) the solubility curve of another alcoholate containing less alcohol. The diagram greatly resembles that obtained for the system  $\text{CaCl}_2\cdot\text{H}_2\text{O}$  (Roozeboom, Abstr., 1889, 752).

The solubility curves of  $\text{CaCl}_2 \cdot 4\text{MeOH}$  and  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  are similar and so also are those of  $\text{CaCl}_2 \cdot 3\text{MeOH}$  and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ; the curve for  $\text{CaCl}_2 \cdot 3\text{MeOH}$  is also analogous to that for  $\text{MgBr}_2 \cdot 6\text{MeOH}$ . Tables are given showing the solubility of  $\text{CaCl}_2 \cdot 4\text{MeOH}$  in methyl alcohol between  $0^\circ$  and  $56^\circ$  and of  $\text{CaCl}_2 \cdot 3\text{MeOH}$  between  $55^\circ$  and  $177^\circ$ .

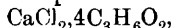
With ethyl alcohol, calcium chloride forms only one compound,  $\text{CaCl}_2 \cdot 3\text{EtOH}$ , m. p.  $97^\circ$ , which separates in large crystals; its solubility in ethyl alcohol has been determined between  $0^\circ$  and  $97^\circ$ . Compounds of analogous composition are also obtained with propyl, *isobutyl*, and *isoamyl* alcohols, but their solubilities in the corresponding alcohols could not be accurately determined, as they form very viscous solutions.

Thus the alcoholates of calcium chloride are of the general type  $\text{CaCl}_2 \cdot 3\text{ROH}$ , and crystallise more readily than those of magnesium bromide, which have the formula  $\text{MgBr}_2 \cdot 6\text{ROH}$  (compare Abstr., 1906, i, 131, 132). The m. p.'s. of the two series of compounds are as follow:

$\text{CaCl}_2 \cdot 3\text{MeOH}$ .....	$177^\circ$	$\text{MgBr}_2 \cdot 6\text{MeOH}$ ..	$190^\circ$
$\text{CaCl}_2 \cdot 3\text{EtOH}$ .....	$97^\circ$	$\text{MgBr}_2 \cdot 6\text{EtOH}$ .....	$108.5^\circ$
$\text{CaCl}_2 \cdot 3\text{PrOH}$ .....	$87-88^\circ$	$\text{MgBr}_2 \cdot 6\text{PrOH}$ .....	$52^\circ$
$\text{CaCl}_2 \cdot 3\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$	$105^\circ$	$\text{MgBr}_2 \cdot 6\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$	$80^\circ$

With *isopropyl* alcohol, calcium chloride forms an *alcoholate*,  $\text{CaCl}_2 \cdot 3\text{Pr}^i\text{OH}$ , crystallising in small needles, whilst with tertiary alcohols it gives alcoholates, which apparently contain only  $1\text{ROH}$  and do not melt, but decompose, on heating.

On dissolving dehydrated calcium chloride in a dehydrated monobasic fatty acid, a crystalline compound is obtained, which can be crystallised from the corresponding acid (compare Benrath, Abstr., 1905, i, 734). In the system  $\text{CaCl}_2 \cdot \text{C}_2\text{H}_4\text{O}_2$ , the m. p. first falls from  $16.2^\circ$ , that of acetic acid, to  $11.1^\circ$ , which corresponds with a content of 42% of the compound  $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_4\text{O}_2$ ; it then rises to  $73^\circ$ , the m. p. of  $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_4\text{O}_2$ , which crystallises in rhombohedra. The solubility curve of this compound in acetic acid is very similar to that of  $\text{MgBr}_2 \cdot 6\text{C}_2\text{H}_4\text{O}_2$ . Formic acid dissolves calcium chloride, but deposits no compound on cooling. Propionic acid gives the compound,

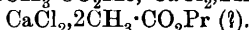


and butyric acid,  $\text{CaCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$  (?), both crystallising in leaflets.

The compound of calcium chloride with ethyl acetate, obtained by Liebig (*Annalen*, 1833, 5, 36—37), has the composition



and is almost insoluble in ethyl acetate. Compounds of similar constitution are  $\text{CaCl}_2 \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{Me}$ ,  $\text{CaCl}_2 \cdot 2\text{H} \cdot \text{CO}_2\text{Et}$ , and



With methylal, calcium chloride forms  $\text{CaCl}_2 \cdot \text{CH}_2(\text{OMe})_2$ , which crystallises in small needles, insoluble in methylal, and with acetal,  $\text{CaCl}_2 \cdot \text{CH}_2(\text{OEt})_2$ , which forms long leaflets.

T. H. P.

**Preparation of Optically Active Butyl Alcohol.** RICHARD METH (*Ber.*, 1907, 40, 695—697).—The author describes a novel

method of resolving an inactive alcohol into its optically active components, the principle of which depends on the formation of a hydrogen ester from the alcohol and a dibasic acid, the resolution of this acid-ester by the ordinary alkaloidal method and the subsequent hydrolysis of the optically active acid-ester obtained in this manner.

*sec.*-Butyl alcohol was converted into butyl hydrogen sulphate (compare Marckwald, *Abstr.*, 1902, i, 418). *Barium sec.-butyl sulphate*,  $(C_4H_9SO_4)_2Ba \cdot 2H_2O$ , is readily soluble in water; the calculated amount of brucine sulphate was added to its aqueous solution, and the precipitated barium sulphate filtered off. The brucine salt of the *d*-acid was readily obtained pure from the filtrate; it has m. p.  $210^\circ$ , decomposing; this brucine salt was then converted into *barium d-sec.-butyl sulphate*,  $(C_4H_9SO_4)_2Ba \cdot H_2O$ , which, in aqueous solution, has  $[\alpha]_D + 0.57^\circ$  ( $C = 41.85$ ). The barium salt was hydrolysed by boiling with dilute sulphuric acid for three hours; the resulting alcohol had  $[\alpha]_D + 0.32^\circ$ . Partial racemisation probably occurred during the hydrolysis of the barium salt.

A. McK.

**Various Syntheses of Dimethylisopropylcarbinol**,  $CMe_2Pr \cdot OH$ . LOUIS HENRY (*Compt. rend.*, 1907, 144, 308—313).—The author having obtained Butleroff's pentamethylethanol (*Abstr.*, 1875, 1248) by the action of magnesium methyl bromide on ethyl- $\alpha$ -chloro- $\alpha$ -methylpropionate, expected that under the same conditions  $\alpha$ -chloro- $\beta$ -methylpropaldehyde would give Friedel's pinacolyl alcohol,  $CMe_3 \cdot CHMe \cdot OH$ , but obtained instead dimethylisopropylcarbinol. The reaction is explained by the scheme  $CMe_2Cl \cdot CHO \rightarrow CMe_2Cl \cdot CHMe \cdot OMgBr \rightarrow$

$$O \begin{array}{c} \diagup CMe_2 \\ \diagdown CHMe \end{array} \rightarrow MgBr \cdot O \cdot CMe_2 \cdot CHMe_2 \rightarrow OH \cdot CMe_2 \cdot CHMe_2.$$

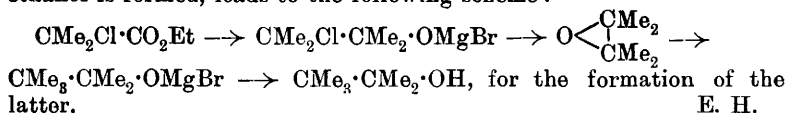
In support of this the author adduces the facts that (1) by the action of magnesium methyl bromide on Brochet's  $\alpha\beta$ -dichlorodiisobutyl ether,  $CMe_2Cl \cdot CHCl \cdot O \cdot C_4H_9$  (*Ann. Chim. Phys.*, 1897, [vii], 10, 289 and 347),  $\beta$ -chloro- $\alpha$ -methyl-diisobutylether,  $CMe_2Cl \cdot CHMe \cdot O \cdot C_4H_9$ , b. p.  $178-179^\circ$  is obtained. (If the  $\alpha\beta$ -dichlorodiisobutyl ether is added to excess of magnesium methyl bromide in ethereal solution, hydrogen chloride is eliminated giving the unsaturated ether,  $CMe_2 \cdot CMe \cdot O \cdot C_4H_9$ , b. p.  $162-164^\circ$ .)

(2)  $\beta$ -Methylbutylene- $\beta\gamma$ -oxide,  $O \begin{array}{c} \diagup CHMe \\ \diagdown CMe_2 \end{array}$  (b. p.  $75^\circ$ ), very readily gives  $\beta\gamma$ -dimethyl- $\beta$ -butanol by reaction with magnesium methyl bromide in the usual way.

*iso*Amylene monochlorohydrin,  $CMe_3Cl \cdot CHMe \cdot OH$ , formed by the action of hydrogen chloride on  $\beta$ -methylbutylene oxide, also reacts with magnesium methyl bromide, giving almost entirely dimethylisopropylcarbinol instead of the secondary pinacolyl alcohol expected, which, however, seems to be found in small amount. The course of the reaction must be similar to that in the case of  $\alpha$ -chloro- $\beta$ -methylpropaldehyde, since the first action of magnesium methyl bromide is to cause the evolution of methane and formation of the compound  $CMe_2Cl \cdot CHMe \cdot OMgBr$ .

The fact that the group  $CMe_2Cl$ , which in  $\alpha$ -chloro- $\beta$ -methylpropaldehyde is not attacked by the magnesium methyl bromide, is also

present in ethyl  $\alpha$ -chloro- $\alpha$ -methylpropionate from which pentamethyl-ethanol is formed, leads to the following scheme :



**Conversion of Ethylene Glycol into Acetaldehyde.** ALEXEI E. FAWORSKY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 741—755).—Although the end products resulting from the action of dehydrating agents or of aqueous mineral acids on the  $\alpha$ -glycols are well known, the actual mechanism of the reaction is purely hypothetical, owing largely to the fact that in no case have the intermediate substances been isolated. Wurtz's experiments on ethylene glycol have been repeated with slight modifications, and acetaldehyde and ethylidene ethylene ether have been obtained, but the main product was diethylene ether, a substance identical with Wurtz's dioxyethylene and Laurenço's glycolic ether. It has all the properties of an ether, and its refractive index corresponds with the formula  $\text{O} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{O}$ , but it very readily forms oxonium salts with iodine, sulphuric, and picric acids of the type  $\text{O} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{O} \begin{array}{c} \text{X} \\ | \\ \text{X} \end{array}$ . When carefully distilled with sulphuric acid or zinc chloride, the distillate consists mainly of acetaldehyde, hence diethylene ether must be taken as a true intermediate product formed by the action of these reagents on ethylene glycol, its mode of formation being exactly analogous with that of any other ether, whilst the formation of acetaldehyde and ethylidene ethylene ether is assumed to be due to the successive formation and decomposition of its oxonium salt. Contrary to Krassuski's supposition (*Abstr.*, 1903, i, 8), it is considered very unlikely that ethylene oxide should be an intermediate compound in these reactions. The *oxonium iodide* of ethylene ether, m. p.  $84^\circ$ , is immediately decomposed by water and air, is soluble in benzene and chloroform which also decompose it. The *sulphate*, m. p.  $100^\circ$ , is dissolved and decomposed by water. The *picrate*, m. p.  $66^\circ$ , forms pale yellow crystals. Z. K.

**Constitution of Dioxyethylene.** EMANUALE PATERNÒ and ROSARIO SPALLINO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 87—92. Compare preceding abstract).—Dioxyethylene bromide, m. p.  $65^\circ$ , prepared by the method given by Wurtz (*Ann. Chim. Phys.*, 1863, [iii], 69, 321), has the formula  $(\text{C}_2\text{H}_4\text{O})_2\text{Br}_2$  in freezing benzene.

Dioxyethylene, b. p.  $101^\circ$ , m. p.  $9^\circ$ , also combines readily (1) with iodine, giving the *iodide*,  $(\text{C}_2\text{H}_4\text{O})_2\text{I}_2$ , m. p.  $85^\circ$ ; (2) with concentrated sulphuric acid, giving the *sulphate*,  $(\text{C}_2\text{H}_4\text{O})_2\text{H}_2\text{SO}_4$ , m. p.  $101^\circ$ , and (3) with mercuric chloride, giving the *compound*,  $(\text{C}_2\text{H}_4\text{O})_2\text{HgCl}_2$ , which dissolves in water, alcohol, or ether and can be crystallised.

When heated with concentrated hydriodic acid in a sealed tube at  $140^\circ$ , dioxyethylene yields ethyl iodide (?) and acetic acid. Oxidation with permanganate yields carbon dioxide and oxalic acid.

These results show that dioxyethylene exhibits both the behaviour

of compounds containing a double linking and that characteristic of substances in which basic oxygen is present. Its constitution is most probably represented by the formula  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{O} : \text{O} < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ . T. H. P.

**Preparation of Alkyloxy-glycols.** AUGUSTE BÉHAL and MARCEL SOMMELET (D.R.-P. 177615).—The alkyloxy-glycols,  $\text{OH} \cdot \text{CRR}' \cdot \text{CH}_2 \cdot \text{OX}$ , are of importance in the synthesis of aldehydes, but hitherto they have been obtained only with great difficulty. A general method of preparation has now been devised based on the action of organomagnesium compounds either on the alkyloxy-ketones,  $\text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OX}$ , or on the esters,  $\text{CO}_2\text{R} \cdot \text{CH}_2 \cdot \text{OX}$ , of the alkyloxy-acetic acids.

The alkyloxy-groups do not interact providing that excess of the organomagnesium compound is avoided. One molecule of this reagent is required for the alkyloxy-ketone,  $\text{RCO} \cdot \text{CH}_2 \cdot \text{OX} + \text{R}' \cdot \text{MgBr} = \text{CRR}'(\text{OMgBr}) \cdot \text{CH}_2 \cdot \text{OX}$ , and two for the alkyloxy-acid,  $\text{OX} \cdot \text{CH}_2 \cdot \text{CO}_2\text{R}' + 2\text{MgRBr} = \text{OX} \cdot \text{CH}_2 \cdot \text{CRR} \cdot \text{OMgBr} + \text{MgBr} \cdot \text{OR}'$ . On treatment with water the additive compounds yield respectively  $\text{OH} \cdot \text{CRR}' \cdot \text{CH}_2 \cdot \text{OX}$  and  $\text{OH} \cdot \text{CR}_2 \cdot \text{CH}_2 \cdot \text{OX}$ .

The patent contains a table of new alkyloxy-glycols which have been thus obtained. G. T. M.

**Fixation of Methyl Alcohol on Camphene and Trimethylethylene.** ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1907, 21, 71—74).—When a mixture of methyl alcohol and methyl iodide is heated in a closed tube at 120—140° during two hours, the reactions represented by the following equations occur:  $\text{MeOH} + \text{MeI} = \text{Me}_2\text{O} + \text{HI}$ ,  $\text{MeOH} + \text{HI} = \text{H}_2\text{O} + \text{MeI}$ . Similarly, when a mixture of camphene, methyl iodide, and methyl alcohol is heated in a closed tube for five hours at 130—140°, methyl isobornyl ether is produced. This property of acting as a catalytic agent under these conditions is not confined to hydrogen iodide, since Bertram and Walbaum have shown that acetic acid and camphene react in presence of sulphuric acid to form isobornyl acetate, and similar cases are recorded by Semmler (*Abstr.*, 1901, i, 90) and Hesse (*Abstr.*, 1906, i, 375). When  $\beta$ -methyl- $\Delta^2$ -butylene, methyl alcohol and sulphuric acid are heated together at 95° in a closed vessel, a yield equivalent to 50% of the theoretical of the corresponding *methyl amyl ether*, b. p. 86°, is obtained. T. A. H.

**Structure of Phosphorous Acid and its Derivatives. IV. The Conversion of Tervalent into Quinquevalent Derivatives of Phosphorus.** ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 687—718. Compare this vol., i, 8, 174).—When the tervalent derivatives of phosphorus are acted on by water or alcohol, quinquevalent derivatives are mostly obtained. The reason for this seems to be the unsaturated character of the tervalent compounds which under certain physico-chemical conditions tend to utilise their reserve of energy and pass into a more stable form. Thus, when compounds of the type  $\text{P}(\text{OR})_3$  react with  $\text{R}'\text{X}$  (where

R' stands for hydrogen, or a fatty radicle either identical with or different from R, and X a halogen or hydroxyl), they are converted into compounds of the type  $O:PR'(OR)_2$ . R'X acting as a catalyst, the course of the reaction being  $R'X + P(OR)_3 = PR'(OR)_3X = O:PR'(OR)_2 + XR$ . Various ethyl, propyl, and methyl compounds of this character have been prepared in this way. The intermediate compounds being very unstable can seldom be isolated, but the compound  $PMe(OPh)_3I$ , prepared by the action of methyl iodide on triphenyl phosphite, has been obtained, and on distillation yields iodobenzene and diphenyl methyl phosphite, b. p. 201—202°/11 mm. (compare Abstr., 1898, i, 417). Thus, water or alcohol acts on phosphorus trichloride thus:  $PCl_3 + 3ROH = P(OR)_3 + 3HCl$ ;  $P(OR)_3 + HCl = P(OR)_3HCl \rightarrow O:P(OR)_2H$ , and to obtain a good yield of such a compound it is necessary (1) to remove too great an excess of hydrochloric acid which might react further and ultimately produce phosphorous acid itself, and (2) to work at low temperatures (Levitsky, Abstr., 1903, i, 733). All the reactions adduced by Levitsky in proof of the tervalency of the phosphorus in the ethyl compound of this type and in its acid are shown to be equally well explained by assuming the quinquevalency of the phosphorus which is more in accordance with its behaviour towards the copper halides. Again, when trimethyl phosphite is mixed with water, its characteristic odour vanishes immediately, great heat is developed, and the compound  $O:P(OMe)_2H$  is formed; if this reaction takes place as explained above, then the fact that it is immediate and seemingly independent of the mass of the reacting substance is explained by its irreversibility, whilst the development of heat might be due to the oxygen changing from a single to a double linking with the phosphorus. Finally, the hydroxyl derivatives of tervalent phosphorus cannot exist, and when formed are at once converted into derivatives of quinquevalent phosphorus in exact analogy with  $>C:CH:OH \rightarrow >CH:CHO$ .  
Z. K.

**Crystalline Compound of Acetic Acid with Hydrogen Bromide.** ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1104—1105).—McIntosh (Abstr., 1906, i, 481) has stated that acetic acid does not unite with hydrogen bromide at low temperatures, but the author finds that, when glacial acetic acid is saturated with dry hydrogen bromide, heat is developed, and the viscous liquid obtained, when kept in a cold place, solidifies to a mass of crystals of the compound  $2C_2H_4O_2.HBr$ , m. p. 7—8°.

A similar viscous liquid is obtained on mixing glacial acetic acid with concentrated sulphuric acid, but no crystalline compound could be separated.  
T. H. P.

[Preparation of Bromides of Dialkylacetic Acids.] KALLE & Co. (D.R.-P. 175585).—Instead of transforming the dialkylmalonic acids into the dialkylacetic acids and then converting the latter into the dialkylacetamides, the dialkylmalonic acid may be treated directly with bromine and the bromoalkylacetic acid produced then converted

into the amide.  $\alpha$ -Bromo- $\alpha$ -ethylbutyric acid,  $\text{C}_2\text{H}_5\text{Br}\cdot\text{CO}_2\text{H}$ , b. p. 200—201°, is obtained by heating diethylmalonic acid with an equal weight of bromine at 160—180°, liberating hydrogen bromide.  $\alpha$ -Bromo- $\alpha$ -methylvaleric acid has b. p. 204—205°.  $\alpha$ -Bromo- $\alpha$ -ethylvaleric and  $\alpha$ -bromo- $\alpha$ -propylvaleric acids have b. p. 212—213° and 228—230° respectively. These acids are readily converted into the corresponding amides.

G. T. M.

**Theory of Saponification.** II. RICHARD FANTO and MILAN J. STRITAR (*Annalen*, 1907, 351, 332—343. Compare Abstr., 1904, i, 843).—In Geitel's method of "cold saponification" (Abstr., 1897, ii, 547) three reactions may take place: (1) formation of a soap and glycerol by saponification of the triglyceride; (2) ester formation by displacement of glycerol by the solvent alcohol, and (3) formation of a soap by hydrolysis of the ester formed intermediately. The course of these reactions must be studied before the results obtained by Geitel's method of saponification can be interpreted.

Two series of saponification experiments with rape-seed oil are described, and the results tabulated and expressed in curves. The oil is shaken with a known volume of alcoholic potassium hydroxide, the reaction stopped after a given time by addition of a measured amount of acetic acid, and, after addition of alcohol and ether, the excess of acetic acid titrated; from this is calculated the ions,  $\text{OH}'$ , taking part in the hydrolysis. An excess of acid is then added, the alcohol and ether distilled off, and the total liberated glycerol determined in the residue. The difference of the total glycerol and that corresponding with the ions,  $\text{OH}'$ , required for the hydrolysis is the amount of glycerol displaced in the ester formation. It is noticeable that the curves do not show any irregularities in the neighbourhood of the point of clearance of the hydrolysis mixture. An apparent decrease in the amount of the "ester-glycerol" must be caused by partial hydrolysis of the ester in presence of still unchanged triglyceride.

The unchanged triglyceride is isolated by distillation in a current of steam (Henriques, Abstr., 1899, ii, 258) and successive extraction of the residue with light petroleum and alcohol; when hydrolysed with alcoholic potassium hydroxide, the residual triglyceride of rape-seed oil yields erucic and arachidic acids. From the quantitative results obtained, the conclusion is drawn that the saturated triarachin is more stable towards alkalis than the unsaturated trierucin and trirapin.

G. Y.

**Catalytic Hydrogenation of Unsaturated Esters.** GEORGES DARZENS (*Compt. rend.*, 1907, 144, 328—331).—The author has applied to unsaturated esters the method of hydrogenation in the presence of nickel obtained by reducing the oxide at 280° (Abstr., 1905, i, 172). Ethyl acrylate and dimethylacrylate give ethyl propionate and isovalerate respectively. Ethyl pelargonate is obtained from ethyl  $\Delta^8$ -nonenoate, while the series of  $\beta\beta$ -methylalkylacrylic esters of the type  $\text{CMeR}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  give the homologous fatty acid esters of the general formula  $\text{CHMeR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ . The disubstituted

acrylic esters were obtained by condensing the ketones,  $R \cdot \text{COCH}_3$ , with ethyl chloroacetate, and dehydrating the  $\beta$ -hydroxy-acid formed, by means of phosphoric oxide. Ethyl undecenoate,

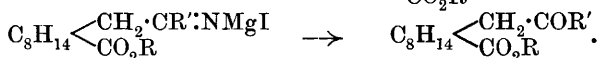


prepared by distilling castor oil in a vacuum, gives ethyl undecenoate. Ethyl cinnamate and ethyl phenylcrotonate give ethyl phenylpropionate and ethyl phenylbutyrate.  $\Delta^{1:2}$  cyclohexenecarboxylic acid is obtained from cyclohexanone. The bisulphite compound of this ketone is treated with potassium cyanide, and the nitrile obtained is hydrolysed by cold hydrochloric acid, forming hydroxycyclohexanecarboxylic acid of which the ethyl ester after dehydration by phosphoric oxide gives ethyl  $\Delta^{1:2}$  cyclohexenecarboxylate by hydrogenation. The *o*-, *m*-, and *p*-methyl homologues of this acid are similarly prepared. In the same manner hexahydrophenylacetic acid is obtained from cyclohexanone after condensing the latter with ethyl chloroacetate.

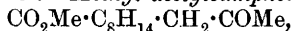
The method of catalytic hydrogenation differs from Bouveault and Blanc's method, using sodium and boiling alcohol (Abstr., 1903, i, 597, 673; 1904, i, 642; 1905, i, 11, 12, 13), in that the latter transforms the group  $\text{CO}_2\text{K}$  into  $\text{CH}_2 \cdot \text{OH}$ , and often hydrogenates the aromatic nucleus and the ethylenic grouping in the  $\alpha\beta$ -position, while catalytic hydrogenation does not affect the  $\text{CO}_2\text{H}$  group or the aromatic nucleus unless it is partially hydrogenated already, and reduces the ethylenic grouping in all positions.

The reactions give a practical method for the synthesis of an acid,  $\text{C}_{n+2}$ , from an aldehyde or ketone  $\text{C}_n$ . E. H.

**Preparation of Acylcampholic Esters and a New Method of Formation of Hydroxyphenylhomocampholic Acid.** ALBIN HALLER and CHARLES WEIMANN (*Compt. rend.*, 1907, 144, 297—301. Compare Haller, Abstr., 1889, 1205; Blaise, Abstr., 1901, i, 133).—When organomagnesium compounds act on the cyanocampholic esters, imino-compounds are formed, and these are hydrolysed by dilute sulphuric acid into keto-derivatives,  $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH}_2 \cdot \text{CN} \\ \text{CO}_2\text{R} \end{smallmatrix} \rightarrow$



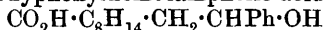
Under the conditions employed, the organomagnesium compound does not attack the group  $\cdot \text{CO}_2\text{R}$ . The esters so obtained are very difficult to saponify, and as they resemble in this respect the  $\beta$ -camphoric esters they probably contain the  $\cdot \text{CO}_2\text{R}$  group in a similar position in the molecule. Their ketonic nature is proved by the formation of semicarbazones. *Methyl acetylcampholate*,



is an oil with an agreeable odour, almost colourless when freshly distilled, b. p.  $190^\circ/50$  mm.,  $[\alpha]_D +73.29^\circ$ ; the *semicarbazone*,  $\text{C}_{14}\text{H}_{25}\text{O}_3\text{N}_3$ , forms white needles, m. p.  $251^\circ$ . *Ethyl propionylcampholate*,  $\text{CO}_2\text{Et} \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}_2 \cdot \text{COEt}$ , is an oil, b. p.  $198^\circ/25$  mm., slightly yellow when freshly distilled, and becoming distinctly yellow on contact with light and air; the *semicarbazone*,  $\text{C}_{16}\text{H}_{29}\text{O}_3\text{N}_3$ , forms silky needles, m. p.  $180.5^\circ$ . *Methyl benzoylcampholate*,  $\text{CO}_2\text{Me} \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}_2 \cdot \text{COPh}$ , crystallises from light petroleum in spangles, m. p.  $71^\circ$ ; its *semi*-



*carbazone* has m. p. 222°. The *ethyl* ester has m. p. 48—49°, b. p. 225°/15 mm.; its *semicarbazone* has m. p. 180°. *Benzoylcampholic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CH}_2\cdot\text{COPh}$ , which is the keto-derivative corresponding with hydroxyphenylhomocampholic acid,



(Haller and Minguin, *Abstr.*, 1900, i, 452), is obtained by heating the ester with hydrochloric acid in a sealed tube to 120—225° for five days. The product is insoluble in concentrated, but soluble in dilute, potassium hydroxide, from solution in which it is thrown down by acids as a white, flocculent precipitate, which crystallises from alcohol or ether in needles, m. p. 163°,  $[\alpha]_D + 69^\circ 28'$  (in methyl alcohol). The *semicarbazone*,  $\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}_3$ , has m. p. 210° (partial decomp.). On reduction with sodium amalgam the acid gives hydroxyphenylhomocampholic acid, which crystallises from methyl alcohol in white, transparent lamellæ containing methyl alcohol of crystallisation; it loses the alcohol at 130° and then melts at 200—202°. The acid obtained by the hydrolysis of benzylidenecamphor (Haller and Minguin, *loc. cit.*) behaves in exactly the same manner, and a mixture of the two products has m. p. 200—202°. It follows that the representation of hydroxyphenylhomocampholic acid as an  $\epsilon$ -hydroxy-acid is correct.

E. H.

**Some Derivatives of Dehydrocampholenic Acid.** MICHAEL N. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 718—721).—In order to explain the structure of some nitro-derivatives of camphene, it was found necessary to investigate some derivatives of dehydrocampholenic acid,  $\text{C}_{10}\text{H}_{14}\text{O}_2$ . The *sodium* and *silver* salts were analysed. The *chloroanhydride*,  $\text{C}_{10}\text{H}_{13}\text{OCl}$ , is prepared by dissolving the perfectly dry acid in an excess of phosphorus trichloride; b. p. 116—117°/15 mm., 229—230°/745 (slight decomp.), m. p. 37.5—38.5°. Cold alcohol converts it into the *ethyl* ester,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{Et}$ , which distils with slight decomposition under the ordinary pressure,  $D_4^{16.5} 1.0215$ ,  $n_D^{16.5} 1.47446$ . By saturating the chlorine compound with ammonia, the *amide*,  $\text{C}_{10}\text{H}_{13}\text{O}\cdot\text{NH}_2$ , is obtained, and crystallises from alcohol in thin, long prisms, m. p. 114.5—115.5°. The chemical and physical properties of the derivatives both point to the saturated character of campholenic acid.

Z. K.

**The van't Hoff-Wislicenus Configuration Theory.** ARTHUR MICHAEL (*J. pr. Chem.*, 1907, [ii], 75, 105—120).—A reply to Lossen (*Abstr.*, 1906, i, 796) and a general criticism of Wislicenus's views on stereochemical structure.

G. Y.

**Ethyl Lactyl-lactate.** ÉMILE JUNGFLISCH and MARCEL GODCHOT (*Compt. rend.*, 1907, 144, 425—427).—From the product of heating pure ethyl lactate in a sealed tube at 250° for seven to eight hours, there were isolated ethyl alcohol, ethyl lactate, and *ethyl lactyl-lactate*,  $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , a colourless liquid with an ethereal odour, b. p. 215—226°,  $D_4^{10} 1.096$ . A cryoscopic determination in benzene

solution gives the molecular weight 199 (theory 192); it seems to be identical with the monoethyl dilactate of Wurtz and Friedel (*Ann. Chim. Phys.*, 1861, [iii], 63, 112). Alkalis resolve it into lactic acid. The formation of ethyl alcohol and ethyl lactyl-lactate is explained by the reaction  $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} + \text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} = \text{EtOH} + \text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , which being reversible, attains an equilibrium. The reverse reaction is rapid, mere dissolution of ethyl lactyl-lactate in ethyl alcohol giving a mixture not precipitable by water. Ethyl lactyl-lactate is much more stable than the corresponding acid, which cannot be transformed directly into either salt or ester.

A fourth product of the reaction is *dl*-dilactide. Its formation is due to the elimination of a molecule of ethyl alcohol from the ethyl lactyl-lactate; this reaction also is reversible and when the alcohol is lost during rectification the proportion of dilactide increases.

The explanation given of the formation of ethyl lactyl-lactate and dilactide is confirmed by the results of the following experiments. (1) When, after heating the ethyl lactate in a sealed tube at  $260^\circ$  the ethyl alcohol formed is distilled off and the residue again heated under the same conditions, the yield of ethyl lactyl-lactate is increased to an amount equivalent to half the ethyl lactate used. (2) When ethyl lactate is heated under the same conditions with an equal volume of ethyl alcohol, no trace of ethyl lactyl-lactate can be isolated from the product.

Thus the products of the action of heat on ethyl lactate are in character analogous to those obtained from lactic acid itself (Abstr., 1906, i, 333), but the mechanism of the changes is different.

E. H.

**The Pyran Series. V.  $\alpha\epsilon$ -Diketopimelic Acids.** EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. Chim.*, 1907, [iv], 1, 75—95. Compare this vol., i, 147, 148).—A *résumé* of the properties of these acids has already been given (Abstr., 1906, i, 300) and their method of formation is also dealt with in this vol., i, 181.

*$\alpha\epsilon$ -Diketopimelic acid*,  $\text{CH}_2[\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}]_2$ , m. p.  $127^\circ$ , crystallises from hot acetic acid or from a mixture of this with ether or from ethyl acetate on addition of benzene. The *sodium* salt crystallises from a mixture of water and alcohol. The *methyl* ester separates from a mixture of ether and light petroleum in crystals, m. p.  $62^\circ$ , and furnishes a *disemicarbazone*, m. p.  $250$ — $251^\circ$  (decomp.), which crystallises from a mixture of formic acid and alcohol. The *ethyl* ester furnishes a crystalline *disemicarbazone*, m. p.  $250^\circ$ , a *diphenylhydrazone*, m. p.  $147^\circ$ , which crystallises from dilute alcohol in yellow needles, and a crystalline *dioxime*, m. p.  $144^\circ$ .  *$\alpha\epsilon$ -Diketopimelic anhydride*, obtained by heating the acid with acetyl chloride, could not be isolated in a pure state; with aniline it forms the *dianilide* of the acid, m. p.  $192$ — $193^\circ$ , which crystallises from boiling benzene.  *$\alpha\epsilon$ -Diketopimelic acid* yields a *disemicarbazone*, m. p. about  $210^\circ$  (decomp.), which crystallises with  $2\text{H}_2\text{O}$  from boiling water. The *diphenylhydrazone*, m. p.  $130^\circ$  (decomp.), separates from dilute alcohol in yellow needles.

With hydrazine acetate the acid furnishes the corresponding *azine*, m. p. 210° (decomp.),  $\text{CH}_2 \begin{matrix} \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{N} \\ \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{N} \end{matrix}$ , which forms small needles from dilute alcohol. The three foregoing substances are soluble in an aqueous solution of potassium hydrogen carbonate. The *dioxime*, obtained by treating the acid with hydroxylamine hydrochloride, is crystalline, m. p. 175° (decomp.), and when boiled with water furnishes glutaronitrile, b. p. 162°/25 mm. (compare Ferkin, Trans., 1889, 55, 702). On reduction with sodium amalgam,  $\alpha\epsilon$ -diketopimelic acid furnishes the corresponding  $\alpha\epsilon$ -dihydroxypimelic acid, which was not obtained pure. This on further treatment with phosphorus and hydriodic acid is converted into pimelic acid.

$\alpha\epsilon$ -Diketo- $\beta$ -methylpimelic acid, m. p. 140° (decomp.), obtained by the hydrolysis of ethyl ethylidenebisoxalacetate, crystallises from ethyl acetate. The *methyl* ester has b. p. 172—176°/15 mm. The *dianilide*, m. p. 135°, crystallises from boiling alcohol. The *disemicarbazone*, m. p. 210° (decomp.), crystallises from boiling water. The *dioxime*, obtained by the action of hydroxylamine hydrochloride on the acid, is crystalline and, on solution in boiling water, furnishes  $\beta$ -methylglutaronitrile, b. p. 140°/10 mm., the latter on hydrolysis with potassium hydroxide in alcohol yields  $\beta$ -methylglutaric acid the *anilide* of which, m. p. 117°, crystallises from benzene.

$\alpha\epsilon$ -Diketo- $\beta$ -ethylpimelic acid is obtained only in small quantities by the acid hydrolysis of ethyl propylidenebisoxalacetate and is better prepared by boiling the corresponding dianhydride with water. It crystallises from ethyl acetate and has m. p. 140° (decomp.). The *methyl* ester, m. p. 86°, obtained by heating propylidenebisoxalacetic dianhydride with methyl alcohol, crystallises from a mixture of ether and light petroleum. The *dianilide*, m. p. 114°, crystallises from dilute alcohol and is insoluble in potassium hydrogen carbonate solution. The *disemicarbazone*, m. p. about 210° (decomp.), crystallises from a mixture of chloroform and alcohol. The *dioxime* is crystalline and like its homologues is unstable, being converted by heating at 170°, or by boiling its aqueous solution, into  $\beta$ -ethylglutaronitrile, b. p. 144°/12 mm. This on treatment with potassium hydroxide in alcohol furnishes  $\beta$ -ethylglutaric acid, which is converted by boiling with acetic anhydride into  $\beta$ -ethylglutaric anhydride, b. p. 158°/13 mm., and this furnishes the corresponding crystalline *anilide*, m. p. 110°.

$\alpha\epsilon$ -Diketo- $\beta$ -n-hexylpimelic acid, obtained by the hydration of heptylidenebisoxalacetic dianhydride, crystallises with  $2\text{H}_2\text{O}$ , which it retains after recrystallisation from benzene. The *methyl* ester, b. p. 206°/10 mm., is obtained by the action of methyl alcohol on heptylidenebisoxalacetic dianhydride. The *dianilide*, m. p. 104°, crystallises from dilute alcohol. The *disemicarbazone* crystallises with  $2\text{H}_2\text{O}$  from a mixture of alcohol and chloroform. The *dioxime*, m. p. 180° (decomp.), forms small needles from benzene and, when its aqueous solution is boiled, passes into  $\beta$ -hexylglutaronitrile, b. p. 180°/14 mm. This, on treatment with potassium hydroxide in alcohol, yields the corresponding acid, m. p. 37—38°, which crystallises from a mixture of benzene and light petroleum, cooled in ice and salt.

$\beta$ -n-Hexylglutaric anhydride, b. p. 194°/12 mm., obtained by boiling

the acid with acetic anhydride, is a viscous liquid at the atmospheric temperature, but separates from methyl chloride in crystals. The *anilide*, m. p. 73°, crystallises from benzene. T. A. H.

**Preparation of Fatty, Aromatic, and Hydroaromatic Aldehydes.** AUGUSTE BÉHAL and MARCEL SOMMELET (D.R.-P. 177614. Compare this vol., i, 275).—On heating the alkyloxy-glycols,  $\text{OH}\cdot\text{CRR}\cdot\text{CH}_2\cdot\text{OX}$ , with acids the alcohol,  $\text{X}\cdot\text{OH}$ , is eliminated and the aldehyde,  $\text{CHRR}'\cdot\text{CHO}$ , is obtained. The method seems to be quite general, the alkyloxy-glycols being heated either with 20% sulphuric acid or dehydrated oxalic acid. The patent contains a table of certain aldehydes obtained by this process. G. T. M.

**Compounds of Thiosulphuric Acid with Aldehydes. II.** OTTO SCHMIDT (*Ber.*, 1907, 40, 865—873. Compare Abstr., 1906, i, 711).—The existence of formaldehydethiosulphuric acid in a solution containing the two constituents is indicated by the following experiments.

If the reaction can be represented by  $\text{OH}\cdot\text{CH}_2\cdot\text{S}_2\text{O}_3\text{H} \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2\text{S}_2\text{O}_3$ , then  $c/c'c'' = k$  (where  $c$ ,  $c'$ , and  $c''$  are the concentrations of the three substances in the order given); for a given initial value of  $c''$ ,  $c$  must increase with  $c'$ , and consequently  $c''$  must diminish. This is the case; as the concentration of the formaldehyde increases, that of the thiosulphuric acid, as measured by the time required for the separation of sulphur in the presence of hydrochloric acid, diminishes.

Regarded as  $\text{CH}_2(\text{OH})_2 + \text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{OH}\cdot\text{CH}_2\cdot\text{S}_2\text{O}_3\text{H} + \text{H}_2\text{O}$ , the reaction is one of ester-formation, and should be favoured by mineral acids; hydrochloric acid does indeed increase very markedly the stability of the formaldehydethiosulphuric acid. Thus a solution containing 47 c.c. of *N*/1 sodium thiosulphate, 3 c.c. of water, 10 c.c. of 39.95% formaldehyde, and 5 c.c. of 25% hydrochloric acid remains clear until after prolonged boiling, trithioformaldehyde is deposited in accordance with the equations: (i)  $\text{OH}\cdot\text{CH}_2\cdot\text{S}_2\text{O}_3\text{H} = \text{CH}_2\text{S} + \text{H}_2\text{SO}_4$ ; (ii)  $3\text{CH}_2\text{S} = (\text{CH}_2\text{S})_3$ .

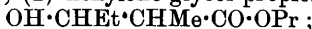
In dilute solution the reaction (ii) does not take place, and (i) becomes reversible, the  $k$  value, calculated for a unimolecular reaction, exhibiting a fairly constant value.

The presence of formaldehyde does not influence appreciably the oxidation of sodium thiosulphate by iodine, but the velocity of oxidation of the free acid is retarded enormously in the presence of the aldehyde; in fact, the velocity is retarded under any of the conditions which favour the formation of formaldehydethiosulphuric acid, such as an increase of the concentration of the formaldehyde or of the hydrochloric acid, or of the total concentration.

C. S.

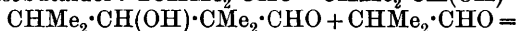
**Action of Aluminium Alkyl oxides on Aldehydes. Ester-condensation as a New Form of Aldehyde-condensation.** VETCHESLAV E. TISTSHENKO (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 482—540).—The reaction between aluminium propoxide and propaldehyde is similar to that between aluminium ethoxide and acet-aldehyde, the principal product being propyl propionate, b. p.

122—124°/769 mm. The following compounds are also formed : (1) *parapropaldehyde*, b. p. 172—173°/773 mm.,  $D_0^0$  0.9643,  $D_4^0$  0.9641,  $D_{20}^0$  0.9443,  $D_{40}^0$  0.9441 (compare Reformatsky, *J. Russ. Phys. Chem. Soc.*, 1890, 22, 197); (2) *hexylene glycol propionate*,



(3) *propyl  $\beta$ -hydroxy- $\alpha$ -methylvalerate*, resulting from the condensation of the aldehyde according to the equations:  $2\text{Et} \cdot \text{CHO} = \text{OH} \cdot \text{CHEt} \cdot \text{CHMe} \cdot \text{CHO}$ ;  $\text{OH} \cdot \text{CHEt} \cdot \text{CHMe} \cdot \text{CHO} + \text{Et} \cdot \text{CHO} = \text{OH} \cdot \text{CHEt} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{COEt} = \text{OH} \cdot \text{CHEt} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{OPr}$ . Part of the propaldol formed decomposes into an unsaturated aldehyde, which was only yielded in small quantity and was not separated, and water, which acts on the aluminium propoxide, giving propyl alcohol,  $\text{Al(OPr)}_3 + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + 3\text{PrOH}$ .

Under the action either of potassium carbonate, as solid or saturated aqueous solution, or of dilute aqueous or alcoholic sodium hydroxide in the cold, *isobutaldehyde* gives *isobutaldol*,  $2\text{CHMe}_2 \cdot \text{CHO} = \text{CHMe}_2 \cdot \text{CH(OH)} \cdot \text{CMe}_2 \cdot \text{CHO}$ . When, however, potassium hydroxide at ordinary or high temperatures, or sodium acetate at 180°, is used, the aldol is accompanied by octylene glycol *isobutyrate* or its products of hydrolysis. With aluminium *isobutoxide* and *isobutaldehyde*, the principal product of condensation is *isobutyl isobutyrate*, b. p. 147—149°,  $2\text{CHMe}_2 \cdot \text{CHO} = \text{CHMe}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CHMe}_2$ . Products yielded in smaller proportion are: (1) *isobutyl alcohol*, and (2) octylene glycol *isobutyrate*, which is formed from the aldehyde by way of *isobutaldol*:  $2\text{CHMe}_2 \cdot \text{CHO} = \text{CHMe}_2 \cdot \text{CH(OH)} \cdot \text{CMe}_2 \cdot \text{CHO}$ ;



$\text{CHMe}_2 \cdot \text{CH(OH)} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CHMe}_2$ . The formation of *isobutyl alcohol* may be due to the decomposition of the aluminium *isobutoxide*, thus,  $\text{Al(OC}_4\text{H}_9)_3 = \text{Al(OH)}_3 + \text{CMe}_2 \cdot \text{CH}_2$ , the aluminium hydroxide then reacting as follows:  $\text{Al(OC}_4\text{H}_9)_3 + \text{Al(OH)}_3 = \text{Al}_2\text{O}_3 + 3\text{C}_4\text{H}_9 \cdot \text{OH}$  or  $3\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CHMe}_2 + \text{Al(OH)}_3 = 3\text{C}_4\text{H}_9 \cdot \text{OH} + \text{Al(C}_4\text{H}_7\text{O}_2)_3$ .

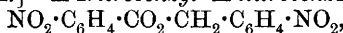
The action of potassium hydroxide or carbonate on ordinary *isovaleraldehyde* gives: (1) the aldol and the unsaturated aldehyde corresponding with  $\beta$ -methylbutaldehyde; (2) the aldol and decylene glycol *isovalerate*, derived from the  $\alpha$ -methylbutaldehyde; there may also be formed decylene glycol from the hydrolysis of the *isovalerate*, and a substance,  $\text{C}_{20}\text{H}_{38}\text{O}_3$ , resulting from the dehydration of the aldol. The condensation of *isovaleraldehyde* and aluminium *isoamyl-oxide* gives mainly *isoamyl isovalerate*, small quantities of amyl alcohol, *isoamyl hydroxydecoate*, the two decylene glycol *isovalerates* and other compounds being obtained.

[With A. ALEXANDROFF.]—The only compound separated from the condensation products of aluminium ethoxide and heptaldehyde was *heptyl heptylate*,  $\text{C}_6\text{H}_{13} \cdot \text{CO}_2 \cdot \text{C}_7\text{H}_{15}$ , b. p. 276.5—278.5° or 157.5—158.5°/24 mm., which gives the normal molecular weight in freezing benzene.

[With A. A. GRIGORIEFF.]—Aluminium ethoxide reacts with chloral or bromal in benzene solution, giving as principal product trichloroethyl trichloroacetate,  $\text{CCl}_3 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CCl}_3$ , or tribromoethyl tribromoacetate.

[With M. N. WISCHNIAKOFF.]—The principal product of the reaction between aluminium ethoxide and  $\alpha$ -bromoisobutaldehyde is  *$\alpha$ -bromoisobutyl- $\alpha$ -bromoisobutyrate*,  $\text{CMe}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CMe}_2\text{Br}$ , b. p. 114—117°/8.5 mm., which yields  $\alpha\beta$ -dibromo- $\alpha\alpha$ -dimethylethane and  *$\alpha$ -bromoisobutyric acid* when heated with hydrobromic acid in a sealed tube at 140°. Ethyl  *$\alpha$ -bromoisobutyrate* is probably also formed.

[With N. N. SUM.]—*m-Nitrobenzyl m-nitrobenzoate*,



obtained by the interaction of aluminium ethoxide and *m*-nitrobenzaldehyde, separates from benzene in small, yellow crystals, m. p. 143—144°, dissolves readily in chloroform and sparingly in other solvents and has the normal molecular weight in boiling benzene. Hydrogen bromide decomposes the ester into *m*-nitrobenzyl bromide and *m*-nitrobenzoic acid.

[With M. GUSHOFF.]—*o-Nitrobenzyl o-nitrobenzoate* (?), prepared by the action of aluminium ethoxide on *o*-nitrobenzaldehyde, separates from benzene in nodular masses of small crystals, m. p. 104—106°. *p-Nitrobenzyl p-nitrobenzoate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , obtained by the interaction of aluminium ethoxide and *p*-nitrobenzaldehyde in benzene solution, separates from benzene in pale yellow crystals, m. p. 171—172°, dissolves sparingly in water, alcohol, ether, light petroleum, and other ordinary solvents, and is resolved into *p*-nitrobenzoic acid and *p*-nitrobenzyl bromide by hydrogen bromide; this ester is apparently accompanied by ethyl *p*-nitrobenzoate.

Attempts to investigate the reaction between aluminium alkyloxides and unsaturated aldehydes, such as acraldehyde, crotonaldehyde, and cinnamaldehyde, gave no definite results, owing to the readiness with which these aldehydes are resinified or oxidised by the aluminium alkoxide.

The reactions of the saturated aliphatic and aromatic aldehydes with aluminium alkyloxides are hence similar to those occurring with alkalis, except that in the latter case the esters formed undergo hydrolysis to the corresponding acids and alcohols. In the conversion of aldehydes into esters by this means, the aldehyde groups, but not the radicles, combined with them, take part. This reaction does not, however, take place with esters of formic acid which contain the CHO group, nor with ketones, nor with acetal or paraldehyde. The reaction occurs with aluminium alkyloxides derived from secondary and tertiary, as well as primary, acids. The alkyloxides of sodium, magnesium, or zinc also bring about this reaction, but those of acid-forming elements, such as boron, do not do so.

The author is of opinion that none of the various hypotheses put forward to explain the action of alkalis or alkyloxides on aldehydes is sufficient to account for the facts. No conversion of ester into aldehyde has yet been observed.

T. H. P.

**Action of Magnesium Amalgam on *iso*Butaldehyde.**  
VETCHESLAV E. TISTSHENKO and G. N. GRIGOREEFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 540—547).—The fact that the action of sodium on *isobutaldehyde* yields octylene glycol *isobutyrate* and a small pro-

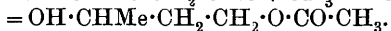
portion of *isobutyl* alcohol was explained by Lederer (Abstr., 1901, i, 669) as due to the action of the moisture of the air on the sodium giving sodium hydroxide and hydrogen, the latter then reducing the aldehyde to the alcohol. To test the accuracy of this explanation, the authors replace the sodium by magnesium amalgam, which, with the moisture of the air, forms magnesium hydroxide, a compound incapable of forming either aldol or ester at the ordinary temperature; *isobutyl* alcohol should thus form the sole product of the reaction.

The action of 4 grams of magnesium in the form of amalgam on 100 grams of *isobutaldehyde* yields *isobutyl* alcohol, *isobutyl isobutyrate*, octylene glycol mono- and di-*isobutyrate*s, the *isobutyl* ester of the acid,  $C_8H_{16}O_3$  (compare Brauchbar, Abstr., 1897, i, 137), the *isobutyrim* of *isobutyl* hydroxyoctoate (?) and octylene glycol. The same products are obtained by the action of aluminium ethoxide on acetaldehyde.

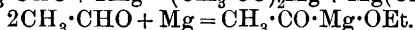
The conclusion is drawn that the first change occurring in the action of magnesium amalgam on *isobutaldehyde* is represented by:  
 $2CHMe_2 \cdot CHO + Mg = CHMe_2 \cdot CO \cdot Mg \cdot O \cdot CH_2 \cdot CHMe_2$  or  $4CHMe_2 \cdot CHO + 2Mg = (CHMe_2 \cdot CO)_2Mg + (CHMe_2 \cdot CH_2 \cdot O)_2Mg$ . The subsequent actions taking place are given by the equations:  $2CHMe_2 \cdot CHO = CHMe_2 \cdot CO \cdot O \cdot CH_2 \cdot CHMe_2$ ;  $2CHMe_2 \cdot CHO = CHMe_2 \cdot CH(OH) \cdot CHMe_2 \cdot CHO$ ;  
 $CHMe_2 \cdot CH(OH) \cdot CHMe_2 \cdot CHO + CHO \cdot CHMe_2 =$  either  
 $CHMe_2 \cdot CH(OH) \cdot CHMe_2 \cdot CH_2 \cdot O \cdot CO \cdot C_3H_7$  or  
 $CHMe_2 \cdot CH(OH) \cdot CHMe_2 \cdot CO \cdot O \cdot C_4H_9$ . T. H. P.

**Action of Magnesium Amalgam on Acetaldehyde.** M. P. VORONKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 547—550).—The results described in the preceding abstracts are not in accord with those of Meunier (Abstr., 1902, i, 335), who obtained  $\beta\gamma$ -dihydroxybutane by the action of magnesium amalgam on acetaldehyde, the latter being reduced in the same way as acetone is reduced to pinacone or benzaldehyde to hydrobenzoin by means of sodium amalgam.

The author was unable to obtain  $\beta\gamma$ -dihydroxybutane by the gradual addition of magnesium amalgam to cooled acetaldehyde, the products formed being aldol, crotonaldehyde, and  $\beta$ -butylene glycol acetate. The last-named compound is formed by the condensation of the aldol with the aldehyde:  $OH \cdot CHMe \cdot CH_2 \cdot CHO + CH_3 \cdot CHO$



The condensing agent causing this reaction is probably a magnesium alkoxide formed by the action of the magnesium amalgam on the aldehyde:  $4CH_3 \cdot CHO + 2Mg = (CH_3 \cdot CO)_2Mg + Mg(OEt)_2$  or



T. H. P.

**Halogen Derivatives of Acetaldehyde.** PAUL FREUNDLER (*Bull. Soc. Chim.*, 1907, [iv], 1, 66—71. Compare Abstr., 1905, i, 326).—When paraldehyde is treated with bromine at  $-10^\circ$  to  $-5^\circ$ , it is transformed almost completely into bromoacetaldehyde. If the temperature is then allowed to rise above  $0^\circ$  the liquid becomes milky,

develops heat, and finally separates into two layers, the upper consisting of dilute hydrobromic acid and the lower of  $\alpha\gamma$ -dibromocrotonaldehyde. The latter is unstable and cannot be readily isolated, but on treatment with excess of bromine is converted into the stable  $\alpha\alpha\beta\gamma$ -tetrabromobutaldehyde. The initial reaction depends on the presence of some acetaldehyde in the paraldehyde used, and the further depolymerisation of the latter is brought about by the hydrogen bromide liberated.

The chlorination of paraldehyde is not strictly analogous with the bromination. Chlorine is absorbed below  $0^\circ$ , but no reaction appears to occur below  $20^\circ$ . At this point chloroacetaldehyde is formed and reacts with some acetaldehyde, yielding  $\alpha$ -chlorocrotonaldehyde which then absorbs chlorine, forming  $\alpha\alpha\beta$ -trichlorobutaldehyde (compare Pinner, Abstr., 1876, i, 552, 553; Lieben and Zeisel, Abstr., 1883, 963, and Natterer, *ibid.*, 964). In the course of the chlorination some oxidation also occurs with the formation of acid products, and in addition a small quantity of chloral is produced.

Chloroacetal may be prepared from paraldehyde by a method similar to that adopted for bromoacetal (compare Freundler and Ledru, Abstr., 1905, i, 326).  
T. A. H.

**Trimethylacetaldehyde** [ $\alpha\alpha$ -Dimethylpropaldehyde]. MAXIMILIAN SAMEC (*Annalen*, 1907, 351, 255—262).—The reactions of  $\alpha\alpha$ -dimethylpropaldehyde have not been studied in consequence of the difficulty of its preparation. It is proposed to work out a convenient method of preparation. In the meantime the author has succeeded in obtaining the aldehyde in a 45% yield by oxidation of *tert*-butylcarbinol, which is prepared in a 4% yield, together with *isobutylene* and other hydrocarbons by Grignard's reaction from *tert*-butyl bromide, magnesium, and paraformaldehyde below  $15^\circ$ .

Oxidation of the alcohol with sodium dichromate and sulphuric acid leads to the formation of  $\alpha\alpha$ -dimethylpropaldehyde, b. p.  $174^\circ$ , methyl *isopropyl* ketone, b. p.  $93^\circ$  (Schindler, Abstr., 1893, i, 71), and  $\beta\beta$ -dimethylpropyl  $\alpha\alpha$ -dimethylpropionate, b. p.  $165^\circ$  (Tisner, Abstr., 1891, 998).  
G. Y.

**Action of Bromine on Polymeric Aldehydes.** ADOLF FRANKE (*Annalen*, 1907, 351, 421—425. Compare Abstr., 1900, i, 427).—The reaction studied previously with *para*isobutaldehyde has been extended now to *parapropaldehyde*.

The action of 1 mol. of bromine on 1 mol. of *parapropaldehyde* in carbon disulphide solution, cooled with ice and salt, leads to the formation of two *parabromopropaldehydes*,  $(C_3H_5OBr)_2$ . Of these, one separates from alcohol as a white, crystalline powder, m. p.  $112.5^\circ$ , resembles *parabromoisobutaldehyde*, does not react with boiling water or reduce ammoniacal silver or Fehling's solution, and at  $160^\circ$  decomposes into the monomolecular  $\alpha$ -bromopropaldehyde (Nef, Abstr., 1905, i, 6). The second isomeride, which is obtained from the alcoholic mother liquors, crystallises in prisms, m. p.  $65^\circ$ , and yields  $\alpha$ -bromopropaldehyde when heated. These substances are considered to be probably



*cis*- and *trans*-isomerides,  $\text{CH}(\text{CHMeBr})\left\langle\begin{smallmatrix} \text{O}\cdot\text{CH}(\text{CHMeBr}) \\ \text{O}\cdot\text{CH}(\text{CHMeBr}) \end{smallmatrix}\right\rangle\text{O}$  and  $\text{CHMeBr}\cdot\text{CH}\left\langle\begin{smallmatrix} \text{O}\cdot\text{CH}(\text{CHMeBr}) \\ \text{O}\cdot\text{CH}(\text{CHMeBr}) \end{smallmatrix}\right\rangle\text{O}$ .

The action of bromide on paraldehyde leads to the formation of a product, m. p. about 85°. G. Y.

**Preparation of Aldol and Crotonaldehyde.** VICTOR GRIGNARD and JEAN REIF (*Bull. Soc. Chim.*, 1907, [iv], 1, 114—117).—To a mixture of equal weights of ether and acetaldehyde, cooled to 0°, a solution of sodium sulphite is added in small quantities at a time and the mixture is vigorously and continuously agitated, the temperature being maintained between 5° and 10° until all the sulphite solution has been added. The temperature is then allowed to rise gradually to 32°. The ethereal layer is separated, washed with sodium hydrogen carbonate solution, dried over calcium chloride, and the ether removed by distillation below 60°; the residue is nearly pure aldol, and on distillation at 84—85° furnishes crotonaldehyde, which may be purified by treatment with calcium chloride and redistillation. The yield is about 48—50% of the theoretical, the loss being due mainly to the volatility of the acetaldehyde, a defect which is not remedied by the use of a reflux condenser. T. A. H.

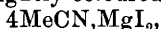
**Some Molecular Combinations of Metallic Halides with Organic Compounds.** VICTOR THOMAS (*Compt. rend.*, 1907, 144, 376—378. Compare Bodroux, *Abstr.*, 1902, ii, 391).—The catalytic effect of certain liquids on the reaction between iodine and the metals magnesium and aluminium is not due to the solvent action of the liquid for iodine, since some liquids, such as benzene, carbon disulphide, chloroform, and carbon tetrachloride, which readily dissolve iodine, are inactive. The aliphatic ketones, such as acetone, methyl ethyl ketone, diethyl ketone, butyrene, and ethyl amyl ketone, the diketones, such as acetylacetone and acetonylacetone, and the aliphatic nitriles, such as acetonitrile, propionitrile, and butyronitrile, react as readily as do ether or anhydrous alcohol. But the aromatic ketones, the aldehydes, except benzaldehyde, and the aromatic nitriles are inactive.

In some cases the reaction with magnesium is so violent that the heat developed renders the mixture red hot and probably causes the formation of magnesium carbide, as on treatment with water the mass gives acetylene. With aluminium, the mixture rapidly becomes incandescent with formation of alumina, owing to the combustion of the iodide formed. The heat developed is so great that the mixture can be used to start the combustion of aluminium in aluminothermal reactions.

In all these reactions the catalyst appears to be of a chemical order, and the combination is due to formation of an additive compound of the iodide and the solvent. A compound of magnesium iodide and alcohol very probably exists (compare Simon, *Abstr.*, 1880, 310). Ketones and nitriles are known to combine easily with iodides.

The experiments with magnesium were effected by the gradual addition of the theoretical quantity of iodine necessary to form mag-

nesium iodide to powdered magnesium contained in a flask and covered with excess of the different ketones and nitriles. The reaction is very violent at first, but slackens rapidly and is completed on a water-bath. From acetone a yellow, crystalline substance,  $\text{COMe}_2, \text{MgI}_2$ , is obtained; it is stable in air, but very easily loses iodine on warming, and is decomposed by water, half the magnesium being precipitated as magnesia and the remainder going into solution. Other ketones under the same conditions give viscous solutions, which, in the case of methyl ethyl ketone after some time, deposits small crystals. Acetonitrile gives a colourless or very slightly coloured mass, probably



which is decomposed by water without precipitation of magnesia. Butyronitrile gives a syrupy liquid which does not crystallise. Aluminium gives similar results, from acetone a brownish-yellow mass decomposed by water, and from acetonitrile several products, including a well crystallised, yellow substance, are obtained. E. H.

**Action of a Solution of Zinc Hydroxide in Ammonia on Sugars.** ADOLF WINDAUS (*Ber.*, 1907, 40, 799—802).—In continuation of previous work on the formation of methylglyoxaline on dextrose (*Abstr.*, 1905, i, 381; this vol., i, 90), the author has studied the behaviour of other sugars towards a solution of zinc hydroxide in ammonia. The various solutions examined were allowed to remain in a closed vessel at the ordinary temperature and in diffused daylight for four months. Working with *d*-mannose, *d*-fructose, *d*-sorbose, *l*-arabinose, and *l*-xylose, the author found methylglyoxaline in every case. With lactose, the yield of 4-methylglyoxaline was much less than with maltose or with dextrose. Methylglyoxaline was not obtained when sucrose was used.

Whilst in the cases quoted no other base, soluble in ether, was obtained in addition to methylglyoxaline, rhamnose formed a mixture of glyoxaline, 4-methylglyoxaline and 2:4-dimethylglyoxaline having been isolated, whilst acetaldehyde was also formed.

A peculiar intermediate product was obtained from *d*-galactose. When the latter remained in contact with an ammoniacal solution of zinc hydroxide for four days, crystals separated, which, when washed with 10% ammonia, were recrystallised from a mixture of alcohol and ammonia. The compound,  $\text{C}_{12}\text{H}_{39}\text{O}_{16}\text{N}_3\text{Zn}$ , obtained in this manner, softens at  $70^\circ$  and has m. p. about  $77^\circ$  (decomp.). When water is added to it, zinc hydroxide separates and the aqueous solution contains free ammonia. It reduces Fehling's solution. When boiled with nitric acid, it forms mucic acid; with phenylhydrazine acetate it yields galactosazone. The formula of a zinc galactosimine,



is suggested. Methylglyoxaline may be obtained by heating the compound with ammonia for two hours at  $100^\circ$  under pressure.

Inositol does not form methylglyoxaline when acted on by an ammoniacal solution of zinc hydroxide. A complex compound, for which the formula  $\text{C}_{12}\text{H}_{37}\text{O}_{18}\text{N}_3\text{Zn}_4$  is suggested, is formed, separating in needles. A. McK.

**Cellulose Esters.** ERNST BERL and WATSON SMITH, jun. (*Ber.*, 1907, 40, 903—908).—Cellulose, according to Cross and Bevan, forms a tetra-acetate (calculated on  $C_6H_{10}O_5$ ) and a trinitrate. The authors are in agreement with Ost, who states (*Abstr.*, 1906, i, 560) that, at the most, only trisubstituted esters are formed.

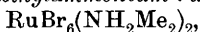
Nitrated cellulose, saturated with glacial acetic acid, is treated with acetic anhydride and concentrated sulphuric acid; the white, powdery product contains more acetic acid and less nitrogen the greater the time occupied in its preparation, but a product free from nitrogen is obtained only under conditions in which the cellulose undergoes extensive degradation.

Reaction does not take place when the acetic anhydride in the preceding preparation is replaced by anhydrous formic acid; the latter, however, reacts with hydrocellulose to form a white powder which is hydrolysed by sodium hydroxide. Béhal's formic acetic anhydride converts hydrocellulose, in the presence of concentrated sulphuric acid, into yellowish-brown formyl compounds of degraded cellulose.

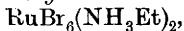
C. S.

**Ruthenium Halogen Salts.** ALEXANDER GUTBIER and H. ZWICKER (*Ber.*, 1907, 40, 690—694).—The ruthenium halogen salts described were obtained either (1) by saturating the ruthenium halide solution with halogen and then mixing with a solution of the hydrochloride or hydriodide of the desired base, or (2) by mixing the ruthenium halide solution with the solution of haloid acid, dissolving any residue formed in dilute halogen acid and then passing chlorine or bromine into the cooled solution. The halogen salts which separate all crystallise well and are very stable and sparingly soluble. They undergo decomposition with water, but may, as a rule, be crystallised from aqueous solutions of the corresponding halogen acid. The chloro-salts are green, forming reddish-brown solutions with hydrochloric acid; the bromo-salts are bluish-black, forming dark blue solutions with hydrobromic acid.

*Methylammonium ruthenichloride*,  $RuCl_6(NH_3Me)_2$ , forms dark greenish-brown, hexagonal leaflets. *Methylammonium ruthenibromide*,  $RuBr_6(NH_3Me)_2$ , forms black, glistening leaflets. *Dimethylammonium ruthenichloride*,  $RuCl_6(NH_2Me_2)_2$ , forms glistening, dark green needles. *Dimethylammonium ruthenibromide*,



forms bluish-black, felted needles. *Trimethylammonium ruthenichloride*,  $RuCl_6(NHMe_3)_2$ , forms dark green needles. *Trimethylammonium ruthenibromide*,  $RuBr_6(NHMe_3)_2$ , forms bluish-black needles. *Ethylammonium ruthenichloride*,  $RuCl_6(NH_3Et)_2$ , forms glistening, green needles. *Ethylammonium ruthenibromide*,



forms bluish-black needles. *Diethylammonium ruthenichloride*,  $RuCl_6(NH_2Et_2)_2$ , forms glistening, brownish-green leaflets. *Diethylammonium ruthenibromide*,  $RuBr_6(NH_2Et_2)_2$ , was prepared. *Propylammonium ruthenichloride*,  $RuCl_6(NH_3Pr)_2$ , forms glistening, dark green needles. *Propylammonium ruthenibromide*,  $RuBr_6(NH_3Pr)_2$ , forms bluish-black, felted needles. *Dipropylammonium rutheni-*

*chloride*,  $\text{RuCl}_6(\text{NH}_2\text{Pr}_2)_2$ , forms dark green needles. *isoButylammonium ruthenichloride*,  $\text{RuCl}_6(\text{C}_4\text{H}_9\cdot\text{NH}_3)_2$ , forms glistening, dark green leaflets. *isoButylammonium ruthenibromide*,

$\text{RuBr}_6(\text{C}_4\text{H}_9\cdot\text{NH}_3)_2$ , forms glistening, bluish-black, felted needles. *Ethylenediammonium ruthenichloride*,  $\text{RuCl}_6(\text{C}_2\text{H}_4\text{N}_2\text{H}_6)_2$ , forms glistening, green needles. *Ethylenediammonium ruthenibromide*,  $\text{RuBr}_6(\text{C}_2\text{H}_4\text{N}_2\text{H}_6)_2$ , forms glistening, black needles. *Propylenediammonium ruthenichloride*,

$\text{RuCl}_6(\text{C}_3\text{H}_6\cdot\text{N}_2\text{H}_6)_2$ , forms greenish-black needles. *Propylenediammonium ruthenibromide*,  $\text{RuBr}_6(\text{C}_3\text{H}_6\cdot\text{N}_2\text{H}_6)_2$ , forms bluish-black needles. A. McK.

**Stereoisomeric Hexamine Salts.** ALFRED WERNER, F. BRÄUNLICH, E. ROGOWINA, and CHR. KREUTZER (*Annalen*, 1907, 351, 65—86. Compare Abstr., 1900, i, 86).—Stereoisomerism has been observed with inorganic salts of the type  $[\text{M}''\text{A}_2\text{B}_2]\text{X}$ , when  $\text{A}_2$  or  $\text{B}_2$  is displaced by an acid group. In the present paper the preparation of stereoisomeric salts, in which this is not the case, is described. These compounds,  $[\text{Co en}_2(\text{NH}_3)_2]\text{X}_3$  ( $\text{En}$  = ethylenediamine), are represented by space formulæ. The members of the *cis*-series, which are characterised by comparatively sparing solubility in water, are formed by the oxidation of dithiocyanodiethylenediaminecobalt salts with chlorine, whilst the *trans*-salts, which are readily soluble in water, are prepared by the action of concentrated ammonia on dinitratodiethylenediaminecobalt nitrate. The configuration of the salts is derived from the genetic relationship of the *cis*-series through the dithiocyanodiethylenediaminecobalt to the 1:2-dichlorodiethylenediaminecobalt salts of the "violeo" series.

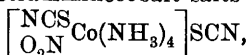
**Diethylenediamine-cis-diamminecobalt Salts.**—The *chloride*,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3\text{H}_2\text{O}$ , prepared by the action of chlorine on dithiocyanodiethylenediaminecobalt chloride in cold aqueous solution, crystallises in long, yellow, asymmetric prisms or thin needles, effloresces, and with nitric acid, hydrobromic acid, and potassium iodide in aqueous solution yields the corresponding salts as glistening, yellow, crystalline powders. Its aqueous solution forms crystalline precipitates also with potassium platinichloride, hydrogen platinichloride, auric chloride, mercuric chloride, and stannous chloride; the *bromide*,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Br}_3$ , crystallises in long, flat prisms; the *iodide*, *nitrate*, *thiocyanate*, *dichromate*, and *mercurichloride*,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3\cdot 5\text{HgCl}_2$ , are described.

**Diethylenediamine-trans-diamminecobalt Salts.**—When heated on the water-bath with nitric acid, D 1.4, 1:2-dinitritodiethylenediaminecobalt nitrate is converted into *dinitratodiethylenediaminecobalt nitrate*,  $[\text{Co en}_2(\text{NO}_3)_2]\text{NO}_3$ , which is obtained in dark red, triclinic crystals, and reacts with liquid ammonia or ammonia in concentrated aqueous solution, forming *diethylenediamine-trans-diamminecobalt nitrate* together with a small amount of the *cis*-salt. The *trans*-nitrate is obtained as a red, viscid syrup, which is soluble in water, and on addition of potassium iodide yields the *iodide*,  $[\text{Co en}_2(\text{NH}_3)_2]\text{I}_3$ ; this

separates from hot water in small, orange-yellow crystals or strongly refracting, rhombic plates.

The *bromide*,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Br}_3$ ; *cobaltchloride*,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3, \text{CoCl}_2$ ; *platinichloride*,  $[\text{Co en}_2(\text{NH}_3)_2]_3\text{PtCl}_6, 12\text{H}_2\text{O}$ , and *aurichloride*, which is a mixture of  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}, 2\text{AuCl}_4$  and  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_2, \text{AuCl}_4$ , are prepared from the iodide by the successive action of silver oxide or nitrate and hydrobromic acid or metallic chloride. G. Y.

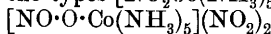
**Structurally Isomeric Thiocyanates and Nitrites.** ALFRED WERNER (*Ber.*, 1907, 40, 765—788).—This research is a contribution to the isomerism of inorganic compounds ("Salzisomerie"). Basing his experiments on the fact that thiocyanic acid forms two series of isomeric compounds of the types  $\text{N}:\text{C}:\text{S} \cdot \text{C}_n\text{H}_{2n+1}$  and  $\text{S}:\text{C}:\text{N} \cdot \text{C}_n\text{H}_{2n+1}$ , the author had previously shown, conjointly with Bräunlich (*Abstr.*, 1900, i, 86), that two isomeric dithiocyanodiethylenediaminecobaltisalts of the types  $[(\text{SCN})_2\text{Co en}_2]\text{X}$  and  $[(\text{NCS})_2\text{Co en}_2]\text{X}$  exist; the structural difference between them is shown by their behaviour on oxidation. In continuation of the work of Werner and Klien (*loc. cit.*) on thiocyanonitrotetramminecobalt salts of the type



the corresponding *isothiocyano*-[thiocarbimide]-compounds are now described, so that the following *isothiocyano*-types are now known in the cobalt series:  $[\text{NCSCo}(\text{NH}_3)_5]\text{X}_2$ ,  $\left[ \begin{array}{c} \text{SCN} \\ \text{H}_2\text{O} \end{array} \text{Co}(\text{NH}_3)_4 \right] \text{X}_2$ ,  $\left[ \begin{array}{c} \text{SCN} \\ \text{O}_2\text{N} \end{array} \text{Co}(\text{NH}_3)_4 \right] \text{X}$ ,  $[(\text{SCN})_2\text{Co en}_2]\text{X}$ , and  $[(\text{SCN})_2\text{Co pn}_2]\text{X}$ , whilst the following thiocyano-types are known:  $\left[ \begin{array}{c} \text{NCS} \\ \text{Cl} \end{array} \text{Co en}_2 \right] \text{X}$ ,

$\left[ \begin{array}{c} \text{O}_2\text{N} \\ \text{NCS} \end{array} \text{Co}(\text{NH}_3)_4 \right] \text{X}$ , and  $[(\text{NCS})_2\text{Co en}_2]\text{X}$ .

Since nitrous acid forms isomeric nitrites and nitro-compounds, isomeric compounds of the types  $[\text{NO}_2\text{Co}(\text{NH}_3)_5](\text{NO}_2)_2$  and

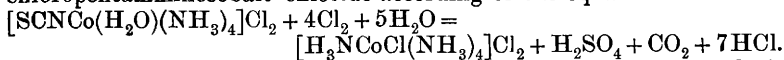


had previously been described by Jörgensen; the latter *isoxantho*-compound, however, had been somewhat imperfectly examined on account of its instability and its slight solubility. The author now places beyond doubt the fact that isomeric compounds of the types in question exist.

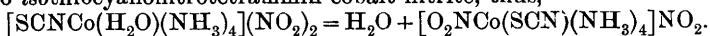
Ammonium thiocyanate was fused and cobalt oxide gradually added. After the addition, first of ammonia and then of water, the resulting red solution was decomposed with concentrated hydrochloric acid and the crude chloride acted on by dilute sulphuric acid, when *isothiocyanopentamminecobaltisulphate*,  $[\text{NCSCo}(\text{NH}_3)_5]\text{SO}_4, 2\text{H}_2\text{O}$ , separates; it crystallises from dilute acetic acid in glistening, yellowish-red leaflets, which, when dehydrated, are transformed into a yellow powder. The

chocolate-coloured powder and on remaining at the ordinary tempera-

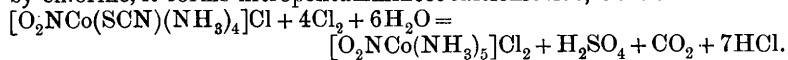
mixture of ammonium thiocyanate and diaquotetramminecobalt sulphate,  $[(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_4]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , is heated with dilute acetic acid and potassium bromide added to the filtrate. Since the bromide could not be obtained pure, the crude product was acted on by concentrated hydrochloric acid, when *isothiocyanatodiaquotetramminecobalt chloride*,  $[\text{SCNCo}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$ , separates as a brick-red precipitate; its aqueous solution is red, and, when acted on by chlorine, forms chloropentamminecobalt chloride according to the equation



The *nitrate* forms dark red, glistening crystals. The *nitrite* is a dark brownish-red, crystalline powder, and, for the preparation of salts of the type  $[\text{O}_2\text{NCo}(\text{SCN})(\text{NH}_3)_4]\text{X}$ , is converted by heating at  $70-80^\circ$  into *isothiocyanonitrotetramminecobalt nitrite*, thus,

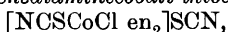


By the addition of potassium bromide to the latter compound, *isothiocyanonitrotetramminecobaltibromide*,  $[\text{O}_2\text{NCo}(\text{SCN})(\text{NH}_3)_4]\text{Br} \cdot \text{H}_2\text{O}$ , is formed; it crystallises in yellowish-brown needles. When oxidised by chlorine, it forms nitropentamminecobaltchloride, thus:



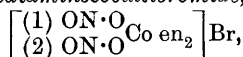
The *nitrate*,  $[\text{O}_2\text{NCo}(\text{SCN})(\text{NH}_3)_4]\text{NO}_3 \cdot \text{H}_2\text{O}$ , is a flesh-coloured, microcrystalline powder. The *iodide* forms a dark flesh-coloured microcrystalline aggregate.

*Chlorothiocyanodiethylenediaminecobalt thiocyanate*,



obtained from potassium thiocyanate and dichlorodiethylenediaminecobalt chloride, forms reddish-violet crystals. The *iodide* forms glistening, reddish-violet leaflets. The *dichromate* forms chocolate-coloured leaflets.

1 : 2-Dinitrodiethylenediaminecobaltibromide,



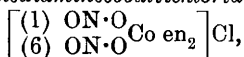
prepared by the addition of sodium nitrite to an aqueous solution of 1 : 2-diaquodiethylenediaminecobaltibromide containing a little acetic acid, is sparingly soluble in water, forming a brownish-orange solution, which, when heated, becomes yellow. After several hours at the ordinary temperature, the brownish-red tint of the dry salt becomes a yellowish-brown, owing to the formation of 1 : 2-dinitrodiethylenediaminecobalt bromide,  $\left[ \begin{array}{l} (1) \text{ O}_2\text{N} \\ (2) \text{ O}_2\text{N} \end{array} \text{Co en}_2 \right] \text{Br}$ . The transformation is

complete when the nitrito-compound is heated at  $80^\circ$  for two hours. The two isomerides differ in their behaviour towards ammonium sulphate. Whilst the addition of ammonium sulphate to a solution of the nitro-bromide causes an immediate precipitation of the sparingly soluble flavo-sulphate, no precipitate is obtained with the nitrito-bromide. The nitrito-compound evolves nitrous fumes when acidified by hydrochloric acid.

The corresponding *nitrate* forms reddish-brown crystals and is readily converted into the isomeric nitro-compound on remaining at the ordinary temperature. The *iodide* forms a microcrystalline,

chocolate-coloured powder and, on remaining at the ordinary temperature, is converted into the chamois-brown isomeride. The *dithionate* forms glistening, silky, brown needles and on remaining at the ordinary temperature is converted into the brownish-yellow isomeride.

1 : 6-Dinitritodiethylenediaminecobaltichloride,

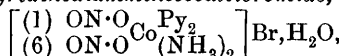


obtained by the action of sodium nitrite on 1 : 6-diaquodiethylenediaminecobaltichloride, forms yellowish-red crystals, which evolve nitrous fumes when acidified by mineral acids. With hydrochloric acid, it forms 1 : 6-diaquodiethylenediaminecobalt chloride. After forty-eight hours at the ordinary temperature, the salt is transformed into the isomeric croceo-chloride,  $\left[ \begin{array}{c} (1) \text{ O}_2\text{N} \\ (6) \text{ O}_2\text{N} \end{array} \text{Co en}_2 \right] \text{Cl}$ , which is only slowly attacked by cold hydrochloric acid and with warm hydrochloric acid is converted into 1 : 6-chloronitrodiethylenediaminecobalt chloride.

The corresponding *bromide* contains  $1\text{H}_2\text{O}$  and forms yellowish-red needles, which, after some hours at the ordinary temperature or more quickly at  $60^\circ$ , are converted into the yellow nitro-compound. The isomerides differ in their behaviour towards hydrochloric acid, the former yielding 1 : 6-diaquodiethylenediaminecobalt chloride and nitrous acid, whilst the latter, when warmed with concentrated hydrochloric acid, gives the red coloration characteristic of croceo-salts, and forms 1 : 6-chloronitrodiethylenediaminecobalt chloride, thus:  $[(\text{O}_2\text{N})_2\text{Co en}_2]\text{Br} + 2\text{HCl} = [\text{O}_2\text{NCoCl en}_2]\text{Cl} + \text{HNO}_2 + \text{HBr}$ .

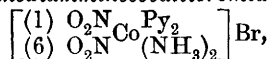
The *iodide* forms brownish-red needles which are readily transformed into the yellow isomeride. The *nitrate* forms dark brownish-red crystals, and at  $110^\circ$  is readily converted into the croceo-salt. The *dithionate* forms brick-red needles. The *thiocyanate* forms glistening, reddish-yellow crystals, which are very readily transformed into a yellow powder.

1 : 6-Dinitritodipyridinediamminecobaltibromide,

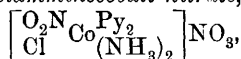


obtained by the action of sodium nitrite on an aqueous solution of hydroxoquodipyridinediamminecobalt chloride containing the requisite amount of acetic acid, forms glistening, copper-coloured leaflets. Nitrous acid is evolved by the action of hydrochloric acid. The *iodide* forms glistening, copper-coloured leaflets and, after some weeks at the ordinary temperature, is transformed into the yellow isomeride. The *nitrate* forms bronze-coloured leaflets and may be kept for weeks at the ordinary temperature without undergoing change. After six weeks, however, the transformation into the yellowish-orange isomeride is complete. The *dithionate* contains  $4\text{H}_2\text{O}$  and forms glistening, yellowish-red crystals and, after some weeks at the ordinary temperature, is converted into the yellow isomeride. The *thiocyanate* forms silvery, reddish leaflets and appears to be the most stable of the dinitrito-compounds studied, since no alteration of its tint was detected.

## 1 : 6-Dinitrodipyridinediamminecobaltibromide,



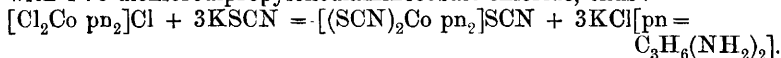
prepared by heating the preceding dinitrito-compound at  $60^\circ$ , separates from dilute acetic acid in yellow needles and is more sparingly soluble in water than the dinitrito-compound. The *nitrate* crystallises from water in brownish-yellow prisms. The *dithionate* contains  $2\text{H}_2\text{O}$  and is a yellow powder.

*Chloronitrodipyridinediamminecobalt nitrate*,

obtained by the action of hydrochloric acid on dinitrodipyridinediamminecobalt bromide, forms a bluish-red, crystalline powder.

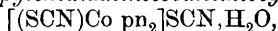
A. McK.

**Disothiocyanodipropylenediamine- and Dipropylenediamine-diammine-cobalti-salts.** ALFRED WERNER and K. DAWE (*Ber.*, 1907, 40, 789—799. Compare preceding abstract).—The *isothiocyano*-compounds described were obtained by heating potassium thiocyanate with 1 : 6-dichlorodipropylenediaminecobalt chloride, thus :



The product of this action is homogeneous and, from its behaviour on oxidation with chlorine, is *disothiocyanodipropylenediaminecobalt thiocyanate*. This result is contrasted with the formation of two isomerides, thiocyano- and *isothiocyano*-compounds, as products of the action of potassium thiocyanate on dichlorodiethylenediaminecobalt chloride.

If a current of chlorine be passed into solutions of the *isothiocyano*-salts described, oxidation occurs with the formation of dipropylene diaminediamminecobalti-salts of the type  $[(\text{H}_3\text{N})_2\text{Co pn}_2]\text{X}_3$ , a proof that the compounds in question are *isothiocyano*-salts.

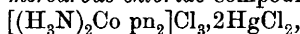
*Düisothiocyanodipropylenediaminecobaltithiocyanate*,

forms tetragonal prisms. The *chloride* forms red, hexagonal prisms and contains  $1\text{H}_2\text{O}$ . The *bromide* has  $1\frac{1}{2}\text{H}_2\text{O}$  and separates from water in rhombic prisms ; it effloresces on exposure to air. The *iodide* has  $1\frac{1}{2}\text{H}_2\text{O}$  and forms brownish-red crystals. The *antimony tetrachloride* compound,  $[(\text{SCN})_2\text{Co pn}_2]\text{SbCl}_4$ , separates in blood-red, glistening, spear-shaped crystals.

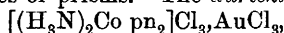
*Dipropylenediaminediamminecobaltichloride*,  $[(\text{H}_3\text{N})_2\text{Co pn}_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ , separates from water in golden-yellow, hexagonal prisms. The *bromide*, prepared by the addition of hydrobromic acid to the chloride, has  $1\text{H}_2\text{O}$  and separates in golden-yellow needles. When potassium iodide is added to an aqueous solution of the chloride, two isomeric *iodides*,  $[(\text{H}_3\text{N})_2\text{Co pn}_2]\text{I}_3 \cdot \text{H}_2\text{O}$ , are formed ; the more sparingly soluble of the two forms dark orange-red, brittle crystals, whilst the crop, which separates from the mother liquor, crystallises in needles of a yellower tint than that of the isomeride. No other isomerides in this series have been observed. The *nitrate* forms straw-yellow leaflets. The *dichromate* forms reddish-yellow needles. The *dithionate* crystal-



lises in orange-coloured leaflets. The *cobalt chloride* compound,  $[(\text{H}_3\text{N})_2\text{Co pn}_2]\text{Cl}_3 \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , forms bright green leaflets or scales, sometimes stellate crystals and prismatic needles. The *stannous chloride* compound,  $[(\text{H}_3\text{N})_2\text{Co pn}_2]\text{Cl}_3 \cdot 2\text{SnCl}_2$ , forms glistening, yellowish-red crystals. The *mercurous chloride* compound,



forms iridescent needles or prisms. The *aurichloride*,



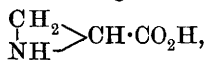
forms golden-yellow needles.

A. McK.

**Two New Methods of Formation of *iso*Serine.** CARL NEUBERG and PAUL MAYER (*Biochem. Zeitsch.*, 1907, 3, 116—120. Compare Abstr., 1904, i, 220, 230; 1906, i, 937).—*iso*Serine is formed by the action of a 50% solution of hydrogen cyanide on a solution of aminoacetaldehyde hydrochloride (Fischer, Abstr., 1893, i, 187, 300) made alkaline with ammonium hydroxide.

The same product may be obtained by the action of ammonia and ammonium carbonate on  $\alpha$ -bromo- $\beta$ -hydroxypropionic acid (Beckurts and Otto, Abstr., 1885, 506) at 100° under pressure. The formation of *isoserine* ( $\beta$ -amino- $\alpha$ -hydroxypropionic acid) and not serine ( $\alpha$ -amino- $\beta$ -hydroxypropionic acid) is probably due to the intermediate formation

of a cyclic compound, for example,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{O} \end{array} \text{CH} \cdot \text{CO}_2\text{H}$  or



and the subsequent addition of ammonia or water.

J. J. S.

### Synthesis of Polypeptides. XVI. Derivatives of *d*-Alanine.

EMIL FISCHER and ARNOLD SCHULZE (*Ber.*, 1907, 40, 943—954).—Glycyl-*d*-alanine has been synthesised in order to determine whether it is identical with one of the hydrolytic products of silk fibroin (Fischer and Abderhalden, Abstr., 1906, i, 326). The synthetical product yields an anhydride which is identical with the anhydro-compound from silk.

*Chloroacetyl-d-alanine*,  $\text{C}_3\text{H}_5\text{O}_3\text{NCl}$ , obtained by the action of chloroacetyl chloride on *d*-alanine in the presence of *N*-sodium hydroxide solution at low temperatures, separates from ethyl acetate in large colourless plates, m. p. 93·5—94·5° (corr.). With ammonia it yields *glycyl-d-alanine*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , which crystallises from a mixture of alcohol and water in long needles, m. p. about 233° (decomp.) after changing colour at 218°;  $[\alpha]_D^{20} - 50^\circ$ . It is completely hydrolysed when heated in a sealed tube in a boiling water-bath for seven hours with 10% hydrochloric acid. When converted into the hydrochloride of its ester and then poured into strongly cooled alcoholic ammonia, which was saturated at 0°, it yields the anhydride (Fischer and Abderhalden, *loc. cit.*). This has  $[\alpha]_D^{20} - 5 \cdot 0^\circ$ , and is more readily prepared by the action of ammonia on the ethyl ester of chloroacetyl-*d*-alanine.

*d*- $\alpha$ -Bromopropionic acid, obtained by the action of bromine and nitric oxide on *d*-alanine, has  $[\alpha]_D + 40 \cdot 28^\circ$ . The chloride of the acid

condenses with *d*-alanine in the presence of sodium hydroxide, yielding *d*-bromopropionyl-*d*-alanine,  $C_6H_{10}O_3NBr$ , which crystallises from water or alcohol in well-developed octahedral crystals, m. p.  $175^\circ$  (corr.) (decomp.),  $[\alpha]_D^{21} - 16.5^\circ$ . The corresponding compound obtained from inactive  $\alpha$ -bromopropionic acid, *dl*- $\alpha$ -bromopropionyl-*d*-alanine, is somewhat sparingly soluble in water, but readily in methyl alcohol. It has no definite m. p.; when heated quickly, it begins to sinter at  $170^\circ$  (corr.) and melts and decomposes at  $173$ – $174^\circ$ . The methyl-alcoholic solution has  $[\alpha]_D^{20} - 26.5$  and the aqueous solution  $[\alpha]_D^{23} - 42.4$ . It is impossible to separate the two components, namely, *d*-bromopropionyl-*d*-alanine and *l*-bromopropionyl-*d*-alanine, which appear to be present in equal amounts. The product, however, is not necessarily a definite compound of the two. *d*-Alanyl-*d*-alanine can be readily isolated from the product obtained by the action of ammonia on the mixed bromo-derivatives.

A discussion on the meaning of the expression "partially racemic" is contained in the paper. J. J. S.

**Influence of Temperature and Concentration on the Rotatory Power of Aqueous Solutions of Certain Alkyl Hydrogen Aspartates.** ARNALDO PIUTTI and GENNARO MAGLI (*Gazzetta*, 1906, 36, ii, 738–781).—The alkyl hydrogen aspartates examined by the authors were the methyl, ethyl, allyl, propyl, *isopropyl*, butyl, *isobutyl*, and amyl esters, which have been prepared by F. Mastrangioli and E. Stanzani, who also carried out some of the polarimetric measurements described below. A description of the above esters is followed by curves and tables giving the rotatory powers at different temperatures of aqueous solutions of 0.4, 0.2, and 0.1-molar concentrations. The rotatory powers of the sodium salts of these esters were also determined in solutions of 0.2-molar concentration at temperatures lying between  $10^\circ$  and  $90^\circ$ .

*Methyl hydrogen aspartate*,  $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO_2Me$ , separates in shining, white plates, m. p.  $180$ – $181^\circ$  (decomp.), and dissolves in water or alcohol. Its *copper* salt,  $(C_5H_8O_4N)_2Cu$ , crystallises from water in nacreous, blue plates.

*Ethyl hydrogen aspartate*,  $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO_2Et$ , crystallises from alcohol in thin, shining plates and from water in thick plates, m. p.  $189$ – $190^\circ$ , decomposing at  $192^\circ$ . The *copper* salt,  $(C_6H_{10}O_4N)_2Cu$ ,

crystallises in laminæ.

*Allyl hydrogen aspartate*,  $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO_2 \cdot C_3H_5$ , forms yellow, acicular crystals, m. p.  $194$ – $195^\circ$ , and dissolves in water. Its *copper* derivative,  $(C_7H_{10}O_4N)_2Cu$ , crystallises in blue plates.

*Propyl hydrogen aspartate*,  $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO_2Pr^a$ , forms nacreous, white scales, m. p.  $200^\circ$ , and dissolves readily in water and sparingly in alcohol. The *copper* salt,  $(C_7H_{12}O_4N)_2Cu$ , was prepared and analysed.

*isoPropyl hydrogen aspartate*,  $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO_2Pr^i$ , crystallises from water in long, white needles, m. p.  $209$ – $210^\circ$ , and is slightly soluble in water. The *copper* derivative,  $(C_7H_{12}O_4N)_2Cu$ , was prepared and analysed.

*Butyl hydrogen aspartate*,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$ , forms pearly, white scales, m. p. 197—198°, and dissolves readily in water and sparingly in alcohol. The *copper* salt,  $(\text{C}_8\text{H}_{14}\text{O}_4\text{N})_2\text{Cu}$ , crystallises in blue plates.

*isoButyl hydrogen aspartate*,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$ , forms white scales, m. p. 197—198°, and is readily soluble in water and slightly so in alcohol. The *copper* derivative,  $(\text{C}_8\text{H}_{14}\text{O}_4\text{N})_2\text{Cu}$ , was prepared and analysed.

*isoAmyl hydrogen aspartate*,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11}$ , crystallises in nacreous, white plates, m. p. 195—196°, and dissolves readily in water and sparingly in alcohol. The *copper* salt,  $(\text{C}_9\text{H}_{16}\text{O}_4\text{N})_2\text{Cu}$ , was prepared and analysed.

All these alkyl hydrogen aspartates are dextrorotatory at the ordinary temperature, but lævorotatory at high temperatures. The following table gives the temperatures at which the aqueous solutions of the three concentrations examined become inactive :

	Mol. Wt.	Temperature of inactivity.		
		0.4 Molar.	0.2 Molar.	0.1 Molar.
Methyl hydrogen aspartate	147	45.2°	35.5°	43.7°
Ethyl                   "                   "	161	63.3°	49.5°	63°
Allyl                   "                   "	173	67.8°	46°	40.5°
Propyl               "               "	175	75.1°	73°	64°
isoPropyl           "           "	175	87.3°	83°	59°
Butyl               "               "	189	74°	76°	78.7°
isoButyl           "           "	189	81.7°	79.5°	73°
isoAmyl           "           "	303	[77°]	91°	80.3°

The results show that the rotatory powers of the alkyl hydrogen aspartates in aqueous solutions are directly proportional to the molecular weight and to the concentration of the solution. The authors regard the change of sign of the optical activity of solutions of these esters to be due to their gradual electrolytic dissociation as the temperature is raised, the free anions being lævorotatory.

The rotatory powers of the sodium salts of these esters are negative between 10° and 90°, except in the case of sodium isopropyl aspartate, which is dextrorotatory below about 22° and lævorotatory above that temperature. As these sodium compounds are undoubtedly more highly dissociated in aqueous solution than the alkyl hydrogen esters themselves, support is lent to the view that the change in sign of the rotation is due to dissociation. T. H. P.

**New Method of Preparing Amides of Substituted Malonic and Acetoacetic Acids.** HANS MEYER (*Monatsh.*, 1907, 28, 1—5. Compare Abstr., 1906, i, 137, 358; this vol., i, 179).—Hitherto, ethylmalonamides have been prepared by way of the acid chlorides, whilst of disubstituted acetoacetamides only the dimethyl and methyl-ethyl derivatives are formed by the action of aqueous ammonia on the esters. The author has found that monosubstituted acetoacetamides, which are formed readily by the action of ammonia on the esters, can

be alkylated by boiling with the sodium alkyl oxide and alkyl iodide. Ethylmalonamide also can be prepared in this manner in good yields from malonamide.

*Diethylacetoacetamide*,  $C_8H_{15}O_2N$ , prepared in an 80% yield from ethylacetoacetamide, crystallises in long needles, m. p. 122—123°.

*Methylpropylacetoacetamide*,  $C_8H_{15}O_2N$ , m. p. 125°, obtained in a 70% yield from methylacetoacetamide, crystallises from water.

Ammonia reacts more easily with methyl- than with ethyl-acetoacetate; with sodium methoxide and methyl iodide, the resulting acetoacetamide forms methyl- or, with an excess of the reagents, dimethyl-acetoacetamide. G. Y.

**Derivatives of Fulminic Acid.** F. CARLO PALAZZO and A. TAMBURELLO (*Chem. Zentr.*, 1907, i, 26—27; from *Estr. Giorn. Sci. Nat. Econ.*, 26).—Determination of the molecular weight of metafulminic or isocyanuric acid, prepared by Scholvien's method (Abstr., 1885, 39; 1886, 137) and dehydrated in a vacuum over sulphuric acid, by Raoult's freezing-point method using glacial acetic acid, gave 129.5, and correspond therefore with the formula  $(CNOH)_3$ . 0.5—1 Gram of the acid is completely dehydrated in a day, and the acid also loses water on exposure to the air. The anhydrous acid explodes at 106°. The anhydrous and the hydrated acids have the same formula, since both yield the same ester,  $C_3N_3(OMe)_3$ , when treated with a solution of diazomethane in ether at -10°. The ester, b. p. 126°/18 mm., is an almost colourless liquid and is insoluble in water or alkalis; the molecular weight determined by the freezing-point method, using glacial acetic acid, was found to be 160.7. When the hydrate of metafulminic acid is boiled with dilute sulphuric acid in a reflux apparatus for an hour, hydrocyanic and oxalic acids can be detected in the distillate, whilst the residue contains ammonia and hydroxylamine; carbon dioxide is also liberated. Hydrochloric acid acts in the same way, but less hydrocyanic acid is formed; when metafulminic acid is heated, however, with either acid at 130—140°, hydrocyanic acid is not formed, but carbon dioxide is evolved. The behaviour of metafulminic acid shows, therefore, that it contains three unchanged oximide groups, and an aqueous solution of sodium fulminate gives the characteristic coloration of hydroxamic acids with ferric chloride.

By the action of methyl sulphate on sodium fulminate the ester,  $OMe \cdot N : C \begin{smallmatrix} \swarrow C : N \cdot OMe \\ \searrow C : N \cdot OMe \end{smallmatrix}$ , m. p. 149°, is obtained; it forms slender, white needles. By the action of benzoyl chloride on the fulminate a compound, m. p. 138°, is formed. The formula of the hydrate of metafulminic acid is probably  $OH \cdot N \begin{smallmatrix} \swarrow CH(OH) \cdot N(OH) \\ \searrow CH(OH) \cdot N(OH) \end{smallmatrix} CH \cdot OH$ .

E. W. W.

**Cyanuric Derivatives.** HERMANN FINGER (*J. pr. Chem.*, 1907, [ii], 75, 103—104).—A preliminary communication.

*Cyanuric trihydrazide*,  $C_3N_3(NH \cdot NH_2)_3$ , is obtained by acting on cyanuric chloride dissolved in cyanomethane with hydrazine hydrate;

it reacts with aldehydes, isatin and ethyl acetoacetate, forming condensation products; its hydrochloride is converted by sodium nitrite into a substance which explodes on heating and is converted by sodium hydroxide into what is probably *cyanuric triazide*,  $C_3N_{12}$ . Cyanuric chloride dissolved in acetone reacts with silver nitrate with the probable formation of *trinitrocyanidine*,  $C_3N_3(NO_2)_3$ . W. H. G.

**Cyanogen, Hydrogen Cyanide, and Acetylene Equilibria.** H. VON WARTENBERG (*Zeit. anorg. Chem.*, 1907, 52, 299—315. Compare Wallis, Abstr., 1906, i, 730).—The experiments have been made chiefly with the object of testing Nernst's equations connecting chemical equilibrium and temperature.

It has been calculated that nitrogen at atmospheric pressure and carbon should be in equilibrium with 44% of cyanogen at  $3500^\circ$ , but, although the spectrum of the latter gas is very prominent in the electric arc, the author finds, in agreement with Wallis (*loc. cit.*), that no cyanogen, but only hydrogen cyanide, can be detected in the gases drawn from the arc chamber. This result may be due partly to the carbon particles in the flame exerting a catalytic action on the decomposition of cyanogen and partly to combination of the latter with hydrogen, which cannot readily be removed from graphite.

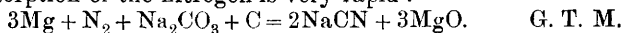
The equilibrium in the reaction  $2C + H_2 + N_2 = 2HCN$ ,  $-59,700$  cal., has been investigated by passing a dry mixture of equal volumes of the gases over a glowing carbon rod in a special apparatus and analysing the resulting gases. At  $1875^\circ$ ,  $1752^\circ$ , and  $1635^\circ$ , the equilibrium concentration of hydrogen cyanide amounts to 4.7, 3.1, and 1.95% respectively, in satisfactory agreement with Nernst's formula.

Corresponding experiments on the formation of acetylene from hydrogen and carbon were carried out in the same apparatus, but as very high temperatures could not be used owing to destruction of the carbon rods, and the reaction is very slow at lower temperatures, the results are only of a preliminary nature. At  $1824^\circ$  the corrected value gives 0.13% of acetylene, whilst Nernst's equation, allowing for the difference of the specific heats of acetylene and hydrogen, gives a considerably higher value; the discrepancy may be due to decomposition of the acetylene as the temperature falls.

The work of Pring and Hutton (*Trans.*, 1906, 89, 1591) on this subject is criticised. G. S.

**Preparation of Alkali Cyanides.** O. SCHMIDT (D.R.-P. 176080).—The nitrides of calcium and magnesium and other allied metals, when heated to redness with carbon and an alkali carbonate, are readily transformed into alkali cyanides. The access of air must be avoided; the reaction when started is exothermic and the best results are obtained when the proportions correspond with the following equation:  $Mg_2N_2 + Na_2CO_3 + C = 2NaCN + 3MgO$ .

It is, however, unnecessary to isolate the nitride; the formation of cyanide takes place in one operation when nitrogen is passed over a mixture of magnesium, sodium carbonate, and carbon heated to redness, and the absorption of the nitrogen is very rapid:



**Alkylation of the Metallic Cyanides.** H. GUILLEMARD (*Compt. rend.*, 1907, **144**, 326—328).—The author has studied the effect of temperature and duration of reaction on the proportions of nitrile and carbylamine obtained by the action of alkylating agents on various metallic cyanides. The quantities of the two isomerides in the reaction product were estimated by the method previously described (this vol., ii, 141). The general conclusion drawn is that the cyanides on alkylation at a low temperature give carbylamines, at a higher temperature a mixture of carbylamine and nitrile, and above a certain temperature nitrile only. This supports Nef's hypothesis that the cyanides correspond with the formula  $MNC$ , at least at low temperatures. The formation of nitriles at higher temperatures can be explained by various hypotheses. (1) By an alteration in the constitution of the cyanides at high temperatures; (2) by a variation in the method of reaction of the cyanide (of fixed constitution) at high temperatures; (3) by isomeric change at high temperature of the carbylamine formed at low temperature into nitrile. The evidence is mostly in support of the last theory, the author having shown previously (this vol., i, 197) that the carbylamines, on dissociating from their compounds with the cyanides, easily change into nitriles.

E. H.

**Allyl Cyanide and Allylthiocarbimide.** CÆSAR POMERANZ (*Annalen*, 1907, **351**, 354—362).—This work was undertaken to throw light on the mechanism of the reaction by which allyl cyanide, the constitution of which as crotononitrile has been established by Lippmann (*Abstr.*, 1892, 27) and Schindler (*ibid.*, 32) is formed from allyl haloids.

In the absence of water, allyl bromide does not react with potassium cyanide in a sealed tube at  $120^{\circ}$ , but a good yield of the nitrile is obtained if a small amount of water is present. This together with the observation that propylene dicyanide, which is formed from allyl chloride and potassium cyanide in dilute alcoholic solution (Pinner, *Abstr.*, 1880, 99), yields potassium cyanide when shaken with aqueous potassium hydroxide, points to the formation of crotononitrile taking place in three stages:  $KCN + H_2O = KOH + HCN$ ;

$CH_2:CH \cdot CH_2Br + KCN + HCN = CN \cdot CHMe \cdot CH_2 \cdot CN + KBr$ ;  
 $CN \cdot CHMe \cdot CH_2 \cdot CN + KOH = CHMe:CH \cdot CN + KCN + H_2O$ . The water being reformed acts as a catalyst. The hydrolysis of crotononitrile with 25% sulphuric acid leads to the formation of isocrotonic acid.

As natural mustard oil contains allyl cyanide, and according to Will and Körner this substance is formed by the action of water on the oil (*Annalen*, 1863, **125**, 273), it seemed probable that the synthetical thiocarbimide might be a mixture of the allyl and propenyl compounds. On oxidation with sodium dichromate and sulphuric acid, it yields formic acid and small amounts of acetic acid which can be formed only from the propenylthiocarbimide. As propenyl compounds boil at higher temperatures than the corresponding allyl derivatives, it is probable that most of the propenyl thiocarbimide formed in the preparation of allylthiocarbimide, is removed in the fractions of higher boiling point.

G. Y.

**Ethyl Oxalylbishydrazoneacetoacetate.** **Decomposition Products of Esters of  $\beta$ -Ketonic Acid Acylhydrazones.** CARL BÜLOW and MARTIN LOBECK (*Ber.*, 1907, 40, 708—719).—*Ethyl oxalylbishydrazoneacetoacetate*,  $C_2O_2(NH \cdot N : CMe \cdot CH_2 \cdot CO_2Et)_2$ , m. p.  $133.5^\circ$ , obtained from oxalylhydrazide and ethyl acetoacetate in 89% yield, forms colourless needles, and reduces silver, gold, and copper salts. When heated at  $187^\circ$ , it decomposes into alcohol, ethyl acetoacetate, a substance,  $C_3H_8O_2N_2$ , m. p.  $247^\circ$ , and a substance, m. p.  $>290^\circ$ , which is insoluble in alcohol. The former is identical with the compound obtained by Rosengarten (*Abstr.*, 1894, i, 546) from hydrazine and ethyl acetylacetoacetate, and is also obtained from 3-methylpyrazolone and ethyl acetoacetate at  $150^\circ$ . The substance, m. p.  $>290^\circ$ , is probably *cyclooxalylhydrazide*,  $\begin{matrix} CO \cdot NH \\ | \\ CO \cdot NH \end{matrix}$ , since the only

products of hydrolysis are hydrazine and oxalic acid. The following reagents decompose ethyl oxalylbishydrazoneacetoacetate: boiling water yields ethyl acetoacetate and oxalylhydrazide; boiling 6% sodium acetate yields ethyl acetoacetate, oxalic acid, hydrazine, and 3-methylpyrazolone, thus disproving Curtius's statement that ethyl acetoacetate-acylhydrazones cannot be transformed into pyrazolone derivatives (*Abstr.*, 1895, i, 32); phenylhydrazine yields oxalylhydrazide and phenylmethylpyrazolone; potassium hydroxide yields methylpyrazolone; boiling acetic anhydride yields *diacetyloxalylhydrazide*,  $C_6H_{10}O_4N_4 \cdot 2H_2O$ , m. p.  $273^\circ$  (decomp.); boiling dilute sulphuric acid causes profound decomposition and hydrazine sulphate is isolated; benzaldehyde and boiling water yield dibenzaldehydeoxalyl dihydrazone; concentrated sulphuric acid and resorcinol produce  $\beta$ -methylumbelliferone and oxalylhydrazide.

C. S.

**Abnormal Metallic Salts of Hydroxyamidines and Allied Compounds.** **Theory of Internally Complex Metallic Salts.** HEINRICH LEY and P. KRAFFT (*Ber.*, 1907, 40, 697—707. Compare *Abstr.*, 1901, i, 759; 1902, i, 445; 1903, i, 282).—In attempting to account for the abnormal colour of the copper, nickel and cobalt salts of substituted hydroxyformamidines of the type  $R_1 \cdot N \cdot CR \cdot NR \cdot OH$ , attention must be given to the following points: (1) the salts are normal and have the metal attached to oxygen (compare *Abstr.*, 1905, i, 175); (2) they have the same colour in solution as in the solid state; (3) they retain the basic character of the parent hydroxyformamidine; (4) they have normal molecular weights in chloroform; (5) potassium hydroxide does not precipitate the metallic hydroxide; (6) azohydroxyamides, hydroxyamidoximes, and hydroxyguanidines, which form similar abnormally coloured salts, all contain the group  $N : X \cdot N \cdot OH$ .

The behaviour of these salts recalls that of internally complex metallic salts (compare Schiff, *Abstr.*, 1898, i, 243; Bruni and Fornara, *Abstr.*, 1904, i, 855). If the assumption is made that, in the salts of amino-acids, the metal, attached to oxygen, is also bound by residual affinity to the aminic nitrogen atom, a parallelism can be drawn between the abnormally coloured metallic salts of amino-acids and the metal-ammonia compounds. The salts of hydroxyformamidines

would thus be formulated,  $R \cdot C \begin{smallmatrix} \nwarrow NR \\ \nearrow NR \end{smallmatrix} O \cdot M$ . (For change of colour in complex salt formation, compare Tschugaeff, Abstr., 1905, i, 865.) Abnormal light absorption seems to be connected with the presence of the metal in the group  $\cdot NH \cdot OM$  containing a singly-linked nitrogen atom, for benzenylamidoxime,  $OH \cdot N : CPh \cdot NH_2$ , and benzenylpiperidylxime,  $C_5NH_{10} \cdot CPh \cdot N \cdot OH$ , do not yield abnormal copper salts.

**3-Hydroxy-1-phenyl-3-benzylformamidine**,  $NPh : CH \cdot N(OH) \cdot CH_2Ph$ , m. p.  $165^\circ$  (decomp.), is obtained from  $\beta$ -benzylhydroxylamine and ethylisoformanilide in absolute alcohol. It forms large, colourless, rhombic plates and exhibits feeble acid properties; the stable *hydrochloride* has m. p.  $185-187^\circ$  (decomp.). The *copper salt*,  $(C_{14}H_{13}ON_2)_2Cu$ , precipitated from an alcoholic solution of the hydroxyamidine by copper acetate, separates from toluene in reddish-brown scales; hydrogen chloride precipitates from its chloroform solution the *hydrochloride*,  $(C_{14}H_{13}ON_2)_2Cu \cdot 2HCl$ , as a microcrystalline, yellow mass which turns brown in the air and is decomposed by water or dilute alcohol, regenerating the brown copper salt. The *nickel salt*,  $(C_{14}H_{13}ON_2)_2Ni$ , forms yellow leaflets, and the *cobalt salt* dark amethyst crystals. When warmed with acetic anhydride, the hydroxyamidine is transformed into the isomeric *s*-phenylbenzyl-carbamide (compare Bamberger and Destraz, Abstr., 1902, i, 538). *Benzenylpiperidylxime*, m. p.  $136-137^\circ$ , forms long, glistening needles. C. S.

**Abnormally Coloured Complex Metallic Salts of Acid Imides.** HEINRICH LEY and F. WERNER (*Ber.*, 1907, 40, 705-707. Compare Abstr., 1906, i, 561; preceding abstract.).—In support of the theory that abnormal light absorption is exhibited by complex metallic salts in which the metal and nitrogen are united by residual affinities, the authors show that the copper salts of succinimide, camphorimide, phthalimide, and dibenzamide are blue, whilst under definite conditions complex salts of the type  $[(RN)_2Cu(NR)_2]K_2$  (where  $NR = \text{acid imide}$ ) are obtained which exhibit abnormal colour.

Potassium copper camphorimide has been described (*loc. cit.*).

*Potassium copper phthalimide*,  $(C_8H_4O_2N)_4CuK_2 \cdot 4H_2O$ , is obtained as a reddish-violet precipitate by adding aqueous copper acetate slowly to aqueous potassium phthalimide. Copper dimethylmaleimide forms sky-blue crystals, whilst the complex sodium copper compound is violet-red. C. S.

**Tetramethylarsonium Iodide and its Pharmacological Action.** EMIL BÜRG (Chem. Zentr., 1907, i, 152; from *Arch. exp. Path. Pharm.*, 56, 101-114).—Tetramethylarsonium iodide,  $AsMe_4I$ , prepared by heating arsenic with methyl iodide at  $220^\circ$  for twenty-four hours, is a white substance which slowly becomes reddish-brown when exposed to light and crystallises from methyl alcohol in tetrahedra; it gives coloured precipitates with many metallic salts.

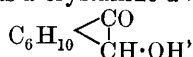
The paralytic action of tetramethylarsonium iodide on the nerve-



centres resembles that of curare; it does not affect the heart of a frog or rabbit. Since in the case of a rabbit only a small portion is decomposed, the rest passing unchanged into the urine, the specific action of arsenic is not apparent. E. W. W.

**The cycloOctane Series. II.** RICHARD WILLSTÄTTER and HANS VERAGUTH (*Ber.*, 1907, 40, 957—970. Compare Abstr., 1905, i, 515).—The *cyclooctadiene* previously described readily yields a *dihydrobromide*, and the readiness with which the hydrocarbon polymerises is in harmony with the presence of conjugated double linkings,  $\text{CH}_2 \begin{smallmatrix} \text{CH}:\text{CH}\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} \text{CH}$ . When the hydrobromide is heated with quinoline, or solid potassium hydroxide, it yields a much more stable unsaturated hydrocarbon, termed *β-cyclooctadiene*, which is readily reduced by Sabatier and Senderens's method (Abstr., 1901, i, 195, 459) to the saturated cyclic compound *cyclooctane*,  $\text{C}_8\text{H}_{16}$ . The presence of an eight-member ring in these compounds is confirmed by the fact that, when oxidised with nitric acid, the saturated hydrocarbon gives a good yield of suberic acid.

In the preparation of the dihydrobromide a certain amount of a *monohydrobromide*,  $\text{C}_8\text{H}_{13}\text{Br}$ , is formed; this can be separated by fractional distillation, and when heated with quinoline yields a *dicyclooctene*,  $\text{C}_8\text{H}_{12}$ . The position of the bridge in this compound has not been established. It is highly probable that a bridged compound is present in the original *α-cyclooctadiene*, as the proportions of mono- and dihydrobromide are always as 1 : 6. *dicycloOctene*, when oxidised with permanganate, yields a crystalline *α-hydroxyketone*,



which, on further oxidation with chromic acid, yields an acid.

*α-cycloOctadiene dihydrobromide*,  $\text{C}_8\text{H}_{14}\text{Br}_2$ , obtained by means of an acetic acid solution of hydrogen bromide, is a colourless, viscid oil with a sweet odour and b. p.  $150-151^\circ/12.5$  mm. (corr.),  $D_4^{20}$  1.662. On exposure to the air it turns to a pink colour, and finally to a dark steel-blue with a reddish-violet fluorescence.

A small amount of a *tetrabromocyclooctane*,  $\text{C}_8\text{H}_{12}\text{Br}_4$ , has been prepared by the action of excess of bromine on the dihydrobromide in presence of iodine or iron. It crystallises in pointed prisms, m. p.  $132.5^\circ$ .

*β-cycloOctadiene* is a colourless, mobile liquid, b. p.  $143-144^\circ$ , and  $D_4^{20}$  0.887. It has an odour of tropilidene and gives an intense orange coloration with concentrated sulphuric acid.

Small amounts of naphthalene are formed when the dihydrobromide is heated with quinoline at a high temperature, and the same hydrocarbon is produced when *o*-xylylene bromide is heated at  $260-270^\circ$  with quinoline, whereas when *o*-xylylene bromide is heated with potassium hydroxide *o*-xylylene oxide,



is formed. This is a colourless, highly refractive oil, b. p.  $192^\circ$  (corr.),  $D_4^{20}$  1.098, and has an odour of bitter almonds.

The *hydrobromide* of *dicyclooctene*,  $C_8H_{18}Br$ , is a clear, viscid liquid, b. p.  $92.5-93^\circ/15$  mm.,  $D_4^0$  1.330, and has a sweet odour. It is stable towards permanganate, but in contact with the air yields black products. *dicycloOctene*,  $C_8H_{12}$ , is a colourless, mobile liquid of high refractive power, b. p.  $137.5-139^\circ$  (corr.),  $D_4^0$  0.9097, and has an odour of tropilidene.

The *hydroxy-ketone*,  $C_8H_{12}O_2$ , crystallises in needles, m. p.  $65-65.5^\circ$ , and yields a *semicarbazone* which decomposes at  $251^\circ$ .

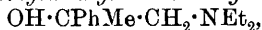
*cycloOctane* is a colourless liquid with an odour resembling camphor, b. p.  $146.3-148^\circ$ ,  $D_4^0$  0.849, and  $D_4^{20}$  0.833, and when cooled solidifies. A slightly impure fraction, b. p.  $145.3-146.3^\circ$ ,  $D_4^0$  0.850,  $D_4^{20}$  0.835, was also obtained, but would not solidify. J. J. S.

**Benzene Hydrocarbons containing a  $\psi$ -Allyl Side Chain; Methoethenylbenzene [ $\beta$ -Allylbenzene] and its Homologues. Study of some Molecular Migrations. Part I. Benzene Hydrocarbons containing a  $\psi$ -Allyl Side Chain.** MAX TIFFENEAU (*Ann. Chim. Phys.*, 1907, [viii], 10, 145-198).—A detailed account of the preparation, properties, and derivatives of hydrocarbons of the type  $R \cdot CMe : CH_2$ , where R denotes the phenyl or *o*-, *m*-, or *p*-tolyl group. The hydrocarbons, prepared by dehydrating the corresponding dimethylcarbinol,  $R \cdot CMe_2 \cdot OH$ , are reduced by the action of sodium and alcohol to the hydrocarbon  $R \cdot CHMe_2$ , or directly by hydrogen in the presence of nickel to form the completely saturated hydrocarbon; they are oxidised directly by oxygen to form trioxymethylene and the corresponding ketone,  $R \cdot COMe$ , which is also the chief product when permanganate is the oxidising agent employed; they react with chlorine or bromine to form the saturated derivatives,  $R \cdot CMeX \cdot CH_2X$  (where X denotes Cl or Br), which, on treatment with alcoholic potash, yield the monohalogen derivatives,  $R \cdot CMe : CHX$ . These hydrocarbons furnish halohydrins of the type  $R \cdot CMe(OH) \cdot CH_2X$ , either by direct union with hypochlorous, hypobromous, or hypoiodous acid, or more conveniently by the action of magnesium methyl bromide or iodide on the monohalogen derivative of acetone; the chloro- or iodo-hydrins condense with dimethyl- or diethyl-amine to form substituted carbinols of the type  $R \cdot CMe(OH) \cdot CH_2 \cdot NAr_2$  (where Ar denotes Me or Et), which yield characteristic methiodides, benzoyl or cinnamyl derivatives; the iodo-hydrins react with potassium hydroxide to form the corresponding methylene oxide,  $O < \begin{smallmatrix} CRMe \\ | \\ CH_2 \end{smallmatrix}$ , and when treated with

silver nitrate lose hydrogen iodide and undergo a molecular migration with the formation of a substituted acetone according to the equation:  $R \cdot CMe(OH) \cdot CH_2I \rightarrow HI + R \cdot CH_2 \cdot COMe$ .

**$\beta$ -Allylbenzene.**—The preparation, properties, and most of the derivatives of this hydrocarbon have already been described (Abstr., 1902, i, 433, 449; 1903, i, 81; 1904, i, 63; 1905, i, 523; 1906, i, 965); the following facts are new:  $\beta$ -allylbenzene, b. p.  $161-162^\circ$ ,  $60-61^\circ/17$  mm. or  $68-69^\circ/27$  mm.,  $D^0$  0.9278 or  $D^{21}$  0.9085, yields the dimeride  $C_{18}H_{20}$  (compare Grignard, Abstr., 1901, i, 681), m. p.  $51-52^\circ$  b. p.  $163-164^\circ/14-15$  mm. or  $299-300^\circ$ , when treated with sulphuric acid, or when a slight excess of methyl iodide is used in the prepara-

tion of the hydrocarbon in which case the polymeride,  $C_{18}H_{20}$ , b. p.  $175^{\circ}/16$  mm.,  $D^0$  1.012, is also formed (compare Klages, Abstr., 1902, i, 666); the *dichloride*,  $CPhMeCl \cdot CH_2Cl$ , b. p.  $115-125^{\circ}/8$  mm., yields  $\beta$ -chloro- $\alpha$ -methylstyrene,  $CPhMe \cdot CHCl$ , b. p.  $210-215^{\circ}$  or  $102-106^{\circ}/14$  mm.; the chlorohydrin, b. p.  $124-125^{\circ}/17$  mm.,  $D^0$  1.168 yields with dimethylamine, phenylmethyldimethylaminomethylcarbinol (compare Fournau, Abstr., 1904, i, 377), and with diethylamine, phenylmethyldiethylaminomethylcarbinol,

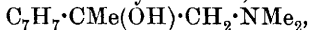


b. p.  $244-247^{\circ}$  or  $138-140^{\circ}/22$  mm., the *cinnamyl* derivative has m. p.  $190-192^{\circ}$ . The *bromohydrin*  $OH \cdot CPhMe \cdot CH_2Br$ , b. p.  $141^{\circ}/19$  mm.,  $D^0$  1.413; the *iodohydrin*, b. p.  $144-145^{\circ}/12$  mm.,  $D^0$  1.541, yields the oxide,  $O \begin{smallmatrix} \diagup CPhMe \\ \diagdown CH_2 \end{smallmatrix}$ , which has  $D^{26}$  1.024,  $n_D^{26}$  1.5161.

*o*-Methoethenyltoluene [*o*- $\beta$ -allyltoluene],  $C_7H_7 \cdot CMe \cdot CH_2$ . The starting point of this hydrocarbon is *o*-tolyl dimethylcarbinol, m. p.  $41^{\circ}$ , b. p.  $217-218^{\circ}$  or  $116^{\circ}/22$  mm., which is obtained by the action of magnesium *o*-tolyl bromide on acetone, or magnesium methyl iodide on methyl *o*-toluate. When distilled with oxalic acid, it yields *o*- $\beta$ -allyltoluene, b. p.  $168-169^{\circ}$ ,  $D^0$  0.9076, which on oxidation with permanganate forms *o*-tolyl methyl ketone, b. p.  $216^{\circ}$ , and the *iodohydrin* yields *o*-tolylacetone, b. p.  $227^{\circ}$ , the *oxime*, m. p.  $75^{\circ}$ , and the semicarbazone, m. p.  $181^{\circ}$ .

*m*-Methoethenyltoluene [*m*- $\beta$ -allyltoluene],  $C_7H_7 \cdot CMe \cdot CH_2$ , b. p.  $183-185^{\circ}$ ,  $D^0$  0.9115, yields *m*-tolyl methyl ketone on oxidation, b. p.  $218-220^{\circ}$ ,  $D^{20}$  0.989, (*oxime*, m. p.  $94^{\circ}$ ), and *m*-cymene on reduction, b. p.  $174-176^{\circ}$ ,  $D^{20}$  0.862; the *iodohydrin* reacts with silver nitrate to form *m*-tolylacetone,  $C_7H_7 \cdot CH_2 \cdot COMe$ , b. p.  $228-229^{\circ}$ ,  $D^0$  1.019; the *semicarbazide* has m. p.  $139^{\circ}$ .

*p*-Methoethenyltoluene [*p*- $\beta$ -allyltoluene],  $C_7H_7 \cdot CMe \cdot CH_2$ , is a colourless, mobile liquid with an odour of thyme, b. p.  $184-185^{\circ}$  (Errera, Abstr., 1891, 1021, gives  $198-200^{\circ}$ ),  $D^0$  0.9122; it yields *p*-cymene, b. p.  $174-176^{\circ}$ ,  $D^{15}$  0.860 on reduction, and *p*-tolyl methyl ketone (*oxime*, m. p.  $88^{\circ}$ ) on oxidation; the *dibromide* is liquid even at  $-15^{\circ}$ , and yields the *glycol*,  $C_7H_7 \cdot CMe(OH) \cdot CH_2 \cdot OH$ , m. p.  $32^{\circ}$ , when treated with barium carbonate. The *dimeride*,  $C_{20}H_{24}$ , has m. p.  $40^{\circ}$ ; the *iodohydrin* reacts with yellow mercuric oxide to form *p*-tolylacetone,  $C_7H_7 \cdot CH_2 \cdot COMe$ , b. p.  $232-233^{\circ}$ ,  $D^0$  1.007 (the *oxime* has m. p.  $90^{\circ}$  and the semicarbazone, m. p.  $158^{\circ}$ ), and with dimethylamine to form *p*-tolylmethyldimethylaminomethylcarbinol,



b. p.  $253-255^{\circ}$  or  $135-136^{\circ}/18$  mm.,  $D^0$  0.982.

M. A. W.

**Reductions with Amorphous Phosphorus. II.** THEODOR WEYL (*Ber.*, 1907, 40, 970-974. Compare this vol., i, 118).—When nitrobenzene is dropped into a boiling mixture of sodium hydroxide solution and red phosphorus, the only reduction product which can be isolated is aniline. The yield is not good, as a large amount of unaltered nitrobenzene is always found. The products formed when the

mixture of nitrobenzene, sodium hydroxide solution, and red phosphorus is heated in a reflux apparatus at 140—170°, consist of aniline, azoxybenzene, and azobenzene, in certain experiments as much as 50% of the nitrobenzene being converted into azobenzene. Calcium hydroxide and ammonium hydroxide are not so efficient as sodium and potassium hydroxides, and the substitution of 95% alcohol for water retards the reduction.

When the reacting substances are heated in sealed tubes at 100—150° the amount of reduction is small, but at 170°, with soda lime and water, some 21% of aniline and 6% of azoxybenzene are formed.

It has been found that phosphine is evolved by the action of ammonium hydroxide solution on amorphous phosphorus. J. J. S.

**Dichlorodiphenylsulphone.** FRITZ ULLMANN and JOHANNES KORSELT (*Ber.*, 1907, 40, 641—648).—Beckurt and Otto's 4:4'-dichlorodiphenylsulphone (Abstr., 1879, 243) is converted quantitatively into 4:4'-dichloro-3:3'-dinitrodiphenylsulphone,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl})_2\text{SO}_2$ , by a mixture of equal volumes of nitric acid (D 1.5) and sulphuric acid at 100°. It crystallises from glacial acetic acid in long, glistening needles, m. p. 202°. 4:4'-Dichloro-3:5:3'-trinitrodiphenylsulphone,  $\text{C}_{12}\text{H}_5\text{O}_8\text{N}_3\text{Cl}_2\text{S}$ , obtained when fuming sulphuric acid (40%  $\text{SO}_3$ ) is used at 150° for a short time, forms almost colourless needles, m. p. 220°, whilst the 3:5:3:5'-tetranitro-derivative,  $\text{C}_{12}\text{H}_4\text{O}_{10}\text{N}_4\text{Cl}_2\text{S}$ , pale yellow needles, m. p. 290°, is the product obtained when the heating is continued for two hours at 150° and 60%  $\text{SO}_3$  sulphuric acid is employed.

Alcoholic solutions of all these nitro-compounds, on being boiled with aniline, lose the two chlorine atoms and give dianilino-derivatives. 3:3'-Dinitro-4:4'-dianilinodiphenylsulphone,  $\text{C}_{24}\text{H}_{18}\text{O}_6\text{N}_4\text{S}$ , forms orange-red crystals from benzene, m. p. 260°; the corresponding trinitro- and tetranitro-compounds are also orange-red, and have m. p. 210° and 250°.

3:3'-Dinitro-4:4'-dihydroxydiphenylsulphone and its methoxy- and ethoxy-derivatives are obtained by the interaction of alcoholic sodium hydroxide, methoxide, or ethoxide, and the dinitrodichlorosulphone (Annaheim, this Journ., 1874, 795). The 3:5:3':5'-tetranitro-4:4'-dihydroxy-derivative is obtained in a similar manner (Annaheim, Abstr., 1879, 294).

3:3'-Diamino-4:4'-dianilinodiphenylsulphone,  $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_4\text{S}$ , crystallising from alcohol in colourless plates, m. p. 186°, gives a phenazonium derivative with 2 mols. of phenanthraquinone in the presence of hydrogen chloride.

When dichlorodinitrodiphenylsulphone is heated with alcoholic ammonia for four hours at 150°, yellow octahedra of 3:3'-dinitro-4:4'-diaminodiphenylsulphone,  $\text{C}_{12}\text{H}_{10}\text{O}_6\text{N}_4\text{S}$ , m. p. 309°, are formed. The tetra-amino-derivative obtained on reduction forms colourless leaflets, m. p. 174°.

Annaheim's dinitrohydroxyanilinodiphenylsulphone (this Journ., 1874, 697) is shown to be an additive compound of the dinitrodihydroxydiphenylsulphone (1 mol.) with aniline (2 mols.). W. R.

**Nature of the Carbon Double Linking II. Addition of Bromine.** HUGO BAUER and H. MOSER (*Ber.*, 1907, 40, 918—924. Compare Abstr., 1905, i, 729; 1904, i, 841).—The interaction of ethenoid compounds and bromine in solution is of the second order (compare Herz and Mylius, this vol., i, 55; Plotnikoff, Abstr., 1906, ii, 12), but the constants obtained vary, especially the first values; this is perhaps explained by the formation of perbromides. The experiments were carried out in the dark in blackened vessels, and it was found that the solvent exercised an important influence in promoting the change. With stilbene in chloroform,  $v = 200$   $t$   $29^\circ$ , the reaction was complete in seven days, whereas in carbon tetrachloride fifty-five days were required. If, however, a methyl group is introduced instead of hydrogen, the reaction velocity is greatly accelerated,  $\alpha$ -methylstilbene in chloroform taking thirty minutes, and in carbon tetrachloride requiring two days ( $v = 200$   $t$   $29^\circ$ ) for complete interaction with bromine.

$\alpha$ -Phenylcinnamonnitrile dibromide (m. p.  $138^\circ$ , V. Meyer and Frost, Abstr., 1889, 598, give  $128^\circ$ ) dissociates slowly in carbon tetrachloride solution at  $30^\circ$  into nitrile and bromine; at  $100^\circ$  the velocity is much increased, so that the equilibrium established between bromine and nitrile was determined by using the dibromide to start with, and in the alternative the two interacting substances; the results obtained were the same by the two methods. In accordance with a reaction of the second order, dilution has a marked effect on the point of equilibrium; with  $v = 200$   $t$   $30^\circ$ , 16.5% of dibromide is obtained; with  $v = 400$  only 9%.

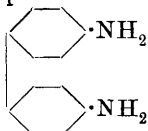
Light favours the production of dibromide, particularly red rays; only 4% of the bromine is taken up by  $\alpha$ -phenyl-*o*-nitrocinnamonnitrile in the dark, whilst in ordinary daylight 34% is absorbed.

The reaction in the case of the stilbenes is practically complete; the introduction, however, of a nitrile group diminishes the reactivity of the ethenoid linking, as is also the case if a hydrogen atom in the phenyl nucleus is replaced by a nitro-group;  $K$  for  $\alpha$ -phenylcinnamonnitrile being 0.02112,  $v = 200$ , whereas for  $\alpha$ -phenyl-*o*-nitrocinnamonnitrile it is 0.01152. W. R.

**Stereochemical Conceptions of Polycyclic Compounds.** FELIX KAUFLEDER (*Annalen*, 1907, 351, 151—160).—The usual formulæ for polycyclic compounds, either of the type of diphenyl or of that of conjugated ring systems, such as naphthalene, which represent the nuclei in one plane, may be displaced with advantage by stereochemical formulæ representing the manner in which the rings of the nuclei are inclined towards one another.

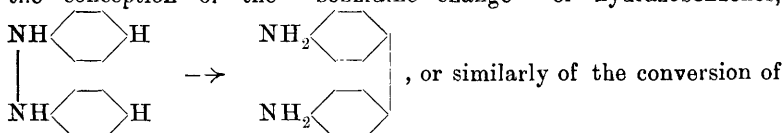
Materials on which may be based a stereochemical formula for diphenyl consist of the benzidine derivatives having the two amino-groups united by one or two carbon atoms, as in carbonylbenzidine (Michler and Zimmermann, Abstr., 1882, 182) or oxalylbenzidine (Strakosch, this Journ., 1872, 25, 503). In consequence, however, of the difficulty of determining the molecular weights of such substances, the bimolecular formulæ could not be looked on previously as excluded. A determination of the molecular weight of Kolber's

phthalylbenzidine (Abstr., 1904, i, 778) by the boiling point method now shows it to have the formula  $C_6H_4 \begin{matrix} \diagup CO \cdot NH \cdot C_6H_4 \\ \diagdown CO \cdot NH \cdot C_6H_4 \end{matrix}$ , and it appears probable that all such substances have unimolecular formulæ. The two amino-groups of benzidine must be much closer together than is represented by the usual formula  $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$ , their relative positions being represented better by the stereochemical formula



. This space formula explains the difficulty of diazo-

tising the second amino-group and the slowness with which the second diazo-group couples as cases of steric hindrance. It also simplifies the conception of the "benzidine change" of hydrazobenzenes,



tetraphenylhydrazine into *s*-diphenylbenzidine (Wielandt and Gambarjan, Abstr., 1906, i, 453).

It is found that 2:7-diaminonaphthalene forms only monosubstitution products when boiled with chlorotrinitrobenzene or chlorodinitrobenzene and potassium acetate in alcoholic solution. 7-*Trinitroanilino*-2-naphthylamine,  $C_{16}H_{11}O_6N_5$ , crystallises in yellow needles, m. p.  $212^\circ$ . 7-*Dinitroanilino*-2-naphthylamine,  $C_{16}H_{12}O_4N_4$ , crystallises in small, dark yellow needles, m. p.  $227^\circ$ . This is explained by mutual steric interference of the groups in positions 2:7, and is

expressed in the spacial formula ; this formula explains also

the difference in the stability of naphthalene-2:6- and naphthalene-2:7-disulphonic acids.

Similar differences are observed between 2:6- and 2:7-disubstituted anthraquinones. Whilst sodium anthraquinone-2:6-disulphonate is converted into 2:6-diaminoanthraquinone by ammonia at  $190^\circ$ , sodium anthraquinone-2:7-disulphonate yields only 2-aminoanthraquinone-7-sulphonic acid,  $C_{14}H_9O_5NS \cdot H_2O$ , which forms light yellow crystals; the barium salt,  $(C_{14}H_8O_5NS)_2Ba \cdot 2H_2O$ , crystallises in dark red leaflets; sodium 2-acetylaminanthraquinone-7-sulphonate,

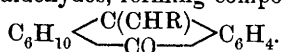


crystallises in orange-red leaflets.

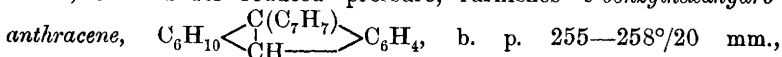
G. Y.

**Constitution of Octahydroanthracene.** MARCEL GODCHOT (*Bull. Soc. Chim.*, 1907, [iv], 1, 121—129. Compare Abstr., 1904, i, 987; 1905, i, 201; 1906, i, 76, 494).—On oxidation with potassium permanganate in presence of water or acetone, octahydroanthracene yields phthalic acid. The hexahydroanthrone produced by oxidising

the octahydride with chromic acid readily condenses in the presence of alkalis with aromatic aldehydes, forming compounds of the type

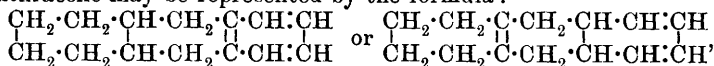


*Benzylidenehexahydroanthrone*, m. p. about 137–138°, forms faintly yellow, prismatic needles, and with bromine in presence of carbon disulphide furnishes a *dibromide*, m. p. 160° (decomp.), which crystallises in small, colourless prisms. On reduction with sodium and alcohol, benzylidenehexahydroanthrone furnishes *9-benzyl-octahydroanthranol*, m. p. 169°, which crystallises in large, colourless needles, and on distillation, even under reduced pressure, furnishes *9-benzylhexahydroanthracene*,



D<sup>n</sup> 1.253, which does not crystallise at –20°, and unlike the foregoing substances yields solutions exhibiting a fine blue fluorescence. The *picrate*, m. p. 120°, forms yellow needles and is resolved into its generators by water. Benzylhexahydroanthracene is also formed when hexahydroanthrone is treated with magnesium benzyl chloride in presence of ether. *Anisylidenehexahydroanthrone*, m. p. about 152°, forms small, yellow tablets, and like its benzylidene analogue does not react with hydroxylamine or semicarbazide. *Cumylidenehexahydroanthrone*, m. p. 148°, forms small, yellow leaflets.

From these results the author concludes that this octahydroanthracene may be represented by the formula :



and of these the first is preferred, since it explains more easily the production of phthalic acid when the hydrocarbon is oxidised with potassium permanganate, and establishes an analogy between the formation of octahydroanthracene from anthracene and that of tetrahydronaphthalene from naphthalene (Leroux, *Abstr.*, 1904, i, 986), both these reactions being brought about by Sabatier and Senderens's method of hydrogenation (*Abstr.*, 1901, i, 459).

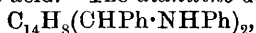
T. A. H.

**Anthracene Series.** EDUARD LIPPMANN and RODOLFO FRITSCH (*Annalen*, 1907, 351, 52–64. Compare *Abstr.*, 1904, i, 865).—

II. *Dibromodibenzylanthracene and its Derivatives.*—Dibromodibenzylanthracene and a number of its derivatives have been prepared and compared with the corresponding monosubstituted dibenzylanthracenes.

The *dibromo*-compound,  $\text{CHPhBr} \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \cdot \text{C} \cdot \text{CHPhBr}$ , prepared by passing a current of carbon dioxide and bromine vapour through dibenzylanthracene in carbon disulphide solution, forms yellow crystals, m. p. 212°, is only partially hydrolysed by boiling potassium hydroxide or carbonate, and does not react with moist silver oxide. The *diacetate*,  $\text{C}_{32}\text{H}_{26}\text{O}_4$ , m. p. 252°, prepared by the action of the dibromide on silver acetate in benzene, or on an alkali acetate in glacial acetic acid, solution, forms solutions with blue fluorescence, and when boiled with

alcoholic potassium hydroxide yields the *monoacetate*,  $\text{OH} \cdot \text{C}_{28}\text{H}_{20} \cdot \text{OAc}$ , which crystallises in red needles, m. p.  $216^\circ$ , and forms solutions with bluish-red fluorescence. The *dibenzoate*,  $\text{C}_{28}\text{H}_{20}(\text{OBz})_2$ , forms white crystals, m. p.  $285^\circ$ , and is only partially hydrolysed by boiling potassium hydroxide. The *dinitrate* forms light yellow crystals, m. p.  $177^\circ$  (decomp.), and when heated at  $140\text{--}180^\circ$  yields nitrogen dioxide, benzaldehyde, and anthraquinone. When boiled with alcohol in benzene solution, the dibromo-compound yields *diethoxydibenzylanthracene*,  $\text{C}_{28}\text{H}_{20}(\text{OEt})_2$ , which forms white crystals, m. p.  $220^\circ$ , dissolves in benzene or chloroform with blue fluorescence and is not hydrolysed by sulphuric acid. The *dianilino*-derivative,

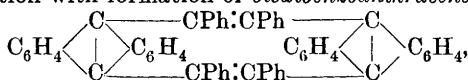


forms yellow crystals, m. p.  $263^\circ$  (decomp.).

III. *Degradation of Dibromodibenzylanthracene*.—The dibromodiffers from the monobromo-compound in that it does not yield hydrogen bromide when heated with quinoline in benzene solution, but resinifies at higher temperatures. An oxygen-free product could not be obtained by the decomposition of the *carbonate* formed by the action of the dibromo-compound on silver carbonate. On prolonged heating at  $212^\circ$ , the dibromo-compound yields hydrogen bromide and

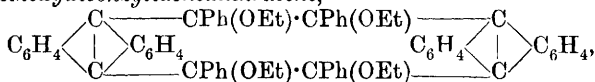
*bromodibenzylideneanthracene*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C} \diagdown \\ | \quad | \\ \diagdown \text{C} \diagup \end{array} \begin{array}{c} \text{CPhBr} \\ \text{C}_6\text{H}_4 \\ \text{CHPh} \end{array}$ , m. p.  $99^\circ$ , which

is reduced to dibenzylanthracene by zinc dust and glacial acetic acid. The dibromo-compound is oxidised by phenylhydrazine in boiling benzene solution with formation of *bisdibenzooanthracene*,



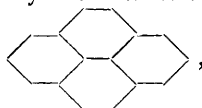
which separates from acetone in yellow crystals, m. p.  $197^\circ$ , decolorises potassium permanganate solution, and yields a *tetrabromide*,  $\text{C}_{56}\text{H}_{36}\text{Br}_4$ , forming yellow crystals, m. p.  $215^\circ$ , and reduced to bisdibenzylideneanthracene by means of zinc dust and acetic acid.

*Bisdiethoxydibenzylideneanthracene*,



prepared by boiling the tetrabromide with alcohol in benzene solution, forms a white, crystalline mass, m. p.  $218^\circ$ . G. Y.

**Structure of Pyrene.** GUIDO GOLDSCHMIEDT (*Annalen*, 1907, 351, 218—232).—Although the investigation of the constitution of pyrene by Bamberger and Philip (Abstr., 1887, 271) established that the nucleus of this hydrocarbon has the structure,

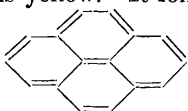


no satisfactory conclusion has been reached as to the distribution of the double linkings.

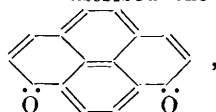
The author now shows by a series of experiments that the yellow



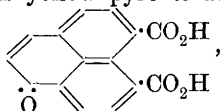
colour of pyrene is that of the substance itself and not of some impurity, the colour disappearing only on change of the pyrene as in its reduction with sodium and amyl alcohol. Contrary to Graebe's statement (this Journ., 1871, 117, 690) pyrene does not become colourless when exposed to sunlight in benzene solution; the apparently colourless leaflets obtained on sublimation of pyrene (Hintz, *Inaug. Diss.*) are yellow when heaped together. The author quotes also the properties of a number of derivatives of pyrene in support of his view that the hydrocarbon is yellow. It follows that pyrene is represented

best by the formula , in which only one of the four

rings is a benzene nucleus, the others having quinonoid structures. To the deep-red pyrenequinone is ascribed the structure



which on oxidation yields yellow pyrenic acid,



and on further oxidation is converted into colourless naphthalenetetracarboxylic acid.

The conversion of pyrene into pyrenequinone is explained also with the aid of Thiele's partial valencies. G. Y.

**A New Exception to Carnelley and Thomson's Rule. Solution Equilibrium between Aniline and *o*-Chloronitrobenzene.** ROBERT KREMANN (*Monatsh.*, 1907, 28, 7—11).—Kremann and Rodinis (Abstr., 1906, ii, 268) found that aniline does not form additive compounds with *m*- or *p*-chloronitrobenzene. It is shown now that this is the case also with aniline and *o*-chloronitrobenzene, the melting point curve for mixtures of these two substances having one eutectic point at  $-18^{\circ}$ , representing a mixture containing about 23% of *o*-chloronitrobenzene.

A comparison of the solubilities of the three chloronitrobenzenes discovers an exception to Carnelley and Thomson's rule (Trans., 1888, 53, 782) that in a group of isomeric organic substances the order of fusibility is the same as that of solubility, the most easily fusible substance being also the most soluble. The solubility curves of *o*- and *m*-chloronitrobenzenes follow this rule to the eutectic points, but that of the *p*-compound only to  $-2.5^{\circ}$ , at which temperature it cuts the curve for the *m*-isomeric; at temperatures below  $-2.5^{\circ}$ , the solubility of *p*-chloronitrobenzene is greater than that of the *m*-chloronitrocompound, although the latter melts at the lower temperature.

An analogous case is found in the solubilities of *p*- and *o*-dinitrobenzenes in aniline (Kremann and Rodinis, *loc. cit.*) which are identical

at 10°; above this temperature, Carnelley and Thomson's rule holds good, but below 10° the ortho-isomeride, which has the lower melting point, is the less soluble. As *m*-dinitrobenzene forms with aniline a 1:1-molecular additive compound, it does not belong to the class of indifferent substances to which alone Carnelley and Thomson's rule is applicable. G. Y.

**Preparation of  $\omega$ -Chloroacetanilide and its Homologues.** ALFRED VON JANSON (D.R.-P. 175586).— $\alpha$ -Chloroacetanilide may be readily obtained by adding phosphorus trichloride or thionyl chloride to a warm mixture of aniline hydrochloride and chloroacetic acid; the product is poured into water and the substance crystallised from alcohol. Other salts of aniline and its homologues may be substituted for the foregoing hydrochloride and the condensation may also be effected with phosphorus pentachloride or oxychloride. G. T. M.

**Preparation of Phenylglycine and its Homologues.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 175797).—Phenylglycine has now been prepared from chloroacetic acid and nitrobenzene in the following manner. Nitrobenzene containing about 10% of aniline is warmed at 70° with iron filings, and dilute chloroacetic acid is slowly introduced. The temperature of this acid should be gradually increased from 50° to 90°. The addition of the acid should suffice to keep the mixture boiling vigorously, and after two hours' heating at 98—100° the solution is neutralised with sodium carbonate. The aniline is distilled off and the phenylglycine isolated in the usual way. G. T. M.

**Preparation of Phenylglycine and its Homologues.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 177491).—The ordinary processes for obtaining phenylglycine by condensing chloroacetic acid with aniline either in excess or with reagents for fixing hydrogen chloride are unsatisfactory, owing to the formation of by-products. This difficulty has now been overcome by operating in the presence of an oxide or a carbonate of a heavy metal by means of which the phenylglycine forms an insoluble salt and is thus removed from the sphere of action. Ferrous chloride is dissolved in water, decomposed with the requisite amount of an alkali, and the mixture heated to 90—100°; chloroacetic acid and aniline are quickly added successively and the heating continued for one and a half hours; after cooling, the precipitated iron salt of phenylglycine is collected and converted into phenylglycine in the usual way. Tolyglycine may be obtained similarly. G. T. M.

**Action of Alkali Alkyloxides on Unsaturated Imides. II.** ARNALDO PIUTTI (*Gazzetta*, 1906, 36, ii, 723—734. Compare Abstr., 1906, i, 657).—The hydroxides of the alkali and alkaline-earth metals, with the exception of calcium, as well as all their derivatives with alcohol or acetone react with substituted imides of maleic, citraconic, and itaconic acids, giving intensely violet compounds which are

insoluble in ether and are decolorised even in solution by the addition of water. In the present paper, the author describes the method used for obtaining certain of these compounds yielded by *p*-ethoxyphenylcitracouimide, the chief difficulty in their preparation being that of rendering and maintaining the reagents and solvents employed absolutely anhydrous.

With sodium ethoxide in alcoholic solution, *p*-ethoxyphenylcitracouimide gives the compound  $C_{13}H_{13}O_3N \cdot EtONa$ , which is obtained as a reddish-violet powder, becoming soft at about  $200^\circ$  and remaining so up to  $300^\circ$ ; water dissolves it, giving a reddish-violet solution which gradually becomes colourless; it is soluble also in alcohol with formation of an intense violet coloration which is weakened by addition of water; it is also soluble in amyl alcohol, ethyl acetate, and acetone.

The compound  $C_{13}H_{13}O_3N \cdot C_5H_{11}ONa$ , formed with sodium amyl-oxide, is a reddish-violet powder, which softens at  $95^\circ$  and decomposes at  $140$ – $150^\circ$ ; its behaviour towards solvents resembles that of the preceding compound, and it is also soluble in toluene or benzene and sparingly so in xylene or carbon disulphide.

The compound  $C_{23}H_{30}O_4NNa$ , formed with sodium bornyloxide, is a reddish-violet powder, which softens at  $180^\circ$ , melts at  $195$ – $210^\circ$ , and behaves towards solvents like the preceding compound.

With the sodium derivative of dimethylacetone, *p*-ethoxyphenylcitracouimide gives a compound  $C_{26}H_{18}O_4NNa$ , which forms a dark reddish-violet powder softening at  $135^\circ$  and melting at  $170$ – $160^\circ$  (?); it is insoluble in benzene, toluene, or carbon disulphide, but towards other solvents it behaves like the borneol derivative. T. H. P.

**Preparation of  $\beta$ -Naphthylamine-3:6:8-trisulphonic Acid.** KALLÉ & Co. (D.R.-P. 176621).—1-Nitronaphthalene-3:6:8-trisulphonic acid when heated at  $150$ – $170^\circ$  for eight hours with concentrated ammonia yields  $\beta$ -naphthylamine-3:6:8-trisulphonic acid.

G. T. M.

**Miscibility of Solutions of Phenols in Aqueous Alkalis with Organic Substances Insoluble in Water.** RUDOLF SCHEUBLE (*Annalen*, 1907, 351, 473–480).—In the course of an investigation of the behaviour of salicylic esters towards potassium hydroxide, the author observed that on boiling thymyl salicylate with the aqueous alkali an increase in the volume of the upper or ester layer took place at the expense of the aqueous solution until after a few minutes a point was reached when the two previously non-miscible layers became completely miscible. This phenomenon is explained by the further observations that a solution of much thymol in concentrated aqueous potassium hydroxide is a solvent for various organic substances otherwise insoluble in water, and that on addition of a certain amount of aqueous potassium hydroxide to the ternary mixture of potassium thymoxide, potassium hydroxide, and the potassium derivative of thymol salicylate, which is formed in the first case, two non-miscible layers are formed. The moment of mixing of the two layers on boiling is not that when the ester has been completely hydrolysed, but when its volume has been diminished in a certain proportion.

This property of thymol is common to all phenols and is known technically in the extraction of phenols from tar distillates, and in the preparation of disinfectants by solution of phenols in alkaline phenol or soap solutions. Contrary to the generally accepted view all phenols can be extracted from their alkaline solutions with more or less ease by ether.

Quantitative experiments show that the amount of phenol, *m*-cresol, *m*-4-xenol, or carvacrol which must be added to a given amount of aqueous potassium hydroxide and octyl alcohol, toluene, or heptane to produce a clear solution increases for these three substances in the order named, and that the addition of water to 21.2% potassium hydroxide solution is at first without effect, but after a certain dilution is reached necessitates a rapid increase in the amount of phenol added.

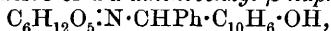
On adding phenol to aqueous potassium hydroxide and octyl alcohol, the liquid becomes apparently homogeneous before the layers are miscible; this occurs in consequence of the two layers having the same refractive index. As this is strictly so only for light rays of a certain wave-length, the liquid exhibits a marked opalescence. G. Y.

**Hydrolysis of Sodium Phenoxide.** ALEXANDER NAUMANN, WILHELM MÜLLER, and EDUARD LANTELME (*J. pr. Chem.*, 1907, [ii], 75, 65—87).—The method employed has been described (Abstr., 1906, ii, 732, 851). Similar results are obtained either by distilling 500 c.c. of the aqueous sodium phenoxide solution and collecting the distillate in 100 c.c. fractions or by distilling one litre of the solution and collecting the distillate in 25 c.c. fractions; from this the conclusion is drawn that the error due to the hydrolysis of further quantities of sodium phenoxide as phenol distils over, and the accumulation of an excess of sodium hydroxide in the distilled solution, is smaller than the experimental error.

To indicate the degree of hydrolysis of sodium phenoxide, the following numbers may be quoted. Aqueous solutions of concentration 1.0, 0.2, 0.1, 0.05, 0.01, and 0.002 mol. per litre are hydrolysed to the extent of approximately 4.4, 8.7, 11.6, 16.0, 29.7, and 56.4% respectively. The presence of a small excess of sodium hydroxide prevents to a great degree the hydrolysis of sodium phenoxide, especially in concentrated solutions. W. H. G.

**Optical Resolution by Means of Dextrose.** MARIO BETTI (*Gazzetta*, 1906, 36, ii, 666—669. Compare Abstr., 1906, i, 950).—Racemic  $\alpha$ -aminobenzyl- $\beta$ -naphthol can be resolved into its optical isomerides by means of dextrose, which forms, with the *d*- and *l*-compounds, derivatives exhibiting different solubilities in alcohol.

The dextrose derivative of *d*- $\alpha$ -aminobenzyl- $\beta$ -naphthol,



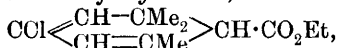
which is the less readily soluble in alcohol, crystallises from this solvent in tufts of white, silky needles, m. p. 192° (decomp.). The *l*- $\alpha$ -aminobenzyl- $\beta$ -naphthol dextrose compound crystallises from alcohol in minute, shining needles, m. p. 163—165° (decomp.). These dextrose

derivatives may be converted into the corresponding  $\alpha$ -aminobenzyl- $\beta$ -naphthols (*loc. cit.*) by hydrolysis with hydrochloric acid. T. H. P.

**Preparation of Aromatic Alcohols by the Electrolytic Reduction of Aromatic Acids.** CARL METTLER (D.R.-P. 177490. Compare Abstr., 1906, i, 497).—The aromatic acids may be readily reduced to the corresponding alcohols when they are electrolysed in an alcoholic sulphuric acid solution with cathodes having a high super-tension. Benzoic acid (200 parts) dissolved in 700 parts of alcohol and 300 parts of concentrated sulphuric acid was electrolysed at 20–30° with a current having a density of 6–12 amperes per 100 square centimetres of cathode surface. The electrodes were of lead, and the anode compartment contained dilute sulphuric acid. During the operation, a further amount (200 parts) of benzoic acid was added and a quantitative yield of benzyl alcohol was obtained. When reduced in a similar manner, *m*- and *p*-hydroxybenzoic acids furnished the corresponding hydroxybenzyl alcohols; 3:5-dichlorosalicylic acid gave rise to 3:5-dichlorosaligenin, and anthranilic and *m*-nitrobenzoic acids yielded respectively *o*-aminobenzyl alcohol and *m*-aminobenzyl alcohol. G. T. M.

**Oxidation of Cholesterol.** Oxysterol; Chollanic Acid. ISAAC LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1907, 50, 436–439. Compare Darmstädter and Lifschütz, Abstr., 1898, i, 470).—The oxidation of cholesterol by dilute permanganate in concentrated acetic acid occurs in three stages. The products of the first two stages are yellow, amorphous, neutral resins; they have no definite melting points and dissolve readily in all solvents with the exception of water. The first product dissolves in a mixture of acetic and sulphuric acids, yielding a red to reddish-violet coloured solution with a characteristic absorption spectrum. The second product, *oxysterol*, yields under similar conditions a green solution. The final product, *chollanic acid*,  $C_{26}H_{40}O_4$ , is a dibasic acid, obtained as a colourless, curdy precipitate on the addition of a large excess of mineral acid to solutions of its salts. Although insoluble in water, it readily forms an emulsion with acid-free water and then cannot be filtered. The *calcium* salt,  $C_{26}H_{38}O_4Ca$ , has been prepared. All three oxidation products occur in wool fat. J. J. S.

**Preparation of  $\Delta^4$ -cycloGeranic Acid (1:3:3-Trimethylcyclo- $\Delta^4$ -hexene-2-carboxylic Acid).** GEORG MERLING (D.R.-P. 175587).—*Ethyl chlorodehydro- $\Delta^{2:4}$ -cyclogeranate*,



is prepared by treating ethyl isophoronecarboxylate with phosphorus pentachloride and distilling the oily product under diminished pressure, when the ester is obtained as a colourless, inodorous oil, b. p. 108°/6 mm. It reduces ammoniacal silver nitrate, and on treatment with alcoholic potash yields chlorodehydro- $\Delta^{2:4}$ -cyclogeranic acid, which separates from benzene or ethyl acetate in lustrous, colourless prisms.

$\Delta^4$ -cycloGeranic acid,  $\text{QH} \begin{matrix} \text{CH} \text{---} \text{CMe}_2 \\ \text{CH}_2 \text{---} \text{CHMe} \end{matrix} \text{CH} \cdot \text{CO}_2\text{H}$ , results from the reduction of chlorodehydro- $\Delta^2$ - $\Delta^4$ -cyclogeranic acid with sodium and ethyl alcohol; it is readily soluble in the ordinary organic solvents, and separates from ethyl acetate or light petroleum in well-defined lustrous prisms, m. p. 102—102.5°, b. p. 123.5°/6 mm.

Ethyl  $\Delta^4$ -cyclogeranate is obtained either by ethylating potassium  $\Delta^4$ -cyclogeranate or by reducing ethyl chlorodehydro- $\Delta^2$ - $\Delta^4$ -cyclogeranate, b. p. 94°/6 mm.  $\Delta^4$ -cycloGerananilide,  $\text{C}_9\text{H}_{15}\text{CO} \cdot \text{NHPh}$ , forms colourless needles, m. p. 157—158°. G. T. M.

**Behaviour of Aromatic Esters towards Phosphorus Pentabromide and Pentachloride.** WILHELM AUTENRIETH and PAUL MÜHLINGHAUS (*Ber.*, 1907, 40, 744—751. Compare Abstr., 1895, i, 511; this vol., i, 31).—The methods of the earlier research have been extended to a number of aromatic and fatty aromatic esters which have been allowed to react directly with the phosphorus haloids at ordinary pressures without the medium of a solvent, moisture being carefully excluded. In most of the cases investigated the esters were easily chlorinated or brominated in the phenyl or naphthalene nucleus, more so in fact than the corresponding phenyl alkyl ethers.

Phenyl acetate and phosphorus pentabromide form a *monobromophenyl acetate*, a colourless liquid, b. p. 235—240° or 129—130°/15 mm., which, when hydrolysed, yields *p*-bromophenol. Small quantities of tri-*p*-bromophenyl phosphate are also obtained.

Phenyl benzoate (1 mol.) and phosphorus pentabromide (2 mols.) yield *dibromophenyl benzoate*, crystallising in long needles, m. p. 96—98°, which, on hydrolysis, forms 2:4-dibromophenol.

$\alpha$ -Naphthyl benzoate, glistening plates, m. p. 56°, prepared by shaking  $\alpha$ -naphthol dissolved in sodium hydroxide with benzoyl chloride, only reacts with phosphorus pentachloride when heated for some hours in an oil-bath at 130—160°. The product, *monochloro- $\alpha$ -naphthyl benzoate*, forms glistening needles, m. p. 100—101°, and on hydrolysis gives a compound, m. p. 118°, crystallising from hot water in long, glistening needles, and probably identical with 4-chloro-1-naphthol (Reverdin and Kaufmann, Abstr., 1896, i, 175). With phosphorus pentabromide,  $\alpha$ -naphthyl benzoate reacts more readily, and on warming a molecular mixture of the two, 4-bromo-1-naphthyl benzoate, plates, m. p. 105—106°, is obtained, since on hydrolysis it yields 4-bromo-1-naphthol (Reverdin and Kaufmann, *loc. cit.*). It forms an ethyl ether, crystallising in needles, m. p. 48°, identical with that obtained from the action of phosphorus pentabromide on  $\alpha$ -naphthyl ethyl ether (this vol., i, 31).

$\beta$ -Naphthyl benzoate and phosphorus pentachloride interact when heated at 130° to form the 1-chloro-2-naphthyl benzoate already obtained by Autenrieth.

$\beta$ -Naphthyl benzoate and phosphorus pentabromide interact very readily and with considerable violence to form 1-bromo-2-naphthyl benzoate, which on hydrolysis forms a product crystallising in needles, m. p. 74°, whereas Armstrong (*Ber.*, 1882, 206) gives 84° for 1-bromo-2-naphthol.

Methyl benzoate and phosphorus pentachloride react first at

160—180° on distillation of the reaction mixture; 11 grams of benzoyl chloride were obtained from 20 grams of ester. E. F. A.

**Formation of Chains from Aromatic Amino-Acids.** HANS MEYER (*Annalen*, 1907, 351, 267—282).—*o*-Aminobenzoylanthranilic acid (Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57) being now readily obtainable (Mohr and Köhler, Abstr., 1906, i, 359; Meyer, *ibid.*, i, 432), the author has investigated its use in the formation of chains. The method of synthesis adopted is the formation of the nitrobenzoyl derivative of the amino-acid by the action of *o*-nitrobenzoyl chloride on the alkali, usually the lithium, salt of the amino-acid, and reduction of the resulting nitrobenzoyl compound with titanium trichloride (Knecht and Hibbert, Abstr., 1903, ii, 509). The solubility of the acid and basic salts of the amino-acids synthesised in this manner decreases with increasing molecular weight; *m*- and *p*-nitrobenzoylanthranilic acids are less soluble than the *o*-compounds.

*o*-Nitrobenzoylanthranilic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , forms a colourless, crystalline mass, m. p. 239°, becoming yellow on exposure to air. *Methyl o-aminobenzoylanthranilate*,

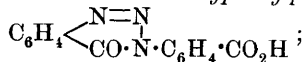
$\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ , crystallises in colourless needles, m. p. 118—119°. *o*-Nitrobenzoylanthranilylanthranilic acid,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , forms almost colourless crystals, m. p. 224°, evolving gas. *Dianthranilylanthranilic acid*,

$\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , forms slightly yellow needles, m. p. 228°, evolving gas. *o*-Nitrobenzoyldianthranilylanthranilic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot [\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4]_2 \cdot \text{CO}_2\text{H}$ , is obtained as a white, microcrystalline powder, decomposing at 170—200°. *Trianthranilylanthranilic acid*,

$\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot [\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}]_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , forms a dirty-white, gelatinous mass, which decomposes when heated.

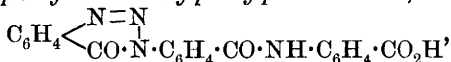
When treated with sodium nitrite in acid solution, anthranilylanthranilic acid gives an intense yellow coloration; this is probably due to the *nitroso*-derivative,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N}(\text{NO}) \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , which loses water, forming the colourless 3-*o*-carboxyphenylphenotriazone,



this separates from methyl alcohol in stout crystals, m. p. 192° (decomp.), explodes when heated, and if boiled with dilute hydrochloric or sulphuric acid, evolves nitrogen and forms *o*-hydroxybenzoylanthranilic acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , which crystallises in colourless needles, m. p. 212° (compare Mehner, Abstr., 1901, i, 470). The *acetoxyanhydride*,  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{O} \cdot \text{CO} \end{array} \text{C}_6\text{H}_4$ , formed by boiling the hydroxy-acid with acetic anhydride and a small amount of sulphuric acid (compare Angeli and Angelico, Abstr., 1901, i, 45), crystallises in long needles, m. p. 154°. The phenotriazone is reduced by titanium chloride in alcoholic hydrochloric acid solution, forming benzoylanthranilic acid.

In concentrated hydrochloric acid solution, the phenotriazone must have the structure  $\text{NCl:N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , in which state it couples with phenols, forming for instance with  $\beta$ -naphthol a scarlet dye; this is remarkable as hydroxyazo-dyes have been prepared exclusively in alkaline or neutral solution.

3-o-Carboxyphenyl-o-carbamylphenylphenotriazone,



formed from dianthranilylanthranilic acid, separates from methyl alcohol in colourless crystals, m. p.  $201^\circ$  (decomp.), and yields a dye on prolonged boiling with  $\beta$ -naphthol and dilute hydrochloric acid.

G. Y.

**Copper Salts of  $\alpha$ -Aminophenylacetic Acid.** GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 943—949. Compare Tiemann and Friedländer, *Abstr.*, 1880, 473; 1882, 56).—For the purpose of characterising the amino-acids, the author has commenced a study of the copper salts of these acids.

The method given by Tiemann (*loc. cit.*) for preparing copper salts of  $\alpha$ -aminophenylacetic acid yields compounds containing amounts of copper varying with the proportions of ammonia, copper sulphate, and amino-acid employed. The author dissolved a weighed quantity of  $\alpha$ -aminophenylacetic acid in excess of ammonia solution and added to the liquid the corresponding amount of standard copper sulphate solution, the excess of ammonia being afterwards removed in a vacuum at  $50$ — $60^\circ$ . In this way the following three compounds were obtained.

The *normal* salt,  $(\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2)_2\text{Cu}\cdot\text{H}_2\text{O}$ , separates in small, pale-blue crystals insoluble in water, but soluble in ammonia solution.

The *basic* salt,  $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\cdot\text{Cu}\cdot\text{OH}\cdot\text{H}_2\text{O}$ , forms small, sky-blue crystals, is insoluble in water, but readily soluble in ammonia solution, and deposits cupric oxide when suspended in water and boiled.

The *complex* salt,  $(\text{Cu}\cdot\text{N}\cdot\text{CHPh}\cdot\text{CO}_2)_2\text{Cu}\cdot\text{CuSO}_4\cdot 3\text{H}_2\text{O}$ , is deposited as a pale-blue powder, dissolves in dilute hydrochloric acid or excess of ammonia solution, and is decomposed by boiling water with formation of cupric oxide.

T. H. P.

**Isomeric Cinnamic Acids.** EMIL ERLNMEYER, jun., C. BARKOW, and O. HERZ (*Ber.*, 1907, 40, 653—663. Compare Erlenmeyer, jun., and Barkow, *Abstr.*, 1906, i, 429).—The authors have endeavoured to ascertain what part the brucine plays during the union of the base with *allocinnamic* acid. This acid does not form a stable brucine salt from which the *allocinnamic* acid can be regenerated; Liebermann's *isocinnamic* acid and Erlenmeyer, jun.'s, *isocinnamic* acid are those obtained (*Abstr.*, 1905, i, 646, 892). Although these two acids melt at the same temperature,  $59^\circ$ , and have the same crystalline form, they are not enantiomorphously related. The hypothesis that *allocinnamic* acid is a racemic mixture of these two acids has been abandoned, as, under the conditions employed, isodynamic change is likely to occur.

The brucine salt, m. p.  $151^\circ$ , is the normal salt, and crystallises in the tetragonal system [ $a:c=1:1\cdot7627$ ]. This salt undergoes isomeric

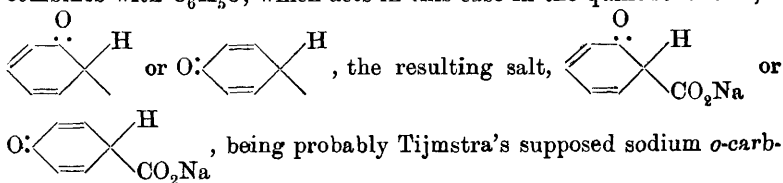


change when recrystallised from absolute alcohol, the crystals obtained from the syrup have m. p. 70—75°, and yield Erlenmeyer's, sen's., isocinnamic acid, m. p. 37—38°. The brucine salt, m. p. 135°, obtained from storax cinnamic acid is the hydrogen salt (compare Marckwald and Meth, Abstr., 1906, i, 880).

A new *cinnamic acid* has been isolated from synthetical cinnamic acid by crystallisation from 75% alcohol, evaporating the mother liquor and repeating this six times, the final mother liquor yields an acid which crystallises from light petroleum in triclinic needles, m. p. 127—128°. This is the eighth cinnamic acid obtained. W. R.

**Chemical Process of Synthesis by Absorption of Carbon Dioxide.** KARL BRUNNER (*Annalen*, 1907, 351, 313—331).—In such reactions as Wanklyn's synthesis of sodium propionate (*Annalen*, 1858, 107, 126), Kolbe and Lautermann's synthesis of salicylic acid (*Annalen*, 1860, 113, 126), Kolbe's reduction of carbon dioxide to formic acid (*Annalen*, 1861, 119, 251; Lieben, Abstr., 1895, ii, 348), Kekule's synthesis of benzoic acid from bromobenzene, sodium, and carbon dioxide (*Annalen*, 1866, 137, 181), and Grignard's and Zelinsky's syntheses (Abstr., 1902, i, 675), which mostly consist of the union of carbon dioxide with a carbon atom of another molecule and take place only in presence of metals such as potassium or sodium, or of the interaction of carbon dioxide and organo-metallic compounds or similar reducing alkali compounds, the carbon dioxide must be considered as undergoing reduction, one of the double carbon oxygen linkings being opened,  $\text{C} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \rightarrow -\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{O} \cdot \text{M} \end{smallmatrix}$ . The formation of

hydroxy-carboxylic acids from phenols is discussed from this point of view. The most convenient method of accomplishing this synthesis is to heat the phenol with glycerol, D 1.26, and potassium hydrogen carbonate in a current of carbon dioxide. Details are given of experiments with a number of phenols at different temperatures; under the most favourable conditions, the carboxylic or dicarboxylic acids are obtained in 40—50% yields. The following explanation is given of the synthesis of salicylic acid; the action of carbon dioxide on sodium phenoxide at the ordinary temperature results in the formation of the complexes  $\text{C}_6\text{H}_5 \cdot \text{O} \cdot$  and  $\cdot \text{CO} \cdot \text{ONa}$ , which combine to form sodium phenyl carbonate; this decomposes at 85° (Tijmstra, Abstr., 1905, i, 439), again forming sodium phenoxide and carbon dioxide. If the temperature is raised and the escape of carbon dioxide prevented, or if carbon dioxide is supplied in a continuous current, the group  $\cdot \text{CO}_2\text{Na}$  combines with  $\text{C}_6\text{H}_5\text{O}$ , which acts in this case in the quinonoid form,



, being probably Tijmstra's supposed sodium *o*-carboxyphenoxide,  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ ; the final stage is the isomeric change into the *o*- or *p*-hydroxybenzoate.

G. Y.

**Preparation of Acetylsalicylamide** KALLE & Co. (D.R.-P. 177054).—Acetylsalicylamide may be conveniently prepared and in good yield by mixing salicylamide (50 parts) with 30 parts of glacial acetic acid and 45 parts of acetic anhydride, and warming for five to six hours at 80–90°; on cooling, the product separates and is crystallised from chloroform. G. T. M.

**Derivatives of 5-Aminosalicylic Acid [5-Amino-2-hydroxybenzoic Acid].** ARNALDO PIUTTI (*Gazzetta*, 1906, 36, ii, 734–738). [With FABRIZIO COBELLIS and DIEGO GANDOLFO].—This preliminary communication merely gives the constitutions and m. p.'s of compounds obtained by the action of oxalic, malonic, succinic, citraconic, or phthalic acid on 5-amino-2-hydroxybenzoic acid or the corresponding aminomethoxybenzoic acid. These compounds are to be fully described later. T. H. P.

**New Case of Wandering of an Alkyl Group.** JACQUES POLLAK and J. GOLDSTEIN (*Annalen*, 1907, 351, 161–171. Compare Goldschmiedt and Herzig, *Abstr.*, 1882, 616; Heinisch, *Abstr.*, 1894, i, 34, 527; Arnstein, *ibid.*, 527; Hübner, *Abstr.*, 1895, i, 366; Malaguti, *Ann. Chim. Phys.*, [ii], 64, 152).—With the object of determining the position assumed by the nitro-group introduced into methyl trimethylpyrogallolcarboxylate on nitration, the nitro-acid was heated in expectation that on loss of carbon dioxide one of the two possible nitrotrimethylpyrogallols would be formed (Will, *Abstr.*, 1888, 1089; Einhorn, Cobliner, and Pfeiffer, *Abstr.*, 1904, i, 238). The product, however, obtained on heating the acid under either the ordinary or reduced pressure, and distillation of the residue in a vacuum, contains neither of the nitrotrimethylpyrogallols, but consists of methyl nitrotrimethylpyrogallolcarboxylate and a small amount of nitropyrogallol dimethyl ether (Graebe, *Abstr.*, 1887, 447; Heintz, *Jahresber.*, 1861, 448).

This wandering of a methyl group from a phenolic to a carboxylic hydroxyl is compared with a number of other similar cases. The lability of the alkyl group is considered to be determined by the presence of the electro-negative nitro-group (compare Salkowski and Rudolph, *Abstr.*, 1878, 72).

The position of the nitro-group in nitrotrimethylpyrogallolcarboxylic acid is determined by reduction to the corresponding amine, which when fused with carbamide at 160–180° yields 2:4-dioxy-5:6:7-trimethoxy-1:2:3:4-tetrahydroquinazoline,  $C_6H(OMe)_3$   $\begin{smallmatrix} \text{CO}-\text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , showing the nitro-group to be in the *o*-position to the carboxyl.

**Methyl 2-nitrotrimethylpyrogallolcarboxylate**,  $NO_2 \cdot C_6H(OMe)_3 \cdot CO_2Me$ , crystallises in colourless needles, m. p. 74°, and is insoluble in aqueous alkalis. The acid,  $NO_2 \cdot C_6H(OMe)_3 \cdot CO_2H$ , forms a colourless, crystalline mass, m. p. 154–155°.

**Nitropyrogallol dimethyl ether**,  $NO_2 \cdot C_6H_2(OMe)_2 \cdot OH$ , separates from

alcohol in light yellow crystals, m. p. 112—114°, and dissolves in aqueous potassium hydroxide, forming an intense orange solution.

*Methyl 2-aminotrimethylpyrogallolcarboxylate*,  
 $\text{NH}_2 \cdot \text{C}_6\text{H}(\text{OMe})_3 \cdot \text{CO}_2\text{Me}$ ,

m. p. 93—98°.

2:4-Dioxy-5:6:7-trimethoxy-1:2:3:4-tetrahydroquinazoline separates from alcohol in colourless crystals, m. p. 261—264° (decomp.), dissolves in aqueous alkalis, forming *alkali* derivatives, and when boiled with fuming hydriodic acid, yields a product, probably the *trihydroxydioxy-tetrahydroquinazoline*, crystallising in white needles, not melted at 300°.

G. Y.

**Santonin Acid.** ANGELO ANGELI and LUIGI MARINO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 159—161).—As a means of ascertaining the constitution of santonin, the authors have attempted to study the products obtained on gradually breaking down the molecule in the manner successfully applied to the terpenes, more especially by Baeyer, Wagner, and Tiemann.

In the present preliminary communication, oxidation by permanganate is considered, and, as santonin is insoluble in water, santonin acid is employed. The oxidation products obtained, in addition to formic and oxalic acids, are: (1) an unstable, yellow, oily, dibasic acid,  $\text{C}_{15}\text{H}_{20}\text{O}_7$ , which reacts readily with hydroxylamine and hydrazines, reduces ammoniacal silver nitrate and Fehling's solutions, and yields iodoform on treatment with iodine and potassium hydroxide. From these reactions it may be regarded as possessing the formula  $\text{CO}_2\text{H} \cdot \text{C}_{10}\text{H}_{14}(\text{CO} \cdot \text{CO}_2\text{H})(\text{COMe}) \cdot \text{OH}$ , and its formation is probably due to the oxidation of a group of the form  $\begin{array}{c} \cdot\text{CO} \cdot \text{CH} \\ | \\ \cdot\text{C} \cdot \text{COMe} \end{array}$  to

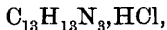
$\cdot\text{CO} \cdot \text{CO}_2\text{H}$  and  $\cdot\text{C} \cdot \text{COMe}$ . (2) A tetracarboxylic acid,  $\text{C}_{11}\text{H}_{16}\text{O}_8$ , m. p. about 165°, at which temperature it loses carbon dioxide and yields a product to be described later; its constitution may probably be represented by the scheme:  $\text{C}_6\text{H}_{12}(\text{CO}_2\text{H})_2 \cdot \text{C}(\text{CO}_2\text{H})_2$ .

The authors regard it as highly probable that santonin acid contains a bridge consisting of a methylene group situated in the ring containing the ketonic group.

T. H. P.

**Benzaldehyde-o-aminophenylhydrazone.** HARTWIG FRANZEN (*Ber.*, 1907, 40, 909—912).—This is the first examination of amino-phenylhydrazones.

*Benzaldehyde-o-aminophenylhydrazone*,  $\text{CHPh} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , obtained by the reduction of the corresponding o-nitrohydrazone in ammoniacal alcohol by sodium hyposulphite, crystallises in slender, yellow needles, m. p. 142°. The unstable *hydrochloride*,



is colourless. When a suspension of the hydrazone in 2% hydrochloric acid is treated with a current of steam for five minutes, it is converted into the hydrochloride of 2-phenylbenziminazole (Pawlewski, *Abstr.*, 1903, i, 661). An attempt to prepare an acetyl derivative also yielded phenyl benziminazole.

W. R.

**$\beta$ -Hydroxynaphthaldehyde.** II. MARIO BETTI and CURIO M. MUNDICI (*Gazzetta*, 1906, **36**, ii, 655—660. Compare Abstr., 1905, i, 213).—The results already described (*loc. cit.*) show that although in many reactions  $\beta$ -hydroxynaphthaldehyde exhibits the normal behaviour of aromatic *o*-hydroxyaldehydes, yet some of the changes which it undergoes are characterised by the ease with which the aldehyde group tends to become detached from the naphthol nucleus. In the present paper are described the results obtained by reducing the hydroxyaldehyde in various ways. A series of compounds is obtained terminated by 1-methyl- $\beta$ -naphthol (compare Fries and Hübner, Abstr., 1906, i, 190), which is the most completely reduced product.

Reduction of  $\beta$ -hydroxynaphthaldehyde by zinc and acetic acid yields: (1) *bisoxynaphthene-ethane*,  $\begin{array}{c} \text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{O} \\ \text{O} \text{---} \text{CH}\cdot\text{C}_{10}\text{H}_6 \end{array}$ , which crystallises from benzene in colourless needles, m. p. 261—262°, gives a yellowish-red coloration with concentrated sulphuric acid and dissolves sparingly in acetic acid or alcohol. (2) A small quantity of *dinaphtholcarbinol*,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}(\text{OH})\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ , which crystallises from alcohol in lemon-yellow, thick needles or flattened prisms, m. p. 232°, dissolves in concentrated sulphuric acid giving a yellow coloration, gives a brown colour with ferric chloride in alcoholic solution, and is readily soluble in alkalis. (3) 1-Methyl- $\beta$ -naphthol, which has the normal molecular weight in freezing acetic acid and dissolves in sulphuric acid giving a yellowish-red solution; it yields a *picrate*, m. p. 162—163°, and a *benzoyl* derivative,  $\text{C}_{18}\text{H}_{14}\text{O}_2$ , m. p. 115—116°.

A better yield of *dinaphtholcarbinol* is obtained if the reduction of the  $\beta$ -hydroxynaphthaldehyde is affected by means of aluminium in alkaline solution.

Reduction with aluminium amalgam gives rise to: (1) *dinaphthol-methane*,  $\text{CH}_2(\text{C}_{10}\text{H}_6\cdot\text{OH})_2$ ; (2) 1-*hydroxymethyl*- $\beta$ -*naphthol*, (*hydroxynaphthoic alcohol*),  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{OH}$ , which crystallises from chloroform in shining, white needles, m. p. 188—189° (decomp.), dissolves in concentrated sulphuric acid giving a reddish-yellow coloration, is soluble in alcohol or benzene, and in alcoholic solution yields a bluish-green coloration with ferric chloride.

T. H. P.

**Action of Nitric Acid on Halogen Derivatives of *o*-Alkyl-phenols.** THEODOR ZINCKE and W. KLOSTERMANN (*Ber.*, 1907, **40**, 679—685. Compare Abstr., 1905, i, 879, 882).—Tribromo-*p*-toluquinone is formed by the vigorous action of concentrated nitric acid (D 1.48—1.5) on tetrabromo-*o*-cresol. If the action of the nitric acid is conducted in the cold or in the presence of glacial acetic acid, *tetrabromo-o-methylquinnitrole*,  $\text{NO}_2\cdot\text{CMe} \begin{array}{c} \text{CBr}\cdot\text{CBr} \\ \text{CO}\text{---}\text{CBr} \end{array} \text{CBr}$ , is formed as a sulphur-yellow, crystalline powder, which softens at 71° and decomposes at higher temperatures. When acted on by moist ether or by methyl alcohol, it forms *tetrabromo-o-methylenequinone*

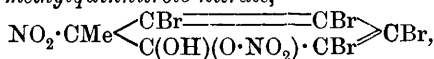
(*tetrabromo-o-quinonemethide*),  $\text{CH}_2\text{:C} \begin{smallmatrix} \text{CBr}\cdot\text{CBr} \\ \text{CO}-\text{CBr} \end{smallmatrix} \text{CBr}$ ; this separates from ether in yellow, glistening leaflets and from methyl alcohol as a sulphur-yellow, granular powder, m. p. about  $130^\circ$ .

Tetrabromo-*o*-methylquinnitrole is converted on reduction into tetrabromo-*o*-cresol.

*Tetrabromo-o-methylquinol*,  $\text{OH}\cdot\text{CMe} \begin{smallmatrix} \text{CBr}\cdot\text{CBr} \\ \text{CO}-\text{CBr} \end{smallmatrix} \text{CBr}$ , prepared by boiling tetrabromo-*o*-methylquinnitrole with light petroleum or with benzene, separates from a mixture of light petroleum and benzene in glistening, yellow needles, m. p.  $135-136^\circ$ . When warmed with glacial acetic acid and a little sulphuric acid, it evolves hydrogen bromide and is converted into tribromo-*p*-toluquinone; when reduced by stannous chloride, it forms tetrabromo-*o*-cresol. Its *acetyl* derivative separates from benzene or glacial acetic acid in yellow leaflets, m. p.  $110^\circ$ . Its *anilide*,  $\text{OH}\cdot\text{CMe} \begin{smallmatrix} \text{CBr}\cdot\text{C}(\text{NHPh}) \\ \text{CO}-\text{CBr} \end{smallmatrix} \text{CBr}$ , separates from a mixture of light petroleum and benzene in glistening leaflets, m. p.  $160-161^\circ$ .

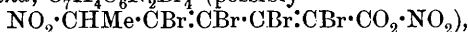
3:4:6-Tribromo-5-nitro-*o*-cresol,  $\text{CMe} \begin{smallmatrix} \text{CBr}\cdot\text{C}(\text{NO}_2) \\ \text{C}(\text{OH})(\text{O}\cdot\text{NO}_2)-\text{CBr} \end{smallmatrix} \text{CBr}$ , obtained by the action of alcoholic sodium hydroxide on tetrabromo-*o*-methylquinnitrole, forms colourless needles, m. p.  $177^\circ$  (decomp.). When reduced by tin and hydrochloric acid, it forms 3:4:6-tribromo-5-amino-*o*-cresol. When oxidised by ferric chloride, it forms 3:4:6-tribromo-*p*-toluquinone.

*Tetrabromo-o-methylquinnitrole nitrate*,



obtained by the prolonged action of nitric acid on tetrabromo-*o*-cresol, separates from a mixture of light petroleum and benzene in colourless needles, m. p.  $99^\circ$ , decomposing with evolution of a red gas.

The compound,  $\text{C}_7\text{H}_4\text{O}_6\text{N}_2\text{Br}_4$  (possibly



obtained either by the action of sodium carbonate on the preceding compound or by the prolonged action of nitric acid on a solution of tetrabromo-*o*-cresol in glacial acetic acid, forms colourless needles, m. p.  $139^\circ$  (decomp.). It reacts vigorously with alkalis and with aniline.

A. McK.

**Preparation of Ketones from Aldehydes by Means of Diazomethane.** HANS MEYER (*Ber.*, 1907, 40, 847-848. Compare *Abstr.*, 1905, i, 87).—The products formed by the action of diazomethane on *m*- and *p*-nitrobenzaldehydes and thought to be possibly enolic compounds, are now found to be identical with the nitroacetophenones, which when pure are colourless, give red colorations with alcoholic alkalis, and are soluble in boiling aqueous alkalis. Contrary to Schlotterbeck's statement (this vol., i, 185) that the reactivity of diazomethane with aldehydes decreases with increasing molecular weight of the latter, the nitrobenzaldehydes enter into the reaction more energetically than does benzaldehyde.

G. Y.

**Stereoisomeric Oximes of Dypnone and Benzylideneacetophenone.** FERDINAND HENRICH [and, in part, RAAB and RUPPENTHAL] (*Annalen*, 1907, **351**, 172—185. Compare Abstr., 1904, i, 431, 751).

—The chemical properties of the substance, m. p. 78°, formed by the action of concentrated sulphuric acid on *syn*-dypnone-oxime

and previously assumed to be the *anti*-oxime,  $\text{CMePh}\cdot\text{CH}\cdot\text{CPh}$   
 $\text{OH}\cdot\text{N}=\text{CPh}$ , ap-

peared to agree better with the isomeric *isooxazoline* structure,

$\text{CH}_2\begin{cases} \text{CMePh}\cdot\text{O} \\ \text{CPh}=\text{N} \end{cases}$ . The present work was undertaken with the object

of deciding between these constitutions. As reduction of both dypnone-oximes, with sodium amalgam in acetic acid solution or with sodium and alcohol, leads to the formation of  $\alpha\gamma$ -diphenylbutylamine, whilst the reduction product of the *isooxazoline* would be the hydroxyamine,  $\text{OH}\cdot\text{CMePh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NH}_2$ , the author decides in favour of the *anti*-oxime formula. The oximes of benzylideneacetophenone also have been examined and compared with those of dypnone.

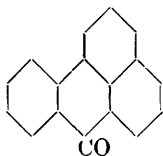
$\alpha\gamma$ -Diphenylbutylamine hydrochloride,  $\text{C}_{16}\text{H}_{19}\text{N}\cdot\text{HCl}$ , crystallises in needles, m. p. 226—228°; the *platinichloride* forms yellow needles, m. p. 195°; the *aurichloride* and *picrate*, m. p. 187°, are obtained as yellow precipitates; the *mercurichloride* forms white needles; the  $\alpha$ -tartrate,  $\text{C}_{16}\text{H}_{19}\text{N}\cdot\text{C}_4\text{H}_6\text{O}_6$ , crystallises in white needles, m. p. 234°, and yields the inactive base.

*anti*-Benzylideneacetophenoneoxime, formed from the ketone and hydroxylamine in alkaline alcoholic solution, crystallises in white needles, m. p. 75° (compare Goldschmidt, Abstr., 1895, i, 422; Claus, Abstr., 1897, i, 189), does not undergo the Beckmann transformation, and on reduction with sodium and alcohol yields  $\alpha\gamma$ -diphenylpropylamine. The *hydrochloride*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NH}_2\cdot\text{HCl}$ , crystallises in colourless needles, m. p. 195°; the *picrate*,  $\text{C}_{15}\text{H}_{17}\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ , long needles or leaflets, m. p. 155°; the *platinichloride*,  $(\text{C}_{15}\text{H}_{17}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$ , was analysed; the *d-tartrate*,  $\text{C}_{15}\text{H}_{17}\text{N}\cdot\text{C}_4\text{H}_6\text{O}_6$ , forms white needles, m. p. 168°, and yields the inactive base.

*syn*-Benzylideneacetophenoneoxime, formed in alcoholic hydrochloric acid solution, separates as a crystalline mass, m. p. 115—116°, is reduced by sodium and alcohol, forming  $\alpha\gamma$ -diphenylpropylamine, and is converted by hot concentrated sulphuric acid into the *anti*-oxime, from which it differs in forming a crystalline *hydrochloride*. The *phenylurethane*,  $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_2$ , crystallises in white needles, m. p. 165°. The *acetyl* derivative of the *syn*-oxime,  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ , forms white crystals, m. p. 135°. When treated with phosphorus pentachloride in ethereal solution, the *syn*-oxime undergoes Beckmann's transformation, forming cinnamoylanilide, m. p. 153°, which is formed also by Werner and Piquet's method (Abstr., 1905, i, 66). G. Y.

**Preparation of Benzanthrone and its Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 176018 and 176019. Compare Abstr., 1906, i, 888).—It was formerly shown that certain aminoanthraquinones condense with glycerol so as to form compounds containing

two new rings, and it has now been discovered that anthraquinone and its sulphonic acids and anthranol and hydroxyanthranol also condense with this reagent to form a new series of ketones, the *benzanthrone*s, the compounds from the aminoanthraquinones being called *benz-anthronequinolines*. *Benzanthrone* is obtained by heating a mixture of anthranol, glycerol, and concentrated sulphuric acid at 120°, a vigorous action sets in and sulphur dioxide is evolved; the product crystallises from alcohol in pale yellow needles, m. p. 170°. This compound may also be prepared from anthraquinone and other condensing agents such as

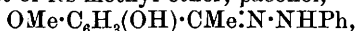


zinc chloride, concentrated hydrochloric acid and aniline sulphate may be employed. *Benzanthrone-β-sulphonic acid* can be produced similarly from the corresponding sulphonic acid of anthraquinone or anthranol. *Benzanthrone* may even be obtained by condensing anthracene itself with glycerol and concentrated sulphuric acid.

G. T. M.

**Hydrazones of Aromatic Hydroxy-ketones. Alkali-insoluble Phenols.** HENRY A. TORREY and H. B. KIPPER (*J. Amer. Chem. Soc.*, 1907, 29, 77—81).—A study has been made of the action of phenylhydrazine on hydroxyacetophenones and hydroxybenzophenones. It was thought that, under certain conditions, not only would the keto-group be attacked, but that possibly the hydroxyl group might react with the hydrogen of the imino-group with the formation of a five-membered ring by a condensation similar to that occurring between phenylhydrazine and ethyl acetoacetate. Although a condensation of this kind did not take place, the character of the hydroxyl group was affected, the hydrazones formed being insoluble in alkali hydroxides. Phenolic compounds which are insoluble in alkali hydroxides have been described previously by Anselmino (*Abstr.*, 1903, i, 121) and by Rogoff (*Abstr.*, 1905, i, 883).

The phenylhydrazone of resacetophenone is soluble in alkali hydroxides, but that of its methyl ether, paeonol,



in which the only free hydroxyl group is in the *o*-position to the keto-side-chain, is insoluble. The insolubility of the latter hydrazone suggests either that the hydroxyl group has formed with the imino-

group a six-membered ring,  $\begin{array}{c} \text{CH} \text{---} \text{CH} : \text{C} : \text{CMe} : \text{N} \\ | \qquad \qquad | \\ \text{C}(\text{OMe}) \cdot \text{CH} : \text{C} : \text{O} \text{---} \text{NH}_2\text{Ph} \end{array}$  or that the

hydrogen is so feebly acid that the alkali salt, if formed, suffers immediate hydrolysis. Resodiacetophenone (2 : 4-dihydroxy-1 : 5-diacetophenone) yields a *bisphenylhydrazone*, m. p. 291°, which, as would be expected, is insoluble in alkali hydroxides. These compounds, however, which do not dissolve in aqueous alkali hydroxides are soluble in potassium ethoxide, but, on adding water, the original compound is precipitated. Another possible explanation of the insolubility of these hydrazones is that they have a quinonoid structure and thus do not contain a hydroxyl group; in this case paeonolphenylhydrazone

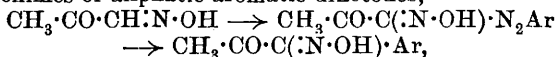
and resodiacetophenonebisphenylhydrazone would be represented respectively by the formulæ

$$\begin{array}{c} \text{CH:CH:C:Me}\cdot\text{NH}\cdot\text{NHPh} \\ \text{OMe}\cdot\text{C}=\text{CH:C:O} \\ \text{NHPh}\cdot\text{NH}\cdot\text{CMe}\cdot\text{C:CH:C:Me}\cdot\text{NH}\cdot\text{NHPh} \\ \text{O:C}\cdot\text{CH:C:O} \end{array}$$

*Dibenzoylresacetophenonephenylhydrazone*,  
 $\text{C}_6\text{H}_5(\text{OBz})_2\cdot\text{CMe:N}\cdot\text{NHPh}$ ,

m. p. 183°, can be obtained either by the action of phenylhydrazine on dibenzoylresacetophenone or by that of benzoyl chloride on a solution of resacetophenonephenylhydrazone in alkali hydroxide. *Dibenzoylresacetophenone* crystallises from alcohol and is insoluble in water. 1:4-Dihydroxyphenylene diphenyl diketone *bisphenylhydrazone*, m. p. 172—174°, forms yellow crystals and is insoluble in alkali hydroxides. 1:3-Dihydroxyphenylene diphenyldiketone *bisphenylhydrazone*, m. p. 292—293°, is a white, crystalline substance insoluble in alkali hydroxides. E. G.

$\alpha$ -Diketones from  $\alpha$ -Ketoaldoximes; a New Synthesis with Diazo-compounds. WILHELM BORSCHKE (*Ber.*, 1907, 40, 737—744).—Although aldehyde-arylhydrazones are easily coupled with aromatic diazo-compounds to form formazyl compounds, this reaction does not succeed with aldoximes. In oximes, such as methylglyoxalmonoxime, in which the  $\cdot\text{CH:N}\cdot\text{OH}$  group is situated immediately next to a carbonyl group the hydrogen atom is more reactive and can be replaced by the diazo-group. Such compounds lose nitrogen and yield monoximes of aliphatic aromatic diketones,



from which the diketones themselves are obtained on heating with dilute sulphuric acid. This at present forms the easiest method of preparing such diketones.

Attempts to carry through the same reaction with isonitrosoacetophenone and so to obtain benzil and its homologues were less successful.

$\beta$ -Keto- $\alpha$ -oximino- $\alpha$ -phenylpropane,  $\text{OH}\cdot\text{N:CPh}\cdot\text{COMe}$ , is obtained from isonitrosoacetone and diazobenzene chloride in faintly yellow plates, m. p. 166—167°, identical with the compound prepared by Kolb (*Abstr.*, 1896, i, 576). Heated with excess of hydroxylamine hydrochloride, it forms the acetylbenzoyldioxime, m. p. 231—233°,  $\text{OH}\cdot\text{N:CPh}\cdot\text{CMe:N}\cdot\text{OH}$ , described by von Pechmann and Müller (*Abstr.*, 1888, 1087). On oxidation with potassium ferricyanide in alkaline solution, phenylmethylglyoxime peroxide,  $\begin{array}{c} \text{CPh:N}\cdot\text{O} \\ \text{CMe:N}\cdot\text{O} \end{array}$ , is formed, crystallising in colourless needles, m. p. 95°.

Acetylbenzoyl, obtained by warming the oxime with dilute sulphuric acid, is a dark yellow oil, volatile in steam, and possessing a characteristic sweet and quinone-like odour (compare Kolb, *loc. cit.*).

$\beta$ -Keto- $\alpha$ -oximino- $\alpha$ -p-tolylpropane,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}\cdot\text{CH}_3$ , forms large, colourless, rhombic plates, m. p. 161—162°; the corresponding dioxime crystallises in colourless needles, m. p. above 230° (decomp.).



*β-Keto-α-oximino-2 : 4-dimethylphenylpropane*,  
 $C_6H_3Me_2 \cdot C(N \cdot OH) \cdot CO \cdot CH_3$ ,

is obtained as colourless, microscopic needles, m. p. 141—142°.

*β-Keto-α-oximino-α-o-methoxyphenylpropane*,  
 $OMe \cdot C_6H_4 \cdot C(N \cdot OH) \cdot CO \cdot CH_3$ ,

crystallises in long needles, m. p. 131—132°.

*β-Keto-α-oximino-α-p-methoxyphenylpropane*,  
 $OMe \cdot C_6H_4 \cdot C(N \cdot OH) \cdot CO \cdot CH_3$ ,

crystallises in short, thick needles, m. p. 152—153°. It forms acetyl-*p*-anisoyl-*amphidioxime*, m. p. 215°, whilst when heated with dilute sulphuric acid, *acetyl-p-anisoyl*,  $OMe \cdot C_6H_4 \cdot CO \cdot CO \cdot CH_3$ , is formed, crystallising in long, citron-yellow needles, m. p. 48°. About half of the oxime is converted in this manner, the rest undergoing a Beckmann rearrangement and yielding pyruvic *p*-aniside,

$OMe \cdot C_6H_4 \cdot NH \cdot CO \cdot CO \cdot CH_3$ ,

crystallising in colourless, minute needles, m. p. 129—130°. The magnitude of the rearrangement is to be attributed to the influence of the *p*-methyl group (compare Werner, Abstr., 1906, i, 180).

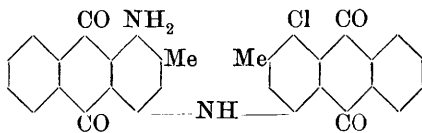
By the interaction of isonitrosoacetophenone and diazobenzene salts, α-benzilmonoxime was obtained.

E. F. A.

**Preparation of Halogen Derivatives of β-Hydroxyanthraquinone.** R. WEDEKIND & Co. (D.R.-P. 175663).—The β-hydroxyanthraquinones readily undergo bromination when suspended in water, giving rise to di- and tri-bromo-derivatives. *Dibromo-2-hydroxyanthraquinone*,  $C_{14}H_6O_5Br_2$ , is produced by adding bromine to a suspension of 2-hydroxyanthraquinone in water acidified with sulphuric acid. Anthraflavic acid yields either di- or tri-bromo-anthraflavic acid, depending on the amount of bromine employed. Flavopurpurin behaves in a similar manner.

G. T. M.

[Preparation of Dianthraquinonylamine Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 176956).—4-Chloro-1-amino-2-methylantraquinone when dissolved in concentrated sulphuric acid and treated with nitrating acid containing 20—21%  $HNO_3$  becomes converted into a substance having the composition  $C_{30}H_{19}O_4N_2Cl$ , which is probably a dianthraquinonylamine having the annexed constitution:



other substituted 1-amino-anthraquinones containing a halogen in position 4 and some other substituent in position 3 undergo this condensation and give rise to analogous dianthraquinonylamines. When

these compounds are condensed with phenols or aromatic amines, blue colouring matters are produced, which dye unmordanted wool in various shades of blue which are characterised by their fastness to light and scouring agents.

G. T. M.

**Camphoformyl-acetic and -α-Propionic Esters.** CHARLES WEIMANN (*Ann. Chim. Phys.*, 1907, [viii], 10, 378—394).—Haller

and Couréménos (Abstr., 1905, i, 523) have shown that two optical isomerides are formed by the introduction of the cyanocamphor group into propionic acid in the  $\alpha$ -position. In the present paper, derivatives of formylcamphor,  $C_8H_{14} \begin{smallmatrix} \diagup \\ C:CH \cdot O \cdot CHR \cdot CO_2R' \\ \diagdown \\ CO \end{smallmatrix}$ , prepared by the

action of sodioformylcamphor (Bishop, Claisen, and Sinclair, Abstr., 1895, i, 62) on bromoacetic and  $\alpha$ -bromopropionic esters in boiling toluene solution, are described, the chief object of the work being to produce evidence as to how far it may be considered to be a general rule that the union of an active molecule with the asymmetric carbon atom of a racemic compound results in the formation of two optical isomerides.

*Ethyl camphoformylacetate*,  $R = H$ ,  $R' = Et$ , separates from light petroleum in white crystals, m. p.  $56^\circ$ , b. p.  $190-210^\circ/20$  mm.,  $[\alpha]_D + 148^\circ 15' 65''$ , and is hydrolysed readily at the ordinary temperature by aqueous alkali carbonates, forming sodioformylcamphor and sodium glycolate, by water under pressure at  $150^\circ$ , yielding formylcamphor, glycollic acid, and ethyl alcohol, or by cold hydrochloric acid, in consequence of which it gives gradually with ferric chloride the violet coloration characteristic of formyl camphor.

*Methyl camphoformylacetate*,  $R = H$ ,  $R' = Me$ , separates from light petroleum in white crystals, m. p.  $91^\circ$ , b. p.  $215/23$  mm.,  $[\alpha]_D + 156^\circ 32' 72''$ , and gives reactions similar to those of the ethyl ester.

*Methyl camphoformyl- $\alpha$ -propionate*,  $R = Me$ ,  $R' = Me$ , separates from methyl alcohol in large, white crystals, m. p.  $71.5^\circ$ , b. p.  $195-205^\circ/20$  mm.,  $[\alpha]_D + 148^\circ 10' 92''$ , and undergoes hydrolysis in the same manner as the camphoformylacetates, yielding formylcamphor, lactic acid, and methyl alcohol; no trace of an optical isomeride could be found on fractional crystallisation from light petroleum.

*Ethyl camphoformyl- $\alpha$ -propionate*,  $R = Me$ ,  $R' = Et$ , is obtained as a yellow oil, b. p.  $205-215^\circ/20$  mm.,  $D_4^{20} 1.078$ ,  $[\alpha]_D + 122^\circ 34'$ .

From the identity of the molecular rotations of methyl camphoformylacetate and methyl camphoformyl- $\alpha$ -propionate and of the specific rotations of methyl camphoformyl- $\alpha$ -propionate and ethyl camphoformylacetate, it is concluded that the camphoformylpropionates are racemic compounds.

G. Y.

**Preparation of Pinene Hydrochloride.** CHEMISCHE FABRIK UERDINGEN LIENAU & Co. (D.R.-P. 175662).—Pinene hydrochloride as usually prepared does not keep unless it has been repeatedly crystallised from alcohol or purified in some other costly manner. It is now found that a stable form of the substance can be cheaply and readily prepared by treating the crude material with hydrolytic agents until the "saponification number" of the product is equal to that of the highly purified compound. This is best carried out by heating the hydrochloride with the calculated amount of an alkali hydroxide in dilute aqueous solution. A further purification is effected by warming the hydrochloride with sulphuric acid,  $D 1.5$ , at  $80^\circ$  to  $100^\circ$ ; this operation removes an oily impurity which lowers the melting point of the hydrochloride. Phosphoric acid may be substituted for sulphuric

acid, and the pinene hydrochloride is distilled off in steam and further purified by distillation or sublimation. G. T. M.

**Synthetical and Natural Phellandrenes.** IWAN L. KONDAKOFF and IWAN SCHINDELMEISER (*J. pr. Chem.*, 1907, [ii], 75, 141—145. Compare Abstr., 1903, i, 845; 1905, i, 801).—Synthetical phellandrene from carvomenthene dibromide resembles the natural hydrocarbon except in its b. p. and molecular rotation. It forms two nitroso-derivatives crystallising in stellate clusters, m. p. 102—103·5°, sparingly soluble in benzene, and in thin needles, m. p. 94—95°, which are more readily soluble; these resemble the  $\alpha$ - and  $\beta$ -nitroso-derivatives of  $\psi$ -phellandrene. The synthetical phellandrene is represented by the formula  $\text{CHPr}^s \begin{matrix} < \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} = \text{CH} > \end{matrix} \text{C} : \text{CH}_2$ .

The action of hydrogen chloride on  $\beta$ -phellandrene in glacial acetic acid solution leads to the formation of a monohydrochloride, m. p. 126°, and an *i-trans*dipentene dihydrochloride, m. p. 50°, b. p. 122·5—125°/16 mm. On treatment with alcoholic potassium hydroxide, the mixture of hydrochlorides obtained from  $\psi$ -phellandrene yields dipentene and a monochloro-compound. The bearing of these changes on the constitution of natural phellandrene and of thujene is discussed (compare Semmler, this vol., i, 145). G. Y.

**Constitution of Terpinene, Origanol, Sabinene, Dipentene, and their Derivatives.** FRIEDRICH W. SEMMLER (*Ber.*, 1907, 40, 751—757; this vol., i, 145).—Polemical. A reply to Wallach (this vol., i, 229). E. F. A.

**Presence of  $\beta$ -Phenylethyl Alcohol in the Essence of Pine-needles of Aleppo, Algeria.** ÉMILIE GRIMAL (*Compt. rend.*, 1907, 144, 434—435).—From the essential oil of pine-needles from Aleppo, Algeria, the author has isolated phenylethyl alcohol, hitherto detected only in the essential oils of neroli and of roses. E. H.

**Autoxidation of Colophony.** WILHELM FAHRION (*Zeitsch. angew. Chem.*, 1907, 20, 356—361. Compare Abstr., 1902, i, 165; 1904, i, 332).—Doubt having been cast on the author's earlier statements by Tschirch and Studer (Abstr., 1904, i, 79), the work has been repeated and verified. The compound,  $\text{C}_{20}\text{H}_{30}\text{O}_2$ , previously called sylvic acid is identical with abietic acid the formula,  $\text{C}_{19}\text{H}_{28}\text{O}_2$ , assigned to the latter by Mach being incorrect; the compound first formed by autoxidation is dioxyabietic acid,  $\text{C}_{20}\text{H}_{30}\text{O}_4$ , which finally passes into tetraoxyabietic acid,  $\text{C}_{20}\text{H}_{30}\text{O}_6$ . Dioxyabietic acid loses water when heated at 120°, also when treated with alcohol, alcoholic sulphuric acid, or an aqueous solution of sodium chloride. The anhydro-acids formed have not been isolated in a pure state, the portion soluble in light petroleum being called  $\alpha$ -anhydrodioxyabietic acid, the insoluble portion,  $\beta$ -anhydrodioxyabietic acid. These substances are also present in colophony which has been exposed in the powdered state for some time to the air. W. H. G.

**Glucoside Hydrolysed by Emulsin: Bakankosin from the Seeds of a Madagascar Strychnos.** EMILÉ BOURQUELOT and HENRI HERISSEY (*Compt. rend.*, 1907, 144, 575—577).—Laurent (*J. Pharm. Chim.*, 1907, [vi], 25, 225) by the application of Bourquelot's method (*Abstr.*, 1902, ii, 55) has ascertained that glucosides occur in the seeds of *Strychnos nux vomica*, *S. Ignatii*, and *S. bakanko* (? *S. vacacoua*). From the last-mentioned the authors by extracting the oil-free seeds with alcohol have obtained *bakankosin*, which forms large, colourless crystals, m. p. 157°, and remelts at about 200°, has  $[\alpha]_D -205.2^\circ$ . The glucoside contains nitrogen and is hydrolysed by boiling dilute mineral acids and slowly by emulsin, furnishing dextrose. Neither *bakankosin* nor its hydrolytic products are toxic. T. A. H.

**New Rhamnoside from Ipomœa Turpethum.** EMIL VOTOČEK and J. KASTNER (*Zeitsch. Zuckerind. Böhm.*, 1907, 31, 307—316).—Roots of *Ipomœa Turpethum* (the drug *radix turpethi*) contains, in addition to turpethin (Spirgatis, *Annalen*, 139, 41; and Kromer, *Abstr.*, 1893, i, 482), two other glucosides,  $\alpha$ -turpethin and in smaller quantity,  $\beta$ -turpethin.

$\alpha$ -Turpethin is readily soluble in light petroleum. When heated with barium hydroxide, the barium salt of  $\alpha$ -turpethic acid is obtained as a light yellowish-brown, amorphous mass readily soluble in water, m. p. 185°. The free acid when hydrolysed with 10% sulphuric acid yields a non-volatile hydroxy-acid,  $C_{16}H_{32}O_3$ , isomeric or identical with jalapic, ipomeolic and tampicolic acids; a volatile fatty acids, probably one of the valeric acids, and rhamnose.

$\beta$ -Turpethin is obtained as a yellow powder insoluble in light petroleum. When  $\beta$ -turpethic acid is hydrolysed, rhodose, dextrose, a non-volatile higher fatty acid, and volatile fatty acids are obtained.

N. H. J. M.

**Grasshopper-Green not Chlorophyll.** HANS PRZIBRAM (*Annalen*, 1907, 351, 44—51).—Spectroscopic examination having failed to decide the question of the identity of the colouring matter obtained from grasshoppers (*Locusta*, *Orphania*, *Mantis*, *Bacillus*, &c.) with chlorophyll, the author has investigated these substances chemically and now describes experiments which show that they are different.

The ethereal extract of grasshopper-green remains unchanged in the dark, but is bleached on exposure to light; when boiled with alcoholic potassium hydroxide, it becomes turbid and wine yellow, and on repeated boiling with fresh quantities of the alkali, deposits a yellow precipitate. A chlorophyll solution treated in the same manner becomes a deep green and yields a substance separating in black drops.

On addition of concentrated sulphuric acid, the grasshopper-green solution becomes a turbid yellow and after some time reddish-brown, whilst chlorophyll forms a clear, deep bluish-green solution gradually resuming its original yellowish-green colour.

The action of fuming nitric acid on grasshopper-green leads to the formation of a colourless, opalescent liquid, and of a whitish-green precipitate, but on chlorophyll to the formation of a turbid, yellow solution, gradually becoming transparent. G. Y.

**Constitution of Tannin. II.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1907, 40, 916—918. Compare Abstr., 1905, i, 914).—The acetyl product, m. p. 129°, obtained from tannin is a mixture of two penta-acetyltannins and not a hexa-acetyl derivative; Dekker's phthalic anhydride formula for tannin contains seven hydroxyl groups and would be expected to yield a hepta-derivative (Abstr., 1906, i, 686, 974). One of the *penta-acetyltannins*,  $C_{14}H_6O_9Ac_5$ , m. p. 203—206°, gives, on oxidation with potassium persulphate in acetic acid, ellagic acid, and on hydrolysis with dilute sulphuric acid, gallic acid; the other has m. p. 166°.

W. R.

**Cannabinol, the Active Constituent of Hashish.** MAX CZERKIS (*Annalen*, 1907, 351, 467—472).—On fractional distillation of the light petroleum extract of hashish, Fränkel (*Arch. exp. Path. Pharm.*, 1903, 49, 266) obtained a substance, cannabinol,  $C_{21}H_{30}O_2$ , b. p. 215°/0.5 mm., and found it to contain a phenolic hydroxyl and to form a trinitro-derivative. He considered, but could not prove, the second oxygen atom to be aldehydic. The author has undertaken the study of the constitution of cannabinol and gives an account of the few results so far obtained.

Cannabinol, b. p. 230°/0.1 mm. (corr.), on treatment with concentrated nitric acid in boiling glacial acetic acid solution, yields a *trinitroacetoxydicarboxylic acid*,  $OAc \cdot C_{19}H_{24}(NO_2)_3(CO_2H)_2$ , which is obtained as an amorphous, orange-yellow powder. The formation of the two carboxyl groups are ascribed to the oxidation of an aldehyde group and of a nucleus methyl, hence cannabinol may be represented by the formula,  $OH \cdot C_{19}H_{25}Me \cdot CHO$ . Oxidation by means of concentrated nitric acid in absence of a solvent leads to the formation of butyric and oxalic acids. On distillation with zinc dust, cannabinol yields a fluorescent oil, boiling at high temperatures. The results obtained suggest that the cannabinol is split into two complexes,  $C_{13}H_{18}O$  and  $C_8H_{12}O$ ; this requires further investigation. G. Y.

**Preparation of a Soluble, Crystalline, Nitrogenous Constituent of Ergot (*Secale cornutum*).** ERNST VAHLEN (*D.R.-P.* 175590 and 175591).—See Abstr., 1906, i, 876. G. T. M.

**Columbin.** I. TH. ULRICH (*Annalen*, 1907, 351, 363—371. Compare Hilger, Abstr., 1896, i, 623).—The investigation of columbin was undertaken as neither the formula nor the molecular weight of this substance had been determined with certainty by previous authors.

Columba root contains berberine and columbin, but contrary to the statements of previous authors, not columbic acid, which is formed when the only partially extracted root is treated with an aqueous alkali. The analytical results and molecular weight determination by the boiling point method show columbin to have the formula  $C_{28}H_{30}O_9$ , and to contain neither methoxy nor acetyl groups. It crystallises in rhombic needles, which are biaxial and show negative double refraction. G. Y.

**Columbin.** II. OTTO FREY (*Annalen*, 1907 351, 372—378. Compare preceding abstract).—The partially structural formula,

$C_{27}H_{26}O_5(OH)_2 \begin{smallmatrix} O \\ \diagup \diagdown \\ CO \end{smallmatrix}$ , is ascribed to columbin, since, contrary to Hilger's statement (Abstr., 1896, i, 623), when boiled with acetic anhydride and sodium acetate, it yields a *diacetyl* derivative,  $C_{28}H_{28}O_9Ac_2$ , crystallising in white needles, m. p.  $218^\circ$ , and, when boiled with potassium hydroxide and a small amount of water in a current of hydrogen, forms columbic acid,  $OH \cdot C_{27}H_{30}O_7 \cdot CO_2H$ , crystallising in rosettes, m. p.  $220^\circ$ . Columbin contains four ethylene linkings, as it forms an *additive* compound with 4 mols. of bromine in chloroform solution. The *product* obtained on heating columbin with dilute hydrochloric acid in a sealed tube at  $160^\circ$ , probably contains acetone, as it gives the iodoform reaction and is coloured a weak red by sodium nitroprusside and sodium hydroxide. G. Y.

**Picrotoxin.** FRANCESCO ANGELICO (*Gazzetta*, 1906, 36, ii, 645—654).—The author's researches deal with the isolation of picrotoxinin and picrotin from picrotoxin by treatment with either barium hydroxide or bromine (compare Meyer and Brugger, Abstr., 1899, i, 226) and with various derivatives obtained on oxidation.

Bromopicrotoxinin, which separates from solution when picrotoxin is suspended in boiling water and treated with bromine water, is readily oxidised by potassium permanganate in faintly alkaline solutions, yielding: (1) a small proportion of a white compound; (2) mainly a bromo-acid, which crystallises from water in white needles, m. p.  $248-250^\circ$  (decomp.), and may be identical with the acid obtained by Meyer and Brugger (*loc. cit.*) by decomposing bromopicrotoxinin dissolved in sodium hydroxide solution by means of acid. Its ethyl ester has m. p.  $170^\circ$  (decomp.). The acid is not attacked by potassium permanganate or dilute acids and does not reduce Fehling's solution. Oxidation with chromic acid in presence of dilute sulphuric acid oxidises it to another bromo-acid which crystallises from water in large, shining needles, decomposing at  $170-180^\circ$  and is sparingly soluble in water; this acid, when reduced by means of zinc and acetic acid, or boiled with alkali, or heated at its decomposition temperature, gives rise to products which react with phenylhydrazine.

Oxidation of picrotin by permanganate in a faintly acid solution yields: (1) a compound,  $C_{15}H_{18}O_8$  or  $C_{13}H_{18}O_7$ , crystallising from acetic acid in nacreous leaflets, m. p.  $254-255^\circ$ ; (2) a compound separating from acetic acid in small, mammillary crystals, m. p. about  $245^\circ$ . T. H. P.

**The Pyran Series. VI. 4-Pyran-2:6-dicarboxylic Acids.** EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. Chim.*, 1907, [iv], 1, 129—146. Compare Abstr., 1904, i, 762; 1906, i, 300; this vol., i, 147, 148, 181).—The  $\alpha$ -diketopimelic acids already described are converted by treatment with excess of sulphuric acid at the atmospheric temperature into 4-pyran-2:6-dicarboxylic acid,  $CH_2 \begin{smallmatrix} CH:C(CO_2H) \\ CH:C(CO_2H) \end{smallmatrix} O$ , which yields characteristic copper salts, usually containing water of crystallisation, which are stable at  $100^\circ$ , furnish unstable acid dichlorides, and cannot be transformed into the corresponding pyrans

or the related pyridine or pyrone derivatives. Similarly, they do not form additive compounds of the types described by Fosse (Abstr., 1903, i, 357; 1905, i, 607), but yield unstable dibromides, the two atoms of bromine being attached to the cyclic oxygen.

4-Pyran-2:6-dicarboxylic acid, obtained by the general method, crystallises from boiling water in long, colourless needles, and is infusible without decomposition. The *methyl* ester, m. p. 121°, crystallises from dilute alcohol; the *ethyl* ester, m. p. 37°, separates in crystals from a mixture of ether and light petroleum. On treatment with phosphorus pentachloride, the acid yields the *dichloride*, m. p. 112°, which crystallises from benzene and, when dissolved in ammonia solution, yields the corresponding *diamide*, m. p. about 250°, which is crystalline and insoluble in most organic solvents. The *dianilide*, similarly obtained, m. p. 255°, crystallises from hot formic acid. Pyran-2:6-dicarboxylic acid is not hydrolysed by boiling water, but is readily attacked by alkalis. When boiled with an aqueous solution of mercuric chloride it is completely hydrolysed to the corresponding  $\alpha$ -diketopimelic acid. It is assumed that in this reaction a molecule of mercuric chloride becomes attached to the cyclic oxygen, and that the derivative so formed is hydrolysed, forming diketopimelic acid, hydrochloric acid, and mercuric oxychloride, the two latter then regenerating mercuric chloride.

Pyran-2:6-dicarboxylic acid suspended in carbon disulphide or acetic acid, absorbs bromine, forming a *dibromide* which separates from ethyl acetate in colourless crystals containing 1 mol. of the ester. From the latter, the dibromide may be obtained as a colourless, crystalline powder, m. p. 205° (decomp.), by heating at 100°. It is readily soluble in water, which hydrolyses it, even in the cold, probably with the fission of the pyran ring. It displaces iodine from iodides in presence of alcohol or water, and in the former case regenerates the acid, which is also formed in presence of water under certain conditions. The reaction in alcohol may be employed as an iodometric method of estimating the dibromide. Attempts were made to form the corresponding pyryl salt by elimination of a mol. of hydrogen bromide, but these were unsuccessful, the elimination of the hydrogen bromide leading to complete decomposition. These results when compared with those of Fosse (*loc. cit.*), Bülow and Wagner (Abstr., 1901, i, 400), indicate that when the pyran nucleus is associated with the naphthalene nucleus the atoms of hydrogen in the 4-position with respect to the cyclic oxygen are more mobile than they are in simple pyran derivatives such as those now studied.

4-Methylpyran-2:6-dicarboxylic acid, m. p. about 260° (decomp.), obtained from  $\beta$ -methyl- $\alpha$ -diketopimelic acid, separates from warm water in small, colourless crystals. The *methyl* ester, m. p. 79–80°, crystallises from dilute alcohol; the *dibromide*, obtained by the addition of bromine to the acid suspended in acetic acid, decomposes about 190°, and separates from a mixture of ethyl acetate and light petroleum as a colourless powder. Its properties are similar to those of the dibromide of the lower homologue.

4-Ethylpyran-2:6-dicarboxylic acid, m. p. about 225° (decomp.), crystallises from warm acetic acid; the *methyl* ester, m. p. 64°, forms

faintly yellow, long needles from dilute alcohol. 4-n-Hexylpyran-2:6-dicarboxylic acid, m. p. 220° (decomp.), crystallises from dilute alcohol in long needles containing 1H<sub>2</sub>O. The methyl ester, m. p. 72°, crystallises from dilute alcohol in long, slender needles.

T. A. H.

**Rupture of the Furan Ring in Catechin.** STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1907, 40, 720—722. Compare this vol., i, 73).—Catechin tetramethyl ether is reduced by sodium and alcohol to an oil which by treatment with methyl sulphate yields *deoxyhydrocatechin pentamethyl ether* (2:4:6:3':4'-pentamethoxy-3-ethylidiphenylmethane), C<sub>6</sub>H<sub>5</sub>(OMe)<sub>2</sub>·CH<sub>2</sub>·C<sub>6</sub>H(OMe)<sub>3</sub>Et, m. p. 83—84°, which crystallises in colourless, prismatic needles. The same reducing agent converts benzhydrol into diphenylmethane; leucobenzophloroglucinol trimethyl ether into 2:4:6-trimethoxydiphenylmethane, m. p. 91—93°, and leucomaclurin pentamethyl ether into 2:4:6:3':4'-pentamethoxydiphenylmethane, m. p. 107—108°.

For a similar rupture of the coumaran ring, compare Alexander, (*Abstr.*, 1892, 1318).

C. S.

**Thiophen-2-and-3-carboxylic Acids.** ARNOLD F. HOLLEMAN and GERARDUS L. VOERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 514—524).—The authors have worked out a very satisfactory method of preparing the 2-acid. Acetothienone is first oxidised by alkaline permanganate to thienylglyoxylic acid, which is subsequently oxidised to thiophen-2-carboxylic acid by hydrogen peroxide. For the preparation of the 3-acid, 3-methylthiophen is chlorinated in the presence of phosphorus pentachloride; from the chlorinated product there is prepared an aldehyde, which is then oxidised to the thiophen-3-carboxylic acid. The yield of 3-acid obtained in this way is very poor, but is slightly better than that given by the older method, of preparation.

A study of the freezing and melting point curves for mixtures of the two acids shows that they form isomorphous mixtures, but that there is a gap in the mixture series from 25% to 61% of the 3-acid. The freezing point curve exhibits a eutectic at 42·5% of 3-acid and 111°. From the conductivity of aqueous solutions of the mixed acids, it appears unlikely that there is any condensation of the molecules of the two acids in such solutions.

The paper contains also crystallographic details of the two acids.

J. C. P.

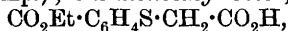
**Derivatives of Thionaphthen and Thioindigotin.** PAUL FRIEDLÄNDER (*Annalen*, 1907, 351, 390—420).—The resemblance of ketocoumaran, C<sub>6</sub>H<sub>4</sub> $\langle \begin{smallmatrix} \text{C(OH)} \\ \text{O} \end{smallmatrix} \rangle$ CH, to indoxyl, C<sub>6</sub>H<sub>4</sub> $\langle \begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix} \rangle$ CH, was studied by Friedländer and Neudörfer (*Abstr.*, 1897, i, 424; *Abstr.*, 1899, i, 675). The author has extended the investigation to the corresponding sulphur compound, C<sub>6</sub>H<sub>4</sub> $\langle \begin{smallmatrix} \text{C(OH)} \\ \text{S} \end{smallmatrix} \rangle$ CH, which is found to resemble, on the one hand, indoxyl, and on the other, α-naphthol.



[With G. MÜLLER.]—A detailed account of the work published previously (Abstr., 1906, i, 378). The following are new.

*o*-Thiocyanobenzoic acid,  $\text{CNS}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , formed by the action of cuprous thiocyanate on diazotised anthranilic acid, crystallises in stout, yellow needles, m. p. 154—155° (decomp.); the *methyl* ester crystallises in small, colourless needles, m. p. 76—77°, and is moderately volatile with steam. The acid is converted by evaporation with aqueous sodium sulphide into thiosalicylic acid, which with methyl sulphate and aqueous sodium hydroxide forms *o*-methylthiolbenzoic acid,  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ ; this crystallises in slender, colourless needles, m. p. 164°, and forms a *methyl* ester crystallising in colourless needles, m. p. 71°.

*o*-Carboxyphenylthiolacetic acid crystallises in small, white needles, m. p. 216—217° (decomp.); the *monoethyl* ester,



m. p. 137°. Whilst 2-hydroxythionaphthen-1-carboxylic acid readily decomposes, its *methyl* ester,  $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\rangle\text{S}\rangle\text{C}\cdot\text{CO}_2\text{Me}$ , formed by the action of sodium ethoxide on methyl *o*-carbmethoxyphenylthiolacetate, is stable; it crystallises in leaflets, m. p. 104°.

2-Methoxythionaphthen,  $\text{C}_6\text{H}_4\langle\text{C}(\text{OMe})\rangle\text{S}\rangle\text{CH}$ , prepared by the action

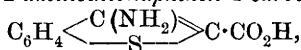
of methyl sulphate on 2-hydroxythionaphthen in alkaline solution, is obtained as a volatile oil, b. p. 260—261° (almost undecomp.), and has the characteristic odour of  $\alpha$ -methoxynaphthalene; the *picrate* forms brownish-red needles, m. p. 112°.

2-Hydroxythionaphthen resembles  $\alpha$ -naphthol in its behaviour towards diazo-salts, the resulting azo-dyes being slightly more yellow, but differs in forming red, crystalline *condensation products* with aromatic aldehydes, ketones, and diketones at high temperatures or in presence of condensing agents in glacial acetic acid solution. Thioindigotin,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{S}\rangle\text{C}:\text{C}\langle\text{CO}\rangle\text{S}\rangle\text{C}_6\text{H}_4$ , prepared by oxidation of 2-hydroxythionaphthen by means of potassium ferricyanide, ferric chloride, chromates, or organic nitro-compounds, melts above 280°, and on reduction yields a yellow *leuco*-compound which is soluble in aqueous alkalis, forming a solution which dyes textile fibres a fast red. On oxidation, 2-hydroxythionaphthen-1-carboxylic acid yields a bluish-violet dye, which can be converted into thioindigotin.

*Derivatives of Aminothionaphthens.*—[With A. LASKE.]—The constitution of 2-keto-3:4-dihydro-1:4-benzothiazine (Unger and Graff, Abstr., 1898, i, 96) is confirmed by formation of the substance on reduction of *o*-litrophenylthiolacetic acid. The ketodihydrobenzothiazine is prepared best by reduction of *o*-aniline disulphide with zinc dust and acid, and treatment of the filtered product with chloroacetic acid; when boiled with aqueous sodium hydroxides and neutralised with ice and hydrochloric acid, it yields *o*-aminophenylthiolacetic acid, which separates in colourless needles, but redissolves, forming the *hydrochloride*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$ , and gradually loses water being converted into the benzothiazine.

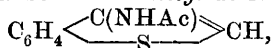
*o*-Cyanophenylthiolacetic acid,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by

the action of copper sulphate and potassium cyanide on diazotised *o*-aminophenylthiolacetic acid, crystallises from water in yellow needles, m. p. 140°, and forms easily soluble *alkali* salts; the *methyl* ester,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , crystallises in white, glistening needles, m. p. 87–88°. When heated with 2½% aqueous alkalis, the cyano-acid is converted into 2-aminothionaphthen-1-carboxylic acid,



which crystallises in brown needles, m. p. 140–146°, evolving carbon dioxide, and has an intense bluish-violet fluorescence in dilute solution; the *barium* salt,  $(\text{C}_9\text{H}_6\text{O}_2\text{NS})_2\text{Ba}$ , crystallises in silvery leaflets. When boiled with dilute acids, the acid evolves carbon dioxide and ammonia, forming thioindoxyl, and on treatment with nitrous acids yields a *diazo*-derivative which couples with  $\beta$ -naphthol, forming a red *azo-dye*.

When boiled with water, made alkaline, and distilled with steam, the amino-acid yields 2-aminothionaphthen,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{NH}_2) \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{CH}$ , which is obtained as a colourless oil, gradually resinifies when exposed to air, and is soluble in dilute acids; the *sulphate*, *hydrochloride*, and *platinichloride* are described. The *acetyl* derivative,



formed from the amine or from the amino-carboxylic acid, crystallises in colourless leaflets or needles, m. p. 169°. The base resembles  $\alpha$ -naphthylamine in giving a characteristic violet coloration with traces of nitrous acid in acetic acid solution, but differs in being readily converted by boiling water into thioindoxyl. G. Y.

**Preparation of Quinine Magnesium Oxyhalides.** VEREINIGTE CHININFABRIKEN, ZIMMER & Co. (D.R.-P. 178172).—Quinine magnesium oxyhalides are obtained on adding the alkaloid to a solution or suspension of a Grignard compound in ether, either at the ordinary or at higher temperatures. In this way the following derivatives were prepared: quinine magnesium oxychloride,  $\text{C}_{20}\text{H}_{28}\text{N}_3\text{O}\cdot\text{O}\cdot\text{MgCl}$ , and oxybromide. These compounds are very reactive and serve for the preparation of other quinine derivatives. G. T. M.

**Preparation of Quinine Esters.** VEREINIGTE CHININFABRIKEN, ZIMMER & Co. (D.R.-P. 178173. Compare preceding abstract).—By treating the quinine magnesium oxyhalides with acyl chlorides or acid anhydrides, the hydroxyl group of quinine becomes esterified and esters are produced.

Acetylquinine was obtained by heating these magnesium oxyhalides with acetyl chloride or acetic anhydride; quinine ethyl carbonate was prepared in a similar manner by means of ethyl chlorocarbonate, and benzoylquinine was produced from the organo-magnesium compounds and benzoyl chloride. G. T. M.

**Constitution of Hordenine.** EUGENE LEGER (*Compt. rend.*, 1907, 144, 488–491).—The presence of the groups  $\text{OH}\cdot\text{C}_6\text{H}_4^-$  and

$\text{-NMe}_2$  in the formula  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$  ascribed to hordenine has already been proved (Abstr., 1906, i, 761; this vol., i, 151). Experimental proof is now given of the presence of the chain  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  in a para-position to the hydroxyl. When hordenine methiodide in sodium hydroxide solution is treated with methyl sulphate, methyl iodide distils, showing that the attack proceeds further than mere methylation of the phenolic hydroxyl, and in fact the product is a mixture of methyl hordenine methiodide (this vol., i, 234) and hordenine methyl sulphate. Methyl hordenine methiodide is converted by moist silver oxide into methyl hordenine methoxide, which decomposes when heated in a vacuum at  $120\text{--}130^\circ$ , yielding trimethylamine and *p*-vinylanisole described by Perkin (Trans., 1877, 668; 1878, 211). The formation of the latter demonstrates the presence in hordenine of the  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  group para to the hydroxyl, and leads to the supposition that the phenol obtained in the decomposition of hordenine methoxide is *p*-vinylphenol or its polymeride. A solution of the normal tartrate of hordenine is apparently not attacked by either neutral hydrogen peroxide or by the oxidising enzyme tyrosinase, but in the presence of both peroxide and enzyme, a stable, cherry-red coloration begins to appear in ten to fifteen minutes. The reaction is accelerated by addition of a few drops of 1% sodium carbonate solution.

E. H.

[Carnosine and Ignotine.] FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1907, 50, 445—448. Compare Amiradžibi and Gulewitsch, Abstr., 1900, i, 516; Gulewitsch, this vol., i, 264).—The identity of carnosine and ignotine is not regarded by the author as being established. The two appear to react differently with silver nitrate, fixed alkalis, and ammonia.

J. J. S.

**Muscle Extract. VIII. Formation of Histidine by the Decomposition of Carnosine.** WLADIMIR VON GULEWITSCH (*Zeitsch. physiol. Chem.*, 1907, 50, 535—537).—Carnosine is a histidine derivative, since when hydrolysed with barium hydroxide solution it yields this base. The other product of hydrolysis is probably alanine, and the hydrolysis may then be represented by the equation:  $\text{C}_9\text{H}_{14}\text{O}_3\text{N}_4 + \text{H}_2\text{O} = \text{C}_6\text{H}_9\text{O}_2\text{N}_3 + \text{C}_3\text{H}_7\text{O}_2\text{N}$ .

J. J. S.

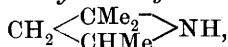
**Preparation of the Alkyl Bromides of the Alkyl Ethers of Morphine.** J. D. RIEDEL (D.R.-P. 175796. Compare Abstr., 1906, i, 692).—It is now found that the alkyl bromides of the alkyl ethers of morphine can be obtained by adding a metallic bromide to the aqueous solution of the dialkyl sulphate of the morphine ether, concentrating or evaporating to dryness and extracting the residue with acetone, or methyl or ethyl alcohol.

Codeine dissolved in chloroform was treated with ethyl sulphate, the solution evaporated, the residue treated with ether, and the resulting oil dissolved in water containing potassium bromide; the aqueous solution was then evaporated to dryness and the final residue extracted with methyl or ethyl alcohol. The codeine ethobromide was

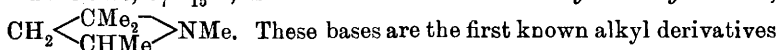
isolated by concentrating the alcoholic solution. Ethylmorphine, ethobromide, and codeine methobromide were prepared similarly.

G. T. M.

**Derivatives of Diacetonalalkamines.** V. MORITZ KOHN *Annalen*, 1907, 351, 134—150. Compare Abstr., 1904, i, 378, 932, 933; 1905, i, 928).—Kahan (Abstr., 1897, i, 494) having shown that diacetonalalkamine combines with hydrogen bromide forming  $\delta$ -bromo- $\beta$ -amino- $\beta$ -methylpentane hydrobromide, it was to be expected that methyl diacetonalalkamine,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NHMe}$ , would be converted similarly into  $\delta$ -bromo- $\beta$ -methylamino- $\beta$ -methylpentane hydrobromide,  $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NHMe}\cdot\text{HBr}$ . That this substance is contained in the resinous product of the reaction is shown by its conversion on treatment with concentrated aqueous potassium hydroxide into a volatile mono-acid base,  $\text{C}_7\text{H}_{15}\text{N}$ , the analogue of which,  $\text{C}_6\text{H}_{13}\text{N}$ , is formed by the action of cooled 33% potassium hydroxide on  $\delta$ -bromo- $\beta$ -amino- $\beta$ -methylpentane hydrobromide. This base is 2:4:4-trimethyltrimethylenimine,

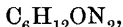


as it forms a nitroso-derivative, a dithiocarbamate, and a quaternary iodide, which is identical with the additive compound of methyl iodide and the base,  $\text{C}_7\text{H}_{15}\text{N}$ ; this must be 1:2:4:4-tetramethyltrimethylenimine,



These bases are the first known alkyl derivatives of trimethylenimine (Howard and Marckwald, Abstr., 1899, i, 749). They differ from ethylenimine (Gabriel and Stelzner, Abstr., 1896, i, 121) and *N*-methylethylenimine (Marckwald and Frobenius, Abstr., 1902, i, 22) in that the ring remains intact on alkylation.

2:4:4-Trimethyltrimethylenimine forms a colourless oil, b. p. 86—88°, which is miscible with water, developing heat, and has an intense amine-like odour; the aurichloride,  $\text{C}_6\text{H}_{13}\text{N}\cdot\text{HAuCl}_4$ , forms glistening needles, m. p. 124—126°; the picrate,  $\text{C}_{12}\text{H}_{16}\text{O}_7\text{N}_4$ , forms needles and plates, m. p. 140—143°. The nitroso-derivative,



is obtained as an aromatic, yellow oil, b. p. 94—95°/20—21 mm. or 198—201°/751 mm. 2:4:4-Trimethyltrimethylenimine, 2:4:4-trimethyltrimethyleniminedithiocarbamate,  $\text{C}_{13}\text{H}_{26}\text{N}_2\text{S}_2$ , prepared by the action of carbon disulphide on the base in cooled ethereal solution, forms white crystals, m. p. 130—133°.

1:2:4:4-Tetramethyltrimethylenimine, b. p. 93—97°, closely resembles the 2:4:4-trimethyl base; the aurichloride,  $\text{C}_7\text{H}_{15}\text{N}\cdot\text{HAuCl}_4$ , m. p. 148—152°; the picrate,  $\text{C}_{18}\text{H}_{18}\text{O}_7\text{N}_4$ , crystallises in slender needles, m. p. 196° (decomp.); the platinichloride,  $(\text{C}_{17}\text{H}_{15}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$ , was analysed.

The methiodide,  $\text{CH}_2\left\langle\begin{array}{c}\text{CMe}_2 \\ \text{CHMe}\end{array}\right\rangle\text{NMe}_2\text{I}$ , formed by the action of methyl iodide on the 2:4:4-trimethyl- or 1:2:4:4-tetramethyl-base in ethereal solution, on successive treatment with silver chloride and auric chloride forms the aurichloride,  $\text{C}_8\text{H}_{17}\text{N}\cdot\text{HAuCl}_4$ , which is obtained as a yellow, crystalline powder, m. p. 176° (decomp.);

the *platinichloride*,  $(C_8H_{17}N)_2H_2PtCl_6$ , forms a yellowish-red precipitate.

On successive treatment with ethyl iodide and silver and auric chlorides, the 1 : 2 : 4 : 4-tetramethyl-base forms the *aurichloride*,

$C_9H_{19}N, HAuCl_4$ ,  
m. p. 161—163° (decomp.); the *platinichloride*,  $(C_9H_{19}N)_2H_2PtCl_6$ , forms glistening, granular crystals.

The *ammonium base*, formed by the action of moist silver oxide on the methiodide, loses  $H_2O$  when distilled, yielding an unsaturated base,  $C_8H_{17}N$ , which is obtained as a colourless, mobile liquid, b. p. 136—139°/750 mm.; the *aurichloride*,  $C_8H_{17}N, HAuCl_4$ , is decomposed by hot water; the *platinichloride*,  $(C_8H_{17}N)_2H_2PtCl_6$ , light yellow crystals, intumescing when heated; the *picrate*,  $C_{14}H_{20}O_7N_4$ , thin needles, m. p. 121—124°. With methyl iodide the unsaturated base forms an *additive* compound, from which are obtained an *aurichloride*,  $C_9H_{19}N, HAuCl_4$ , as a yellow precipitate, and a *platinichloride*,

$(C_9H_{19}N)_2H_2PtCl_6$ ,  
crystallising in prisms or needles. In the same manner, by way of the *additive* compound of ethyl iodide and the unsaturated base, are formed the *aurichloride*,  $C_{10}H_{21}N, HAuCl_4$ , obtained as a yellow precipitate, and the *platinichloride*,  $(C_{10}H_{21}N)_2H_2PtCl_6$ , crystallising in needles.

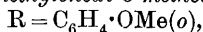
When treated with silver oxide and water, the methyl iodide *additive* product of the unsaturated base yields an *ammonium base*,  $C_6H_{11}NMe_3 \cdot OH$ , which on distillation with water decomposes, forming trimethylamine, water, and a *hydrocarbon*,  $C_6H_{10}$ ; this is a colourless, mobile liquid, b. p. 74—75°. G. Y.

**Formation of 1-Phenyl-5-Methylpyrrolidone by the Simultaneous Electrolytic Reduction of Lævulic Acid and Nitrobenzene.** BRUNO EMMERT (*Ber.*, 1907, 40, 912—916).—The author expected that  $\gamma$ -anilinovaleric acid would be one of the products obtained on reducing nitrobenzene and lævulic acid in an electrolytic cell using a mercury cathode. This is not formed, but a 40% yield of 1-phenyl-5-methylpyrrolidone,  $C_4NH_5MePhO$ , its internal anhydride is obtained as a colourless oil, b. p. 320.5° (corr.)/752 mm., 178.5°/15 mm. By cooling with solid carbon dioxide, it solidifies, m. p. 52—54°, but the liquid exhibits the phenomena of supercooling to a marked extent. It behaves like pyrrolidone (compare Tafel, *Abstr.*, 1900, i, 557), and its constitution was established by preparing it from  $\gamma$ -bromovaleric acid and aniline. W. R.

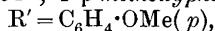
**Steric Hindrance of Ring-formation by *o*-Substituting Groups.** MAX SCHOLTZ and E. WASSERMANN (*Ber.*, 1907, 40, 852—858. Compare *Abstr.*, 1898, i, 305, 383, 471, 565; 1899, i, 881; Scholtz and Friemehl, *Abstr.*, 1899, i, 541; v. Braun, *Abstr.*, 1904, i, 841).—It has been shown previously that *o*-xylylene dibromide and trimethylene dibromide react with *o*-substituted primary aromatic amines, forming substituted diamines, but with other primary aromatic amines forming cyclic compounds. It is now found that  $\alpha$ -dibromopentane behaves towards primary aromatic amines in the same manner; the products formed with *m*- and *p*-substituted amines being

derivatives of piperidine,  $\text{CH}_2\langle\text{CH}_2\cdot\text{CH}_2\text{CH}_2\cdot\text{CH}_2\rangle\text{NR}'$ , whilst those with *o*-substituted amines are pentamethylenediamines,  $\text{NHR}'[\text{CH}_2]_5\cdot\text{NHR}$ . *o*-Naphthylamine behaves as an *o*-,  $\beta$ -naphthylamine as a *m*- or *p*-substituted amine. The reaction takes place, but only slowly, with *oo*-disubstituted amines such as *o*-amino-*m*-xylidine. The following new substances have been prepared.

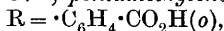
*Pentamethylenedi-o-toluidine*,  $\text{R} = \text{C}_7\text{H}_7(o)$ , colourless prisms, m. p. 76—77°; b. p. 290—291°/20 mm., forms a sparingly soluble *sulphate*; *1-m-tolylpiperidine*,  $\text{R}' = \text{C}_7\text{H}_7(m)$ , colourless prisms, m. p. 126°; *1-p-tolylpiperidine*, needles, m. p. 122°; *pentamethylenedi-o-nitroaniline*,  $\text{R} = \text{NO}_2\cdot\text{C}_6\text{H}_4(o)$ , red needles, m. p. 55—57°; *1-p-nitrophenylpiperidine*,  $\text{R}' = \text{NO}_2\cdot\text{C}_6\text{H}_4(o)$ , yellow needles, m. p. 114°; *pentamethylenedi-cumidine*,  $\text{R} = \text{C}_6\text{H}_2\text{Me}_3[\text{Me}_3 = 2:4:5]$ , colourless leaflets, m. p. 115—116°; *pentamethylenedi-a-naphthylamine*,  $\text{R} = \text{C}_{10}\text{H}_7$ , yellow needles, m. p. 61°; *1-β-naphthylpiperidine*,  $\text{R}' = \text{C}_{10}\text{H}_7$ , leaflets, m. p. 54°; *pentamethylenedi-o-chloroaniline*,  $\text{R} = \text{C}_6\text{H}_4\text{Cl}(o)$ , colourless crystals, m. p. above 300°; *1-p-chlorophenylpiperidine*,  $\text{R}' = \text{C}_6\text{H}_4\text{Cl}(p)$ , scales, m. p. 208°; *pentamethylenedi-o-methoxyaniline*,



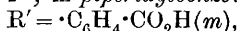
colourless prisms, m. p. 131°; *1-p-methoxyphenylpiperidine*,



glistening crystals, m. p. 37°; *pentamethylenedi-o-carboxyaniline*,



slender needles, m. p. 171°; *m-piperidylbenzoic acid*,



colourless needles, m. p. 227°, forms yellow solutions in aqueous alkalis; the *barium* and *lead* salts are yellow and dissolve to a colourless solution in acetic acid; *p-piperidylbenzoic acid*, colourless needles, m. p. 188°; *pentamethylenedi-2 m-xylidine*,  $\text{R} = \text{C}_6\text{H}_3\text{Me}_2[\text{Me}_2 = 2:6]$ , colourless leaflets, m. p. 228°. G. Y.

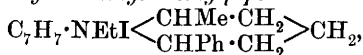
**Stereoisomerism of Compounds containing a Quinquevalent Asymmetric Nitrogen Atom and an Asymmetric Carbon Atom.** MAX SCHOLTZ and E. WASSERMANN (*Ber.*, 1907, 40, 685—690).—It had been shown previously (*Abstr.*, 1904, i, 1044; 1905, i, 296, 473) that, when an asymmetric nitrogen atom is generated in an optically active compound which owes its optical activity to the presence of an asymmetric carbon atom, the case is exactly the same as when an additional asymmetric carbon atom is generated in a compound, already optically active in virtue of asymmetric carbon; two compounds are formed, differing from one another in solubility, melting point, and specific rotation.

*2-Phenyl-6-methyl-1-ethylpiperidine* has two asymmetric carbon atoms. The addition of benzyl iodide to the active forms of this compound has been studied—a change in which the nitrogen atom becomes asymmetric

Since there are two asymmetric carbon atoms in *dl*-2-phenyl-6-methylpiperidine, two *dl*-compounds are known. The one, which forms the more sparingly soluble hydrochloride (m. p. 215—216°), was resolved into its optically active components as described previously (*Abstr.*, 1901, i, 41).

1-2-Phenyl-6-methyl-1-ethylpiperidine,  $\text{NEt} \left\langle \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CHPh} \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{CH}_2$ , obtained by the ethylation of the *sec.-l*-base in question with ethyl iodide and potassium hydroxide, has b. p.  $258^\circ/760$  mm. and  $131^\circ/12$  mm. It has  $D_4^{20}$  0.9519 and  $[\alpha]_D - 64.5^\circ$ . When the mixture with benzoyl iodide remains at the ordinary temperature for two days, a mixture of two compounds is formed, which may be separated by treatment with a mixture of chloroform and ether.

$\alpha$ -1-2-Phenyl-1-benzyl-6-methyl-1-ethylpiperidinium iodide,



has m. p.  $184^\circ$ , and in methyl-alcoholic solution has  $[\alpha]_D^{15} - 7.35^\circ$  ( $c = 6.8$ ).

$\beta$ -1-2-Phenyl-1-benzyl-6-methyl-1-ethylpiperidinium iodide has m. p.  $205^\circ$ , and is formed in larger amount than the  $\alpha$ -compound; in methyl alcoholic solution has  $[\alpha]_D^{15} - 11.03^\circ$  ( $c = 6.8$ ).

*d*-2-Phenyl-6-methyl-1-ethylpiperidine has b. p.  $257^\circ$ ,  $D^{20}$  0.9517,  $[\alpha]_D^{15} + 64.1^\circ$ . The mixture of piperidinium iodides obtained from it by the action of benzyl iodide was separated by means of chloroform, the more sparingly soluble of the two being  $\alpha$ -*d*-2-phenyl-1-benzyl-6-methyl-1-ethylpiperidinium iodide, m. p.  $184^\circ$ . In methyl-alcoholic solution it has  $[\alpha]_D^{15} + 7.35^\circ$  ( $c = 6.8$ ).

$\beta$ -*d*-2-Phenyl-1-benzyl-6-methyl-1-ethylpiperidinium iodide has m. p.  $205^\circ$  and  $[\alpha]_D^{15} + 11.03^\circ$  ( $c = 6.8$ ) in methyl-alcoholic solution.

When equal amounts of the *d*- and *l*- $\alpha$ -compounds are mixed in methyl-alcoholic solution and the product crystallised from water, a product with m. p.  $202^\circ$  was obtained. When a similar experiment was carried out with the *d*- and *l*- $\beta$ -compounds, the product had the same m. p. as that of its components, namely,  $205^\circ$ . A. McK.

Diphenyl-4-pyridylcarbinol. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1105—1108).—Diphenyl-4-pyridylcarbinol,  $\text{C}_5\text{NH}_4 \cdot \text{CPh}_2 \cdot \text{OH}$ , prepared by the action of 4-benzoylpyridine on magnesium phenyl bromide in ethereal solution, crystallises from ethyl or amyl acetate as a granular powder, m. p.  $203^\circ$ , and is sparingly soluble in the ordinary solvents; it acts as a base and dissolves readily in dilute mineral acids. The *platinichloride*,  $(\text{C}_{18}\text{H}_{15}\text{ON})_2, \text{H}_2\text{PtCl}_6$ , m. p.  $188$ — $190^\circ$  (decomp.), and the *picrate*, separating from benzene with benzene of crystallisation, have been prepared.

Attempts to prepare salts of diphenyl-4-pyridylcarbinol, corresponding with the basic dyes, were unsuccessful. The carbinol dissolves, however, in concentrated sulphuric acid, giving an intense red coloration which slowly changes to a dirty brown. With a concentrated solution of zinc chloride containing hydrochloric acid, the carbinol also gives an intensely red solution, which deposits the carbinol unchanged on addition of ammonia, or becomes brown if kept.

T. H. P.

Action of Chloroform on 2-Methylindole and on Certain Pyrroles. GIUSEPPE PLANCHER and U. PONTI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 130—135).—When 2-methylindole is acted on by sodium ethoxide and chloroform under the conditions given by Mag-

nanini (Abstr., 1887, 1113), it yields: (1) the chloromethylquinoline, described by Magnanini (*loc. cit.*), and (2) 2-methylindole-3-aldehyde (2-methyl-3-methylalindole),  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CMe} \end{smallmatrix} \text{C} \cdot \text{CHO}$ , which crystallises from ethyl acetate in rosettes of slender, colourless needles, m. p. 198°. These crystals gradually change into approximately cubical crystals having the same melting point, but whether the two forms are dimorphically or tautomerically related is undecided. 2-Methylindole-3-aldehyde dissolves in water, alcohol, ether, or concentrated potassium hydroxide solution, and gives a faint red coloration with a pine splinter and hydrochloric acid, whilst when it is boiled with dilute sulphuric acid the latter first turns yellow, then red, and ultimately deposits orange-red, acicular crystals (compare Ellinger, Abstr., 1906, i, 696). The aldehyde does not reduce Fehling's solution, but gives a semicarbazone,  $\text{C}_{11}\text{H}_{12}\text{ON}_4$ , m. p. 224° (decomp.), and a p-nitrophenylhydrazone, m. p. 273°, or 250° if placed in a bath at that temperature; it forms a picrate, m. p. 181° (decomp.). Oxidation of the aldehyde with faintly alkaline permanganate solution at about 60° yields acetylanthranilic acid (o-acetylaminobenzoic acid), whilst in the cold, traces of 2-methylindole-3-carboxylic acid are also obtained.

The yield of 2-methylindole-3-aldehyde obtained in the above reaction may be increased by gradually adding an aqueous alcoholic solution of potassium hydroxide to a boiling solution of 2-methylindole in 95% alcohol containing excess of chloroform. T. H. P.

#### Steric Hindrance of Alkyl Substituted Cinchonic Acids.

HANS MEYER (*Monatsh.*, 1907, 28, 33—46. Compare Abstr., 1906, i, 107, 137, 358).—It has been shown previously that the stability of methyl esters or ethers may differ considerably from that of the corresponding ethyl compounds. It is now found that the differences in stability may outweigh the effect of steric hindrance, the hydrolysis of certain methyl esters in which steric hindrance must be assumed taking place more easily than that of analogously constituted ethyl esters not sterically hindered.

The work of Ornstein (*Diss., Berlin*, 1904) and of Mulert (Abstr., 1906, i, 534) is criticised and attention drawn to the author's papers (*loc. cit.*). The action of methyl alcohol on methyl 2-chloro-3-methylcinchonate at 100° leads to the formation of the 2-hydroxy- and not of the 2-methoxy-ester. Butyrylisatin crystallises in long, yellow needles, m. p. 136°.

The following esters are prepared from the acids by the thionyl chloride method: methyl 2-phenylcinchonate,  $\text{C}_9\text{NH}_5\text{Ph} \cdot \text{CO}_2\text{Me}$ , forms colourless leaflets, m. p. 58°, becomes electrified when rubbed, and is converted by aqueous ammonia into the sparingly soluble amide, m. p. 155°; ethyl 2-hydroxy-3-methylcinchonate,  $\text{OH} \cdot \text{C}_9\text{NH}_4\text{Me} \cdot \text{CO}_2\text{Et}$ , crystallises in long needles, m. p. 167°; ethyl 2-hydroxy-3-ethylcinchonate crystallises in long needles, m. p. 133—134°; the chloride of this acid, m. p. 100°, can be recrystallised from boiling alcohol almost without change.

Hydrolysis experiments with these and similar substituted cinchonates on the water-bath gave the following results; the figures are



the percentages hydrolysed by *N*-sodium carbonate and by 5% aqueous potassium hydroxide respectively: methyl cinchonate, 12, 100; methyl 3-methylcinchonate, 0, 0; methyl 2-hydroxycinchonate, 90, 100; ethyl 2-hydroxycinchonate, 60, 100; methyl 2-hydroxy-3-methylcinchonate, 45, 100; ethyl 2-hydroxy-3-methylcinchonate, 7, 100; methyl 2-hydroxy-3-ethylcinchonate, 18, 100; ethyl 2-hydroxy-3-ethylcinchonate, 0, 100.

Contrary to Fischer's rule that the presence of a group, which forms a salt with the hydrolysing agent, retards the hydrolysis (Abstr., 1899, i, 262), the hydrolysis of the cinchonates is favoured by the introduction of a hydroxyl in position 2. The influence of *o*-substitution also is noticeable; the stability of methyl 2-phenylcinchonate is remarkable in view of Findlay and Turner's observations on the acceleration of the rate of hydrolysis by the introduction of phenyl groups (Trans., 1905, 87, 747). Stress is laid on the obvious increase in the stability of the carboxyalkyl consequent on the substitution of ethyl for methyl. G. Y.

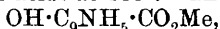
**Wandering of Alkyl Groups in the Pyridine Series.**  
HANS MEYER (*Monatsh.*, 1907, 28, 47—62. Compare Abstr., 1906, i, 604).—The 2- and 4-*O*-ethers and the 4-carboxyalkyl derivatives of pyridine and quinoline are capable of undergoing isomeric change into the corresponding *N*-alkyl compounds. In the present work the behaviour of derivatives of 2-hydroxyquinoline-3-, 2-hydroxyquinoline-4-, and 2-hydroxypyridine-5-carboxylic acids has been studied and the following general conclusions are drawn from the results.

When heated, 2-methoxy- or 2-ethoxy-3-carboxylic acids of the pyridine series lose the methyl or ethyl group and form anhydrides together with small amounts of the alkylated pyridones. 2-Alkyl-oxy-4-carboxylic acids of the pyridine series are converted by the action of heat into the corresponding hydroxy-esters, together with small amounts of the free acids. 2-Alkyl-oxy-5-carboxylic acids, when heated, yield the free hydroxy-acids, together with small amounts of the alkylated pyridones. In no case does the isomeric change of the *O*- into the *N*-ether, typical of other 2-alkyloxy-pyridines, take place if a carbonyl or, as in methyl 2-methoxynicotinate, a carboxyalkyl group is present in the molecule. This behaviour is directly contrary to that of the ester-acids (compare Kirpal, Abstr., 1902, i, 564; 1903, i, 117, 852).

*Methyl 2-methylcinchonate*,  $C_6H_4 \begin{matrix} \text{C}(\text{CO}_2\text{Me})\cdot\text{CH} \\ \text{N}=\text{CMe} \end{matrix}$ , m. p. 61—62°,

prepared by the action of diazomethane on the acid, decomposes partially when distilled. The *amide* crystallises in colourless needles, m. p. 238°, and is converted by the action of bromine and dilute sodium hydroxide into 4-amino-2-methylquinoline.

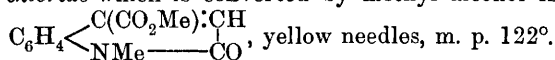
2-Hydroxyquinoline-3-carboxylic acid is prepared best from *o*-nitrobenzylidenemalononic acid (Stuart, Trans., 1888, 53, 143), which is formed almost quantitatively by heating *o*-nitrobenzaldehyde with malonic and glacial acetic acids at 135°. The *methyl* ester,



crystallises in long needles, m. p. 186°. Chlorination of the acid leads

to the formation of 2-chloroquinoline-3-carboxylic acid (Friedländer and Göhring, Abstr., 1884, 1019) and a substance insoluble in aqueous alkalis. 2-Methoxyquinoline-3-carboxylic acid,  $\text{OMe} \cdot \text{C}_9\text{NH}_5 \cdot \text{CO}_2\text{H}$ , formed by heating the 2-chloro-acid with sodium methoxide and methyl alcohol at  $100^\circ$ , crystallises in colourless needles, m. p.  $182^\circ$ , and when heated above its melting point yields the anhydride obtained by Friedländer and Göhring (*loc. cit.*) from 2-ethoxyquinoline-3-carboxylic acid.

It is shown that Königs and Körner's methyl derivative of hydroxycinchonic acid is methyl 2-hydroxycinchonate (Abstr., 1884, 84; Claus, Abstr., 1892, 1488; Roser, Abstr., 1893, i, 177; 1895, i, 155; Decker, Abstr., 1893, i, 365). When treated with thionyl chloride, Roser's 1-methyl-2-quinolone-4-carboxylic acid yields a crystalline chloride which is converted by methyl alcohol into the methyl ester,



2-Methoxypyridine-5-carboxylic acid,  $\text{CH} \begin{array}{l} \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \\ \text{CH} = \text{C}(\text{OMe}) \end{array} \text{N}$ , formed by heating the 2-chloro-acid with sodium methoxide and methyl alcohol at  $110^\circ$ , crystallises in colourless needles, m. p.  $173^\circ$ , and at temperatures above  $260^\circ$  decomposes, forming 2-hydroxypyridine-5-carboxylic acid and traces of 2-methoxypyridine. The methyl ester,  $\text{OMe} \cdot \text{C}_5\text{NH}_3 \cdot \text{CO}_2\text{Me}$  (Abstr., 1906, i, 108), m. p.  $42^\circ$ , b. p.  $256^\circ$ , prepared by the action of diazomethane on the methoxy-acid, remains unchanged when heated at  $330^\circ$ . G. Y.

**Action of Thionyl Chloride on Quinaldinic (Quinoline-2-carboxylic) Acid.** HANS MEYER and RICHARD TURNAU (*Monatsh.*, 1907, 28, 153—162. Compare Meyer, Abstr., 1905, i, 155, 666; Besthorn and Ibele, Abstr., 1905, i, 612; 1906, i, 605).—Contrary to the repeated statements of Besthorn and Ibele, the action of thionyl chloride, whether freshly prepared or distilled from a previous reaction mixture, on quinoline-2-carboxylic acid leads to the formation of only one product, quinoline-2-carboxylic chloride, m. p.  $175^\circ$  (decomp.). The excess of thionyl chloride may be removed by treatment with formic acid with which it reacts energetically, whilst the quinoline-2-carboxylic chloride reacts with formic acid only slowly. The carboxylic chloride forms the ester in an 80%, and the amide in a 75%, yield, whereas if it were an anhydride hydrochloride as suggested by Besthorn and Ibele, it could not form more than 50% of the ester or amide.

Pyridine- and quinoline-carboxylic acids are isolated from their salts most readily by conversion into the hydrochloride or nitrate, and addition of 1 mol. of sodium hydroxide. G. Y.

**Behaviour of Arylated Naphthylamines with Formaldehyde and with Nitrous Acid.** HANS T. BUCHERER and FRANZ SEYDE (*Ber.*, 1907, 40, 859—865. Compare Abstr., 1905, i, 585).—The product, obtained by treating a hot alcoholic solution of an aryl-naphthylamine with formaldehyde and a small quantity of hydrochloric acid, depends on the nature of the aryl group. If this is a para-

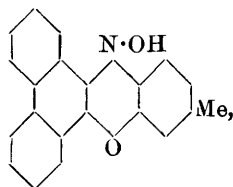
substituted benzene nucleus, the product is a dihydronaphthacridine derivative, whereas, aryl-naphthylamines containing a nucleus with a free para-position, or those of the  $\alpha$ -series, yield dinaphthylmethane derivatives. Thus, *p*-anisyl- $\beta$ -naphthylamine yields 10-methoxy-1:2-dihydronaphthacridine,  $C_{18}H_{15}ON$ , m. p.  $260^\circ$ , and *p*-tolyl- $\beta$ -naphthylamine yields Ullmann's 10-methyl-1:2-dihydronaphthacridine in a pure state, m. p.  $212^\circ$  (compare Abstr., 1900, i, 360), which does not possess basic properties, and is oxidised readily to the corresponding acridine. On the other hand, phenyl- $\beta$ -naphthylamine yields an amorphous substance,  $C_{33}H_{26}N_2$ , m. p.  $80^\circ$ , which has basic properties, couples with diazo salts, and appears to be diphenyldiaminodinaphthylmethane. *p*-Tolyl- $\alpha$ -naphthylamine yields a substance,  $C_{35}H_{30}N_2$ , of a similar character to the preceding dinaphthylmethane derivative.

By the action of nitrous acid on a hot alcoholic solution of *p*-tolyl- $\beta$ -naphthylamine, a substance,  $C_{17}H_{13}N$ , m. p.  $223$ — $224^\circ$ , is obtained, which separates from benzene in red needles, forms a white, crystalline hydrochloride, and an acetyl derivative, m. p.  $231$ — $232^\circ$ ; the examination of the substance is in progress. C. S.

**The Oxime of 1-Methylcinchotoxine and its Transformation by the Beckmann Reaction.** WILHELM KOENIGS (*Ber.*, 1907, 40, 648—652)—[with KARL BERNHART and JOSEF IBELE.]—Rabe's formula for cinchotoxine,  $C_9NH_6 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_7H_{12}N$  (this vol., i, 78; compare also Abstr., 1905, i, 811), where  $C_9NH_6$  is the quinoline and  $C_7H_{12}N$  the 3-vinylpiperidine nucleus, differs from Koenigs, in that it has the carbonyl adjacent to the quinoline group, whereas the author supposed it to be between the two methylene groups. In order to decide this, the oxime of 1-methylcinchotoxine, m. p.  $70$ — $110^\circ$ , was prepared, and on hydrolysing the product from the Beckmann change a 6% yield of cinchoninic acid and a 43% yield of 4-aminoquinoline (Hoogewerff and van Dorp, Abstr., 1892, i, 725) was obtained which supports Rabe's formula for cinchotoxine. W. R.

**Azoxonium Compounds. IV. Phenanthraquinone Azoxine Derivatives.** FRIEDRICH KEHRMANN and ABERT WINKELMANN (*Ber.*, 1907, 40, 613—623. Compare Abstr., 1901, i, 484, 1905, i, 930, 949).—This is a continuation of the inquiry into the action of aminophenols on phenanthraquinone including the aminocresols and nitro-*o*-aminophenols; all show similar changes, the colourless  $\psi$ -bases giving rise to intensely coloured azoxonium salts and yellow  $\psi$ -salts.

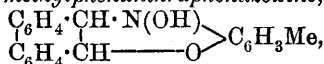
Phenanthraquinone and *o*-amino-*m*-cresol in boiling benzene condense to form the  $\psi$ -base, crystallising in white needles decomposing at  $200^\circ$  without melting. When this is dissolved in a mixture of 2 parts alcohol and 1 part benzene and the bulk of the benzene removed by boiling, almost colourless aggregates of needles, m. p.  $95^\circ$ , separate. Sulphuric acid dissolves the compound with a blue coloration, the solution on carefully adding



ice deposits yellow crystals; these give the  $\psi$ -base on further washing with water. The yellow sulphate could not be analysed, but the corresponding yellow nitrate was. The unstable azoxonium nitrate is almost black.

$\psi$ -3-Methylphenanthraphenazoxine  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}=\text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{O} \end{array} > \text{C}_6\text{H}_3\text{Me}$ , obtained by the reduction of the  $\psi$ -base with stannous chloride, forms greenish-yellow needles, m. p. 163—164°.

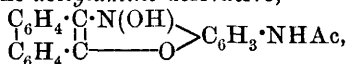
Hydroxydihydro-3-methylphenanthraphenazoxine,



is formed when the  $\psi$ -base dissolved in benzene is heated with phenylhydrazine. It is oxidised at 100°, losing two hydrogen atoms, and is a white, glistening, felt-like substance.

The  $\psi$ -base from *o*-amino-*p*-cresol,  $\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}$ , forms white leaflets, m. p. 195° (decomp.).  $\psi$ -2-Methylphenanthraphenazoxine,  $\text{C}_{21}\text{H}_{15}\text{ON}$ , forms greenish-yellow needles, and gives a green fluorescence in alcoholic solution.

The  $\psi$ -base derived from 5-nitro-3-amino-*p*-cresol,  $\text{C}_{21}\text{H}_{14}\text{O}_4\text{N}_2$ , forms slender, greenish-grey needles, m. p. 202—204° (decomp.). The  $\psi$ -base from 4-nitro-2-aminophenol,  $\text{C}_{20}\text{H}_{12}\text{O}_4\text{N}_2$ , white needles, m. p. 224—225°, gives a dihydro-derivative,  $\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_2$ , which forms orange needles. The acetylamino-derivative,



obtained by reduction of the nitro- $\psi$ -base and acetylation, is a yellowish-white powder, m. p. 220° (decomp.).

The  $\psi$ -base from 3-nitro-2-aminophenol,  $\text{C}_{20}\text{H}_{12}\text{O}_4\text{N}_2$ , m. p. 220° (decomp.), gives the corresponding azoxine, which forms bluish-violet needles from pyridine, and decomposes at 220° without melting.

3-Aminophenanthraphenazoxonium chloride is dark violet, and in aqueous solution is partially hydrolysed. An aqueous solution colours ether yellow when shaken with it. This is due to a yellow  $\psi$ -base which is obtained as a brownish-yellow mass on decomposing the chloride with sodium acetate and a few drops of sodium hydroxide. 3-Dimethylaminophenanthraphenazoxonium salts were obtained from Frie's zinc chloride double salt (D.R.-P. 130743). The nitrate is sparingly soluble in water and gives on long keeping the yellow

$\psi$ -base,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}=\text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \text{---} \text{O} \end{array} > \text{C}_6\text{H}_3 \cdot \text{NMe}_2$ , purified in the same way as the parent substance, it forms lemon-yellow crystals, m. p. 180° (decomp.).

W. R.

**Preparation of *NN'*-Dialkylmethylenediamines and Homologues.** EMIL FRÖHLICH (*Ber.*, 1907, 40, 762—765).—The author describes the preparation of a homologous series of asymmetrical diammonium bases, the first member being *methylenedi-methylaniline*,  $\text{CH}_2(\text{NMePh})_2$ , obtained from methylaniline and formaldehyde as a yellow, viscid oil, b. p. 227°/33 mm.

*Methylenedi-ethylaniline*,  $\text{CH}_2(\text{NEtPh})_2$ , obtained from ethylaniline and formaldehyde, separates from light petroleum in prisms, m. p.  $76-77^\circ$ .

*Ethylenedi-methylaniline*,  $\text{C}_2\text{H}_4(\text{NMePh})_2$ , obtained from methylaniline and ethylene dibromide, is first obtained as a yellow, viscid oil, b. p.  $245^\circ/45$  mm., which soon solidifies and may be crystallised from light petroleum as prisms, m. p.  $47-48^\circ$ . Its *picrate* has m. p.  $180^\circ$  (decomp.).

*Ethylenedi-ethylaniline*,  $\text{C}_2\text{H}_4(\text{NEtPh})_2$ , obtained from ethylaniline and ethylene dibromide, has b. p.  $245^\circ/45$  mm., and separates from light petroleum in prism, m. p.  $75^\circ$ . Its *picrate* has m. p.  $189-190^\circ$  (decomp.).

*Trimethylenedi-methylaniline*,  $\text{CH}_2(\text{CH}_2\cdot\text{NMePh})_2$ , obtained from methylaniline and trimethylene bromide, has b. p.  $270-272^\circ/70$  mm., and separates from light petroleum in prisms, m. p.  $46-47^\circ$ . Its *picrate* has m. p.  $183-184^\circ$  (decomp.).

*Trimethylenedi-ethylaniline*,  $\text{CH}_2(\text{CH}_2\cdot\text{NEtPh})_2$ , obtained from ethylaniline and trimethylene bromide, is a yellow, viscid oil, b. p.  $245-247^\circ/30$  mm. Its *picrate* has m. p.  $177^\circ$  (decomp.).

A. McK.

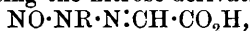
**Preparation of 4'-Nitroso-4-acetylamino-diphenylamine and its *o*-Sulphonic Acid.** LEOPOLD CASSELLA & Co. (D.R.-P. 176046).—4'-Nitroso-4-acetylamino-diphenylamine,  $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , prepared by adding concentrated aqueous sodium nitrite to an alcoholic hydrochloric acid solution of 4-acetylamino-diphenylamine is precipitated with brine as a brown deposit soluble in alkalis and reprecipitated by acids, and dissolving in alcohol to a reddish-brown solution. 4'-Nitroso-4-acetylamino-diphenylamine-2-sulphonic acid is produced similarly, and consists of a brown, crystalline powder which dissolves only sparingly in water and dilute acids, but is somewhat soluble in alcohol. Its alkali salts are readily soluble and separate from their concentrated solutions in brown crystals. These nitroso-compounds are of great technical importance in the production of safranines.

G. T. M.

**Action of Mono- and Di-chloroacetic Acids on Primary Hydrazines. Hindrance of Chemical Reactions.** MAX BUSCH and EDUARD MEUSSDÖRFFER (*J. pr. Chem.*, 1907, [ii], 75, 121-141. Compare Abstr., 1904, i, 97; Fries, Abstr., 1906, i, 644).—The action of chloroacetic acid on arylhydrazines, under the conditions which with phenylhydrazine lead to the formation of *as*-phenylhydrazinoacetic acid, was investigated with the object of determining if the product is always an *as*-hydrazinoacetic acid,  $\text{NH}_2\cdot\text{NR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . It has been found that *o*-tolyl-, *o*-anisyl-, *o*-chlorophenyl-, and  $\alpha$ -naphthylhydrazines, which might have been expected to yield *s*-hydrazinoacetic acids,  $\text{NHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , do not react with chloroacetic acid. This failure of the reaction might be ascribed to steric hindrance, but it is

found further that  $\beta$ -naphthylhydrazine does not enter into the reaction, whilst 4-*m*-xylylhydrazine, despite the presence of an *o*-methyl, yields a mixture of the two isomeric xylylhydrazinoacetic acids.

All *o*- and *p*-substituted phenylhydrazines which have been studied react with dichloroacetic acid, forming hydrazones of glyoxylic acid,  $\text{NHR}\cdot\text{N}:\text{CH}\cdot\text{CO}_2\text{H}$ ; the rate of this reaction is retarded and the yields diminished by the presence of an *o*-bromine, still more by that of an *o*-iodine, atom. The influence of an *o*-substituting group may extend apparently even to the  $\beta$ -nitrogen atom; the formation of arylazoformaldoximes,  $\text{NR}:\text{N}\cdot\text{CH}:\text{N}\cdot\text{OH}$ , by the action of nitrous acid on arylhydrazones of glyoxylic acid (Busch and Wolbring, Abstr., 1905, i, 493) takes place equally well with *o*- and *p*-chlorophenyl-, or with *o*-anisyl- and *p*-nitrophenyl-hydrazones of glyoxylic acid, but fails with the *o*-bromo-, *o*-iodo-, and *o*-nitro-phenylhydrazones. This could be explained by assuming the reaction to take place in two stages, the intermediate product being the nitroso-derivative,



the formation of which would be sterically hindered by the presence of *o*-groups. The difference in the behaviour of the *o*-chloro-, and the *o*-bromo-, and *o*-iodo-compounds must be the result of the differences in the atomic volumes.

Whilst in the presence of potassium carbonate, chloroacetic acid and phenylhydrazine yield only the *as*-hydrazino-acid, in presence of an alkali hydroxide the acid acts in the same manner as the ester, a mixture of the *s*- and *as*-hydrazinoacetic acids being formed.

In one experiment with *o*-tolylhydrazine, a very small amount of a *tolylhydrazinoacetic acid*,  $\text{C}_9\text{H}_{11}\text{O}_2\text{N}_2$ , forming yellowish-white crystals, m. p.  $140^\circ$  (decomp.), was obtained. *o*-Tolylhydrazine does not react, or reacts to only a small extent with ethyl chloroacetate.

*s*-4-*m*-Xylylhydrazinoacetic acid crystallises from dilute alcohol in glistening leaflets, m. p.  $162$ – $163^\circ$ . The *as-isomeride* crystallises in glistening leaflets, m. p.  $178^\circ$ , evolves nitrogen with Fehling's solution, and forms a *m*-nitrobenzylidene derivative, crystallising in yellow needles, m. p.  $151^\circ$ .

*as-p*-Tolylhydrazinoacetic acid crystallises in white needles, m. p.  $158^\circ$ . The benzylidene derivative crystallises in yellow needles, m. p.  $166^\circ$ ; the *m*-nitrobenzylidene derivative, yellow needles, m. p.  $191^\circ$ . The ethyl ester crystallises from ether in slender, white needles, m. p.  $123$ – $125^\circ$ , and forms a *m*-nitrobenzylidene derivative, yellow needles, m. p.  $123$ – $124^\circ$ .

*as-m*-Tolylhydrazinoacetic acid crystallises in white leaflets, m. p.  $160^\circ$  (decomp.); the *m*-nitrobenzylidene derivative crystallises from alcohol in yellow prisms, m. p.  $189^\circ$  (decomp.); the benzylidene derivative forms greenish-yellow needles, m. p.  $158^\circ$  (decomp.).

*as-p*-Anisylhydrazinoacetic acid crystallises in white leaflets, m. p.  $137^\circ$  (decomp.), evolves nitrogen with Fehling's solution, and forms a *m*-nitrobenzylidene derivative, crystallising in yellow needles, m. p.  $159^\circ$ .

*as-p*-Bromophenylhydrazinoacetic acid crystallises in white needles,

m. p.  $138^{\circ}$  (decomp.); the *m*-nitrobenzylidene derivative forms yellow needles, m. p.  $189^{\circ}$  (decomp.).

The action of 2 mols. of *p*-bromophenylhydrazine on 1 mol. of potassium chloroacetate leads to the formation of a mixture of the two hydrazinoacetic acids. *s*-*p*-Bromohydrazinoacetic acid, m. p.  $150^{\circ}$ , is insoluble in aqueous oxalic acid, and reduces Fehling's solution without evolution of nitrogen.

Glyoxylic acid-*o*-anisylhydrazone crystallises in yellow, microscopic plates, m. p. about  $115^{\circ}$ , decomposing at a slightly higher temperature. *o*-Anisylazoformaldoxime, m. p.  $153$ — $154^{\circ}$  (decomp.).

*o*-Chlorophenyl-*m*-nitrobenzylidenehydrazine forms yellow needles, m. p.  $150^{\circ}$ . Glyoxylic acid-*o*-chlorophenylhydrazone crystallises in lemon-yellow needles, m. p.  $145^{\circ}$  (decomp.).

Glyoxylic acid-*p*-chlorophenylhydrazone forms flat spears, m. p.  $142^{\circ}$  (decomp.).

*o*-Bromophenylhydrazine, prepared from *o*-bromoaniline, is obtained as a viscid oil solidifying to white needles, m. p.  $48^{\circ}$ . Glyoxylic acid-*o*-bromophenylhydrazone is formed in two stereoisomeric modifications of which the one, m. p.  $160^{\circ}$ , is identical with Busch and Wolbring's product from diazo-*o*-bromophenyl acetate (*loc. cit.*); the second *stereoisomeride*, which is soluble in benzene, crystallises in orange-yellow needles, m. p.  $154^{\circ}$ . Both modifications yield at most only traces of the corresponding azoformaldoxime.

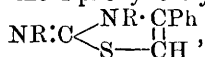
*o*-Iodophenyl-*m*-nitrobenzylidenehydrazine crystallises in yellow needles, m. p.  $170^{\circ}$ .

*p*-Nitrophenylazoformaldoxime, formed from the *p*-nitrophenylhydrazone of ammonium glyoxylate (Busch and Wolbring, *loc. cit.*), crystallises from a mixture of ether and light petroleum in red needles, m. p.  $118^{\circ}$  (decomp.).

G. Y.

**Action of Bromoacetophenone on Thiocarbamides.** REINHOLD VON WALTHER (*J. pr. Chem.*, 1907, [ii], 75, 187—199. Compare Traumann, Abstr., 1889, 414).—It is considered that in the formation of iminothiazolines, the first stage of the reaction consists of the addition of the  $\alpha$ -halogenoketone to the sulphur atom of the thiocarbamide, the loss of the hydrogen haloid forming the second stage.

[With H. GREIFENHAGEN.]—The action of bromoacetophenone on *s*-diarylthiocarbamides in alcoholic solution on the water-bath leads to the formation of 2-arylimino-4-phenyl-3-aryl-2 : 3-thiazolines,

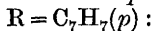


which are strong, monoacid bases, are stable towards hydrochloric acid, and, when heated with carbon disulphide in a sealed tube at  $200^{\circ}$ , yield the corresponding feebly basic 2-thio-4-phenyl-3-aryl-2 : 3-thiazolines,

$\text{CS} \begin{array}{l} \nearrow \text{NR} \cdot \text{CPh} \\ \searrow \text{S} - \text{CH} \end{array}$ . The following iminothiazolines have been prepared; the temperatures are melting points.

From *s*-diphenylthiocarbamide,  $\text{R} = \text{Ph}$ : long, white needles; the *hydrobromide*,  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{S} \cdot \text{HBr}$ , prisms,  $276^{\circ}$ ; the *platinichloride*,  $(\text{C}_{21}\text{H}_{16}\text{N}_2\text{S})_2 \cdot \text{H}_2\text{PtCl}_6$ ,

a brown, crystalline precipitate; the picrate,  $C_{21}H_{16}N_2S_2C_6H_3O_7N_3$ , orange-yellow prisms,  $173^\circ$ . From *s*-di-*p*-tolylthiocarbamide,



long, white needles,  $188^\circ$ ; the *hydrochloride*, prisms,  $235^\circ$ ; the *hydrobromide* remains unchanged at  $242^\circ$ ; the *platinichloride*, a brown, crystalline precipitate. From *s*-di-*o*-tolylthiocarbamide,  $R = C_6H_4Me(o)$ : colourless leaflets,  $120^\circ$ ; the *platinichloride* and the *picrate*,  $208^\circ$ , were analysed. From *s*-di-*m*-tolylthiocarbamide,  $R = C_6H_4Me(m)$ : slender needles,  $103^\circ$ ; the *platinichloride* was analysed.

The following thiothiazolines are described; the temperatures are melting points.

$R = Ph$ : white needles,  $148^\circ$ ;  $R = C_6H_4Me(p)$ : white needles,  $146^\circ$ ;  $R = C_6H_4Me(o)$ : silvery leaflets,  $146^\circ$ ;  $R = C_6H_4Me(m)$ : white needles,  $195^\circ$ .

Of the isomeric iminothiazolines which might be formed by the action of bromoacetophenone on *s*-phenyl-*p*-tolylthiocarbamide, only

2-*p*-tolylimino-3:4-diphenyl-2:3-thiazoline,  $C_7H_7 \cdot N : C \begin{smallmatrix} \nearrow NPh \cdot CPh \\ \searrow S - CH \end{smallmatrix}$ , could be isolated. It crystallises in white needles, m. p.  $209^\circ$ , and, when heated with carbon disulphide, yields 2-thio-3:4-diphenyl-2:3-thiazoline, m. p.  $148^\circ$ , together with *s*-di-*p*-tolylthiocarbamide, m. p.  $176^\circ$ . G. Y.

**Preparation of 5:5-Dialkylbarbituric Acids.** EMANUEL MERCK (D.R.-P. 177694).—Diethylbarbituric acids were formerly obtained by heating diethylmalonyl chloride with biuret when the group  $CO \cdot NH_2$  was eliminated. It has now been found that in a similar manner the dialkylmalonyl chlorides react with the alkyl allophanates so that the group  $CO_2R$  is removed.

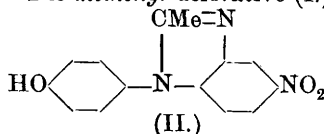
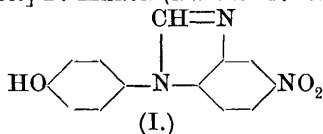
On heating a mixture of ethyl allophanate and diethylmalonyl chloride at  $115$ — $120^\circ$ , hydrogen and ethyl chlorides and carbon dioxide are evolved and the residue contains diethylbarbituric acid. G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** OTTO WOLFES (D.R.-P. 175592).—The iminopyrimidines having the general formula  $X : C \begin{smallmatrix} \nearrow NH \cdot C(:Z) \\ \searrow NH \cdot C(:Y) \end{smallmatrix} > CRR'$ , where X, Y, and Z may be imino-groups or where X is a substituted imino-group, such as  $:N \cdot CN$  or  $:NMe$ , are all converted by alkyl nitrites into the corresponding dialkylbarbituric acids.

2-Imino-4:6-dioxy-5:5-diethylpyrimidine when heated in absolute alcohol with amyl nitrite yields diethylbarbituric acid.

The following compounds also give rise to the same dialkylbarbituric acid when similarly treated: 4-imino-2:6-dioxy-5:5-diethylpyrimidine, 2:4-di-imino-6-oxy-5:5-diethylpyrimidine and 2-methylimino-4:6-dioxy-5:5-diethylpyrimidine. G. T. M.

[Anhydro-Bases from 4'-Nitro-2-amino-4-hydroxydiphenylamine.] D. MARON (D.R.-P. 175829).—The *methenyl* derivative (I.)



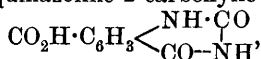


of 4'-nitro-2'-amino-4-hydroxydiphenylamine is prepared by heating this substituted diamine with 25% formic acid and crystallising the product from alcohol, m. p. 267—268°.

The *ethenyl* derivative (II.) is obtained in a similar manner by the action of acetic anhydride, m. p. 187—188°. The *benzenyl* derivative produced by heating the nitroamino-compound with benzoyl chloride in xylene is crystallised from alcohol and melts at 259—260°. These compounds when heated with benzidine and sulphur at 220—240° yield sulphur dyes which give green and yellow shades on unmordanted cotton.

G. T. M.

**Quinazolines. XVII. Synthesis of Quinazolinecarboxylic Acids from 4-Aminoisophthalic Acid and from Aminoterephthalic Acid.** MARSTON T. BOGERT, JOHN DAVID WIGGIN, and J. EDWIN SINCLAIR (*J. Amer. Chem. Soc.*, 1907, 29, 82—87. Compare Abstr., 1906, i, 988, and earlier abstracts).—The only quinazolinecarboxylic acid described previously is the carbamidobenzoylcarboxylic acid (diketotetrahydroquinazoline-2-carboxylic acid),



obtained by Niementowski (Abstr., 1896, i, 578). In the present paper, a number of quinazolinecarboxylic acids are described which were prepared from *m*- and *p*-xylydines. The xylydines were acetylated, the methyl groups oxidised to carboxyl groups, the resulting acetylaminophthalic acids converted into acetylanthranilcarboxylic acids by the action of acetic anhydride, and from these the quinazolines were obtained by the action of primary amines. The non-alkylated quinazolines were prepared by the action of formamide on the ammonium aminophthalates. The quinazolinecarboxylic acids are colourless, crystalline substances which usually melt and decompose above 300°, are sparingly soluble in water, insoluble or nearly so in ether, benzene, chloroform, carbon tetrachloride, or acetone, and soluble in alcohol or aqueous alkali hydroxides; they form salts with the heavy metals. The following substances are described.

*Acetylanthranil-5-carboxylic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3 \begin{array}{l} \text{N}^{\text{Ac}} \\ \text{CO} \end{array}$ , m. p. 264°, minute, colourless crystals. *4-Ketodihydroquinazoline-6-carboxylic acid*

(*4-hydroxyquinazoline-6-carboxylic acid*),  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CH} \\ \text{CO}\cdot\text{NH} \end{array}$  or

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CH} \\ \text{C}(\text{OH})\cdot\text{N} \end{array}$ , small, pale-yellow crystals. *4-Keto-2-methyldihydroquinazoline-6-carboxylic acid* (*4-hydroxy-2-methylquinazolinecarboxylic acid*),  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CMe} \\ \text{CO}\cdot\text{NH} \end{array}$  or  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CMe} \\ \text{C}(\text{OH})\cdot\text{N} \end{array}$ , *4-keto-2:3-dimethyldihydroquinazoline-6-carboxylic acid*, and *4-keto-3-phenyl-2-methyldihydroquinazoline-6-carboxylic acid* form minute, colourless needles.

*2-Acetylaminoterephthalic acid*,  $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$ , crystallises in colourless, feathery needles and, on hydrolysis with sulphuric acid,

yields 2-aminoterephthalic acid together with another substance, m. p. 59°, which forms colourless, pearly scales, and on successive treatment with acetic anhydride and ammonia is converted into a compound, m. p. 92°, which crystallises in colourless, silky needles.

Acetylanthranil-4-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\left\langle\begin{smallmatrix}\text{N}\cdot\text{Ac} \\ \text{CO}\end{smallmatrix}\right\rangle$ , m. p. above 300°,

minute, colourless crystals. 4-Ketodihydroquinazoline-7-carboxylic acid (4-hydroxyquinazoline-7-carboxylic acid) colourless, microscopic crystals. 4-Keto-2-methylidihydroquinazoline-7-carboxylic acid (4-hydroxy-2-methylquinazoline-7-carboxylic acid), resembles the isomeric 6-carboxylic acid. 4-Keto-2:3-dimethyldihydroquinazoline-7-carboxylic acid, m. p. 298°, small, colourless prisms. 4-Keto-3-phenyl-2-methyldihydroquinazoline-7-carboxylic acid forms small, colourless crystals and decomposes above 300° without melting. E. G.

**Seven-Membered Rings from  $\beta$ -Diketones and Ortho-diamines.** JOHANNES THIELE and GERHARD STEIMMIG (*Ber.*, 1907, 40, 955—957).—Acetylacetone readily condenses with *o*-diamines in acid solution, yielding bases free from oxygen; the hydrochlorides of these form dark violet crystals, whereas the bases themselves are colourless. Benzoylacetone reacts less readily than acetylacetone. The bases appear to be formed by the elimination of 2 molecules of water from molecular proportions of the ketone and amine.

Acetylacetone and *o*-phenylenediamine dissolved in a mixture of alcohol and acetic acid yield a base,  $\text{C}_{11}\text{H}_{12}\text{N}_2$ , which can be isolated in the form of its hydrochloride,  $\text{C}_{11}\text{H}_{12}\text{N}_2\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ , when diluted with water and mixed with concentrated hydrochloric acid. The salt crystallises in practically black needles, loses its water of crystallisation when kept in a desiccator, dissolves fairly readily in water, but when boiled with this solvent yields acetone and methylbenziminazole. With phenylhydrazine it yields the *o*-diamine and phenyldimethylpyrazole. The salt dissolves in fuming hydrochloric or concentrated sulphuric acid, yielding a colourless solution, which turns purple on the addition of water. When hydrogen chloride is led into a suspension of the violet salt in hydrochloric acid, a colourless, crystalline salt (+2HCl ?) is formed, but this immediately turns violet when filtered. The base crystallises from ether in colourless plates, m. p. 131—132°, and is more stable than the salts.

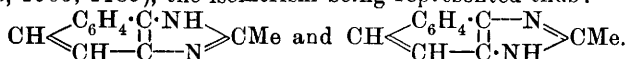
The formula  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CMe} \\ \text{N}=\text{CMe}\end{smallmatrix}\right\rangle\text{CH}$  or  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CMe}\end{smallmatrix}\right\rangle\text{CH}_2$  is suggested, and the compound is undoubtedly a pseudo-base.

The hydrochloride of the product from benzoylacetone and *o*-phenylenediamine has the composition  $\text{C}_{16}\text{H}_{14}\text{N}_2\cdot\text{HCl}\cdot 3\text{H}_2\text{O}$ , and when boiled with water yields methylbenziminazole and acetophenone together with phenylbenziminazole and acetone. The base melts at 87—88°.

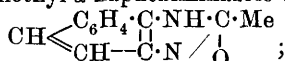
J. J. S.

**Tautomerism of Benziminazoles.** OTTO FISCHER (*J. pr. Chem.*, 1907, [ii], 75, 88—95. Compare Abstr., 1906, i, 895).—The

N-hydrogen atom in 2-methylbenziminazole is assumed by the author vibrate between the two nitrogen atoms; the same view should also apply to the corresponding naphthalene compound, but a second isomeric 2-methylnaphthiminazole, always, however, with a mol. of water of crystallisation, has been described by Meldola, Eyre, and Lane (Trans., 1903, 1185), the isomerism being represented thus:



The anhydrous isomeride known as Prager's base (Abstr., 1885, 1239) is shown to be 2-methyl- $\alpha$ -naphthiminazole (Fischer, Abstr., 1901, i, 414), and the isomeride containing the mol. of water of crystallisation is really 2-methyl- $\alpha$ -naphthiminazole oxide,

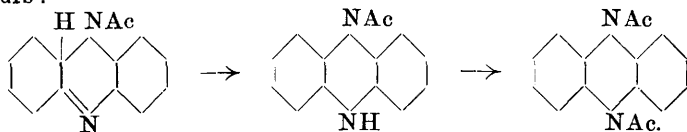


this statement is supported by analysis and also by the fact that on reduction, such as distilling a mixture of it with iron powder, 2-methyl- $\alpha$ -naphthiminazole is obtained.

The action of methyl iodide on the isomeric 1:2:5- and 1:2:6-trimethylbenziminazoles has again been studied with the object of preparing two isomeric 1:2:3:6-tetramethylbenziminazolium iodides, but only one, m. p. 167—168° (Fischer and Rigand, Abstr., 1902, i, 399), was obtained. The author therefore concludes that in both cases the labile iodide,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{NMe} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C} \begin{array}{c} \text{Me} \\ \diagup \\ \text{I} \end{array}$ , is first formed, which then passes into the stable form, m. p. 167—168°.

W. H. G.

**Mono- and Di-acetyldihydrophenazines.** NADEZDY STSCHERBINA (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 613—615).—The action of acetic anhydride on dihydrophenazine in the cold yields the same monoacetyldihydrophenazine as was obtained by Tichwinsky and Wolochowitsch (Abstr., 1905, i, 383) at a high temperature (compare Schaposchnikoff, Abstr., 1905, i, 840). The asymmetrical formula for dihydrophenazine is hence confirmed. On boiling the monoacetyl derivative with excess of acetic anhydride, it is converted into the diacetyl compound, m. p. 180°; it is concluded that the monoacetyl derivative undergoes molecular rearrangement before further acetylation occurs:

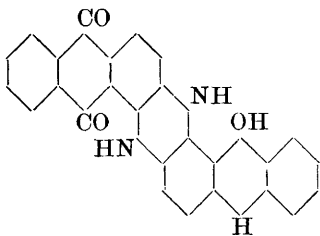


T. H. P.

**Hydroazines.** MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 615—620. Compare preceding abstract).—The author discusses the relation between the hydroazines and azines with especial reference to the work of Schaposchnikoff (Abstr., 1905, i, 840) and of Hinsberg (Abstr., 1902, i, 238). He disagrees with the former author's quinone formula for the azines.

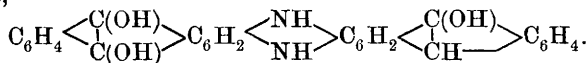
T. H. P.

**Indanthrene and Flavanthrene. VII. Products of Reduction of Indanthrene.** ROLAND SCHOLL and PH. STEGMULLER (*Ber.*, 1907, 40, 924—933. Compare Abstr., 1904, i, 109, 110; this vol., 255, 256, 257).—*N*-Dihydroanthraquinoneanthraquinolazine



(this vol., i, 256) is very easily oxidised to indanthrene; if heated with 28% sodium hydroxide for ten hours at 220—230°, or in an atmosphere of carbon dioxide at 250°, for 1 molecule converted into indanthrene there is another converted into a compound  $C_{28}H_{16}O_3N_2$ . Its constitution was established thus: it is converted into an azine by oxidation and is therefore a *N*-dihydroazine, it

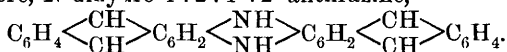
can be reduced with hyposulphite showing it to contain an unaltered anthraquinone complex, and as it gives a sodium salt it is 1:2:1':2'-*N*-dihydroanthraquinone-anthranolazine. It is a brownish-red powder which does not melt at 360°, its *hydrochloride* is blue, the *mono-acetate*,  $C_{30}H_{18}O_4N_2$ , is reddish-brown. 1:2:1':2'-*Anthraquinone-anthranolazine*,  $C_{28}H_{14}O_3N_2$ , is obtained as a violet-brown powder by the oxidation of the corresponding dihydroazine with air or sodium hypochlorite. Reduction of the dihydroazine with sodium hyposulphite at 70° yields 1:2:1':2'-*N*-dihydroanthraquinolanthranolazine,



This may also be obtained directly from indanthrene by reduction with hyposulphite and serves as the most convenient source for *N*-dihydroanthraquinone-anthranolazine; the method of preparation and separation from anthranoneazine (Abstr., 1904, i, 111) is described in detail. The *triacetate* (?) is a brown powder, m. p. 240—243°.

W. R.

**Indanthrene and Flavanthrene. VIII. Products of Reduction of Indanthrene.** ROLAND SCHOLL [with HANS BERBLINGER and A. KÜNZEL] (*Ber.*, 1907, 40, 933—939. Compare preceding abstract).—Distillation of indanthrene with zinc dust yields anthrazine, but digestion with zinc dust and sodium hydroxide gives a compound,  $C_{26}H_{18}N_2$ , containing two hydrogen atoms more in the molecule than anthrazine. It crystallises in red aggregates having a metallic lustre and is converted into the yellow anthrazine on heating at 360°. It is, therefore, *N*-dihydro-1:2:1':2'-anthrazine,

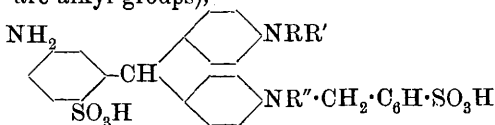


The author discusses the relationship of colour and constitution of the darker coloured dihydroazines and azines, and supports his conclusion that when chromogens containing more than one chromophore are reduced or altered in such a way that one chromophore remains whilst the other is converted into an auxochrome, a deepening in colour results. It is proposed to call such compounds *chromohydro*-compounds in distinction to the *leucohydro*-compounds.

*Anthrazine sulphate*,  $C_{28}H_{16}N_2 \cdot H_2SO_4$ , crystallises in brownish-red, microscopic needles; the *picrate*,  $C_{78}H_{16}N_2(C_6H_3O_7N_3)_2$ , in slender, red needles.

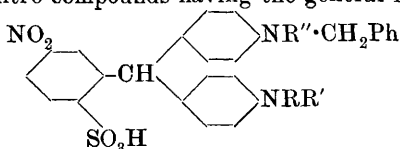
*Octabromoanthrazine*,  $C_{28}H_8N_2Br_8$ , obtained by heating the azine with bromine at  $100^\circ$  for six hours, is yellow. Boiling nitric acid probably gives a pentanitro-tetrahydroxyanthrazine. W. R.

**Preparation of Green Triphenylmethane Derivatives.** FARBERWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 175825 and 175826).—The substituted triphenylmethanedisulphonic acids (where  $RR'$  and  $R''$  are alkyl groups),

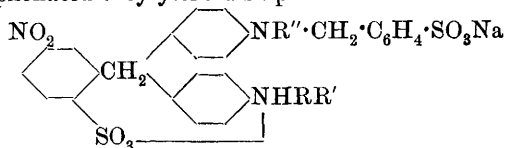


when diazotised and combined with salicylic acid give azo-derivatives which, on subsequent oxidation with lead peroxide furnish green colouring matters.

When the nitro-compounds having the general formula



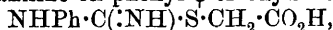
are further sulphonated they yield disulphonic derivatives of the following type



G. T. M.

**Synthesis of Tertiary Amidines** [*iso*Diphenylcarbamidoacetanilide]. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1907, 144, 487—488).—By the action of amines, such as aniline, on a mono-substituted thiohydantoic acid, polysubstituted derivatives can be obtained. The iminic hydrogen is first replaced with loss of ammonia and then the acid is converted into the acid amide, the water liberated then reacting on the product with evolution of hydrogen sulphide and replacement of the sulphur atom by oxygen. It is possible to isolate the intermediate products.

By the action of aniline on phenyl- $\psi$ -thiohydantoic acid,



*isodiphenylcarbamidoacetanilide*,  $NHPh \cdot C(:NPh) \cdot O \cdot CH_2 \cdot CO \cdot NHPh$ , is formed in small, white crystals, m. p.  $289^\circ$ . E. H.

**Condensation of Gallocyanin Dyes with Amino-compounds.** EUGÈNE GRANDMOUGIN and ERNST BODMER (*J. pr. Chem.*, 1907, [ii], 75, 199—200. Compare Abstr., 1906, i, 596; Nietzki and Bossi, Abstr., 1893, i, 44).—The condensation product of prune and *m*-aminobenzoic

acid, formed in presence of sodium acetate in glacial acetic solution, separates in glistening, green crystals, is soluble in aqueous alkalis, and forms a greenish-blue chromium lake. It is considered to have the constitution

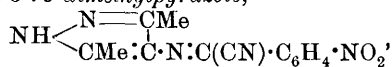
$$\begin{array}{c} \text{NMe}_2 \cdot \text{C} = \text{CH} \cdot \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{C}(\text{OH}) - \text{CO} \\ | \\ \text{CH} : \text{CH} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{C}(\text{CO}_2\text{Me}) : \text{C} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \end{array}$$

The condensation product of prune and *m*-nitroaniline,  $\text{C}_{22}\text{H}_{18}\text{O}_7\text{N}_4$ , forms large, golden crystals, and is insoluble in aqueous alkalis. Condensation products have been formed also from prune with *p*-aminobenzoic acid, anthranilic acid, and *p*-nitroaniline, and from coreine with aniline, *m*-nitroaniline, and *m*-aminobenzoic acid. G. Y.

**Preparation of Cyano-derivatives of Pyrimidine.** EMANUEL MERCK (D.R.-P. 175795).—It is now found that the condensation of dicyanodiamide and the dialkylmalonic esters in presence of alkaline condensing agents takes place readily at  $120^\circ$  under pressure. Thus 2-cyanoimino-4:6-dioxy-5:5-diethylpyrimidine is obtained in good yield by heating at this temperature dicyanodiamide and ethyl diethylmalonate with alcoholic sodium ethoxide. G. T. M.

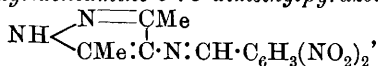
**Condensations of Nitroso-compounds of the Pyrazole Series.** FRANZ SACHS and PAUL ALSLEBEN (*Ber.*, 1907, 40, 664—678).—It had previously been shown by Sachs and his pupils (*Abstr.*, 1899, i, 883; 1900, i, 362; 1901, i, 229) that nitrosodimethylaniline, nitrosophenol, nitrosobenzene, and other nitroso-benzenoid derivatives react with methylene derivatives. A series of analogous condensations with tertiary nitroso-compounds of the pyrazole series is now described.

4-Nitroso-3:5-dimethylpyrazole,  $\text{NH} \begin{array}{c} \text{N} = \text{CMe} \\ | \\ \text{CMe} : \text{C} \cdot \text{NO} \end{array}$ , obtained by condensing hydrazine with isonitrosoacetylacetone according to Wolff (*Abstr.*, 1903, i, 203), was condensed with *p*-nitrobenzyl cyanide in the presence of ammonia or of piperidine; the resulting 4-*p*-nitro- $\alpha$ -cyanobenzylideneamino-3:5-dimethylpyrazole,



separates from alcohol in yellow needles containing  $1\text{H}_2\text{O}$ ; the anhydrous compound has m. p.  $229^\circ$ . When dehydrated, the colour changes to an orange-red. Its solution in concentrated sulphuric acid is colourless.

4-op-Dinitrobenzylideneamino-3:5-dimethylpyrazole,

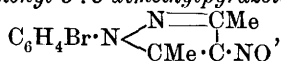


obtained by the condensation of 4-nitroso-3:5-dimethylpyrazole with 2:4-dinitrotoluene, separates from methyl alcohol in yellowish-brown needles, which are transformed at  $195^\circ$  into a red modification, m. p.  $212^\circ$ . Its solution in concentrated sulphuric acid is yellowish-brown.

4-*m*-Nitro- $\alpha$ -cyanobenzylideneamino-1-phenyl-3:5 dimethylpyrazole,  $\text{NPh} \begin{array}{c} \text{N} = \text{CMe} \\ | \\ \text{CMe} : \text{C} \cdot \text{N} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{array}$ , obtained by the condensation of

nitrobenzyl cyanide with 4-nitroso-1-phenyl-3 : 5-dimethylpyrazole (Wolff, *loc. cit.*), separates from alcohol in glistening pyramids, m. p. 160°. It forms a very yellow solution with concentrated sulphuric acid.

4-Nitroso-1-*p*-bromophenyl-3 : 5-dimethylpyrazole,

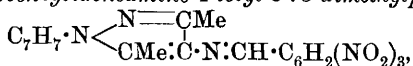


obtained from *p*-bromophenylhydrazine and isonitrosoacetylacetone, separates from dilute alcohol in green needles, m. p. 122°; its solution in concentrated sulphuric acid is ruby-red.

4-*p*-Nitro- $\alpha$ -cyanobenzylideneamino-1-*p*-bromophenyl-3 : 5-dimethylpyrazole,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{N} \begin{array}{l} \text{N}=\text{CMe} \\ \text{CMe}\cdot\text{C}\cdot\text{N}\cdot\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \end{array}$ , obtained by condensing the preceding compound with *p*-nitrobenzyl cyanide, separates from a mixture of chloroform and methyl alcohol in fan-shaped needles, m. p. 218.5°. Its solution in concentrated sulphuric acid is yellow.

4-Nitroso-1-*p*-tolyl-3 : 5-dimethylpyrazole,  $\text{C}_7\text{H}_7\cdot\text{N} \begin{array}{l} \text{N}=\text{CMe} \\ \text{CMe}\cdot\text{C}\cdot\text{NO} \end{array}$ , obtained from *p*-tolylhydrazine and isonitrosoacetylacetone, separates from acetic acid in glistening, emerald-green needles, m. p. 109.5°. Its solution in concentrated sulphuric acid is cherry-red.

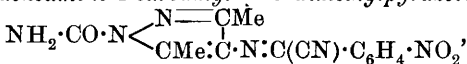
4-*oo'*-*p*-Trinitrobenzylideneamino-1-tolyl-3 : 5-dimethylpyrazole,



obtained from the preceding compound and 2 : 4 : 6-trinitrotoluene, separates from toluene in silky, orange-coloured needles, m. p. 235°, its solution in sulphuric acid is yellow. It is very stable towards dilute acid.

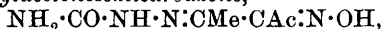
4-Nitroso-1-carbamyl-3 : 5-dimethylpyrazole,  $\text{NH}_2\cdot\text{CO}\cdot\text{N} \begin{array}{l} \text{N}=\text{CMe} \\ \text{CMe}\cdot\text{C}\cdot\text{NO} \end{array}$ ,

obtained by the action of a mixture of semicarbazide hydrochloride and sodium acetate on isonitrosoacetylacetone, crystallises from benzene in glistening, green needles, m. p. 130° (decomp.). When boiled with much water it forms a blue solution. Its solution in concentrated sulphuric acid is yellowish-brown; with alkalis it forms red salts. When condensed with *p*-nitrobenzyl cyanide, it forms 4-*p*-nitro- $\alpha$ -cyanobenzylideneamino-1-carbamyl-3 : 5-dimethylpyrazole,



which crystallises from acetic acid in glistening, orange-coloured needles, m. p. 227°. Its solution in concentrated sulphuric acid is slightly yellow.

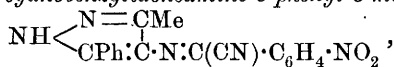
3-iso-Nitrosoacetylacetonesemicarbazone,



obtained together with 4-nitroso-1-carbamyl-3 : 5-dimethylpyrazole by the action of semicarbazide on isonitrosoacetylacetone, crystallises from glacial acetic acid in yellow needles, m. p. 192.5°. Its solution in con-

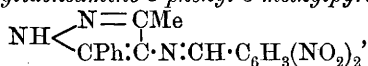
concentrated sulphuric acid is faintly yellow, and it forms yellow salts with alkalis.

4-Nitroso-5-phenyl-3-methylpyrazole,  $\text{NH} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CPh}:\text{C}:\text{NO} \end{smallmatrix}$ , obtained by the action of hydrazine on isonitrosobenzoylacetone, crystallises from dilute alcohol in dark green, serrated needles, m. p. 153° (decomp.). It forms red salts with alkalis. Its solution in concentrated sulphuric acid is dark red. When condensed with *p*-nitrobenzyl cyanide, it forms 4-m-nitro- $\alpha$ -cyanobenzylideneamino-5-phenyl-3-methylpyrazole,



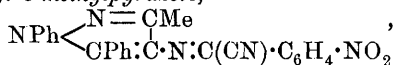
which crystallises from glacial acetic acid in bright red, rhombic plates, m. p. 136°. Its alkali salts are purple. It forms a red solution with concentrated sulphuric acid.

4-op-Dinitrobenzylideneamino-5-phenyl-3-methylpyrazole,



prepared by the condensation of 4-nitroso-5-phenyl-3-methylpyrazole with *op*-dinitrotoluene, crystallises from glacial acetic acid in yellowish-red pyramids, m. p. 240°. Its solution in concentrated sulphuric acid is yellowish-brown. Its alkali salts are dark red.

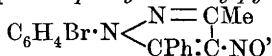
4-Nitroso-1:5-diphenyl-3-methylpyrazole,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CPh}:\text{C}:\text{NO} \end{smallmatrix}$ , obtained from phenylhydrazine and isonitrosobenzoylacetone, separates from dilute acetic acid in bright green, rhombic plates, m. p. 137.5°. Its solution in concentrated sulphuric acid is dark red. When condensed with *p*-nitrobenzyl cyanide, it forms 4-p-nitro- $\alpha$ -cyanobenzylideneamino-1:5-diphenyl-3-methylpyrazole,



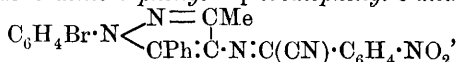
which separates from alcohol in brick-red needles or in hexagonal prisms, m. p. 156°. Its solution in concentrated sulphuric acid is bright yellow.

The azoxy-derivative of 4-nitroso-1:5-diphenyl-3-methylpyrazole,  $\text{C}_{32}\text{H}_{26}\text{ON}_6$ , obtained by the addition of a few drops of sodium hydroxide to a boiling alcoholic solution of the nitrosopyrazole, separates from a mixture of chloroform and alcohol in glistening, serrated, bright brown leaflets, m. p. 211°.

4-Nitroso-5-phenyl-1-p-bromophenyl-3-methylpyrazole,

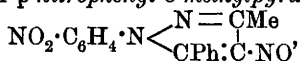


crystallises from alcohol in glistening, bright green, tetragonal plates, m. p. 130°. Its solution in concentrated sulphuric acid is dark brown. When condensed with *p*-nitrobenzyl cyanide, it forms 4-p-4-nitro- $\alpha$ -cyanobenzylideneamino-5-phenyl-1-p-bromophenyl-3-methylpyrazole,

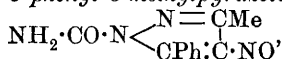


which separates from glacial acetic acid in cinnabar-red, rhombic crystals, m. p. 194°. It forms a yellow solution with concentrated sulphuric acid.



*4-Nitroso-5-phenyl-1-p-nitrophenyl-3-methylpyrazole,*

obtained by the condensation of *p*-nitrophenylhydrazine with isonitrosobenzoylacetone, separates from glacial acetic acid in olive-green, rhombic crystals, m. p. 135°. Its solution in concentrated sulphuric acid has a claret tint. In addition to the pyrazole, the condensation in question leads to the formation of 3-isonitrosobenzoylacetone-*p*-nitrophenylhydrazone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CBz} : \text{N} \cdot \text{OH}$ , which separates from methyl alcohol in hexagonal, glistening, dark yellow pyramids, m. p. 211° (decomp.). Its solution in concentrated sulphuric acid is red.

*4-Nitroso-1-carbamyl-5-phenyl-3-methylpyrazole,*

obtained by the action of semicarbazide on isonitrosobenzoylacetone, separates from acetic acid in green needles, m. p. 128° (decomp.). Its solution in concentrated sulphuric acid is ruby-red.

*4-p-Nitro-α-cyanobenzylideneamino-1-carbamyl-5-phenyl-3-methylpyrazole*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \begin{array}{l} \text{N} = \text{CMe} \\ \text{CPh} : \text{C} \cdot \text{N} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{array}$ , obtained in the usual manner, separates from alcohol in cinnabar-red needles, m. p. 235°. Its solution in concentrated sulphuric acid is wine-red.

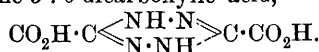
*4-p-Nitro-α-cyanobenzylideneamino-1-phenyl-2:3-dimethyl-5-pyrazolone*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CN}) : \text{N} \cdot \text{C} \begin{array}{l} \text{CMe} \cdot \text{NMe} \\ \text{CO} - \text{NPh} \end{array}$ , obtained by the condensation of nitrosoantipyrine with *p*-nitrobenzyl cyanide, separates from alcohol in glistening, yellowish-red leaflets, m. p. 270°. Its solution in concentrated sulphuric acid is colourless. A. McK.

**Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXIII. Constitution of *s*-Dihydropyrazines.** ROBERT STOLLE (*J. pr. Chem.*, 1907, [ii], 75, 94—98. Compare Abstr., 1906, i, 709).—Polemical. The author contends that the arguments employed by Bülow (Abstr., 1906, i, 905) in support of his proposition that *s*-dihydropyrazine is really 1-amino-3:4-triazole are not conclusive and that the constitution of this compound is still unsettled. W. H. G.

**So-called Trisbisdiazomethanetetracarboxylic Acid and the Related Bisdiazomethane.** THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, 40, 815—837. Compare Abstr., 1906, i, 939; this vol., i, 21; Curtius and Lang, Abstr., 1889, 369; Curtius and Thompson, Abstr., 1906, i, 404, 940; Hantzsch and Silberrad, Abstr., 1900, i, 261; Silberrad, Trans., 1900, 77, 1185).—The authors have repeated Hantzsch and Silberrad's investigation of Curtius and Lang's tridiazooacetic acid (bisdiazooacetic acid) and its

decomposition products. The conversion of trisbisdiazomethane tetracarboxylic acid into bisdiazomethane has been studied quantitatively and the results obtained found to agree with the empirical formula,  $C_2H_3N_4 \cdot CO_2H \cdot \frac{1}{2}H_2O$ , for the supposed tetracarboxylic acid, which is shown now to be identical with *C*-aminotriazolecarboxylic acid (Thiele and Manchot, Abstr., 1899, i, 167); bisdiazomethane formulated by Hantzsch and Silberrad as 3:6-dihydro-1:2:4:5-tetrazine being identical with *C*-aminotriazole.

The substance termed trimethinetriazoimide by Curtius and Lang, or *N*-dihydropottrazine,  $CH \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{N} \cdot \text{NH} \end{smallmatrix} CH$ , by Hantzsch and Silberrad, is considered by Bülow (Abstr., 1906, i, 905; this vol., i, 99) to be *N*-aminotriazole,  $NH_2 \cdot N \begin{smallmatrix} \text{CH} : \text{N} \\ \text{CH} : \text{N} \end{smallmatrix}$ ; from this it follows that the action of potassium hydroxide on bisdiazooacetic acid leads to the simultaneous formation of *C*-aminotriazolecarboxylic acid and *N*-aminotriazole-dicarboxylic acid,  $NH_2 \cdot N \begin{smallmatrix} C(CO_2H) : N \\ C(CO_2H) : N \end{smallmatrix}$ , previously considered to be 1:4-dihydropottrazine-3:6-dicarboxylic acid,



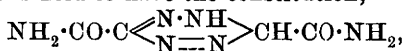
It is found now that Hantzsch and Silberrad's supposed dicarboxylic acid, m. p. 287°, is the *potassium hydrogen dicarboxylate*; when boiled with water, it decomposes forming *N*-aminotriazole. *N*-Aminotriazole-dicarboxylic acid, m. p. 77°, is formed by the action of an excess of very dilute sulphuric acid on the potassium salt.

Contrary to Hantzsch and Silberrad's statement, *C*-aminotriazole (bisdiazomethane) is not converted into *N*-aminotriazole hydrochloride (dihydropottrazine hydrochloride) by the action of boiling dilute hydrochloric acid. It is found that *C*-aminotriazole hydrochloride and *N*-aminotriazole hydrochloride melt at exactly the same temperature, 153°. The bases are distinguished by their behaviour with nitrous acid, *C*-aminotriazole being diazotised, whilst *N*-aminotriazole is converted into triazole.

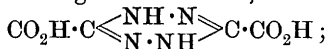
Dihydropottrazine,  $CH \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ \text{N} \text{---} \text{N} \end{smallmatrix} CH$ , formed by reduction of tetrazine with hydrogen sulphide (this vol., i, 262), crystallises in yellow prisms, m. p. 125—126°, and is readily oxidised by air, more completely by nitrous acid, forming tetrazine; the dihydropottrazine is hydrolysed rapidly by sulphuric acid, forming hydrazine sulphate and formic acid, which is analogous to the formation of hydrazine and oxalic acid by the hydrolysis of bisdiazooacetic acid. As *N*-aminotriazole-dicarboxylic acid is converted by the action of hot acids into *N*-aminotriazole, which is stable towards dilute acids, it cannot be formed as an intermediate product in the hydrolysis of bisdiazooacetic acid as supposed by Bülow (*loc. cit.*). When fused, dihydropottrazine undergoes isomeric change into *N*-aminotriazole, which explains the formation of this substance by the action of heat on bisdiazooacetic acid.

Of the four possible dihydropottrazines, that described above is the

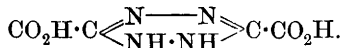
only one which has been prepared. Of derivatives of dihydrotetrazines,  $\psi$ -diazooacetamide is held to have the constitution,



whilst the formation of bisdiazooacetic acid from ethyl *isodiazooacetate* points to its having the structure,



it is possible that this is tautomeric with the structure,



The condensation product of salicylaldehyde and bisdiazomethane, considered by Ruhemann (*Trans.*, 1906, **89**, 1268) to be a derivative of *C*-dihydrotetrazine, must be derived from *C*-aminotriazole. *Benzylidene-C-aminotriazole*,  $\text{CHPh} \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{NH} \cdot \text{N} \\ \text{N} - \text{N} \end{array} > \text{CH}$ , prepared by the action of benzaldehyde and pyridine on *C*-aminotriazole in absolute alcoholic solutions, forms a sparingly soluble, white, crystalline precipitate, *m. p.* 210°.

G. Y.

**Preparation of 4 : 6-Di-imino-5 : 5-dialkyl-2-cyanoimino-pyrimidines.** *FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 175588 and 175589).*—By the interaction of dialkylmalononitriles and dicyanodiamide in the presence of alkaline condensing agents, pyrimidine derivatives are produced which probably have the general formula  $\text{CN} \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{NH} \cdot \text{C}(\text{NH}) \\ \text{NH} \cdot \text{C}(\text{NH}) \end{array} > \text{CR}_2$ , where R is an alkyl group. These substances have the valuable property of being easily converted by hydrolytic agents into the technically important dialkylbarbituric acids. The condensation product from dicyanodiamide and diethylmalononitrile crystallises from boiling water in needles, *m. p.* 270°.

These condensations may be effected by prolonged warming on the water-bath, but the action is accelerated and the yield increased by heating at higher temperatures under pressure.

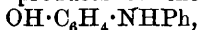
The foregoing condensation is thus carried out in alcoholic potash at 120°.

G. T. M.

**Reaction between Hydrogen Peroxide and Diphenylamine in Sulphuric Acid Solution.** A. USCHAKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 959—962. Compare *Abstr.*, 1906, i, 159).—Further study of the compound, *m. p.* 240°, obtained by the action of zinc dust on the compound  $\text{C}_{30}\text{H}_{49}\text{O}_2\text{N}_5$  (*loc. cit.*), shows it to be diphenylbenzidine,  $\text{NHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NHPh}$ , *m. p.* 242°; the best yield of the latter is obtained by gradually raising the temperature of the mixture of zinc dust and the compound in a combustion tube. When diphenylamine itself is heated with zinc dust in this way, no diphenylbenzidine is formed.

The two compounds obtained by the interaction of hydrogen peroxide and diphenylamine in presence of sulphuric acid must be

regarded as condensation products of the compound,



the sulphuric acid acting as condensing agent. The action of benzoyl chloride on these condensation products indicates that they contain hydroxyl groups.

The same compounds are obtained by the action of an electric current on a sulphuric acid solution of diphenylamine as by the action of hydrogen peroxide.

T. H. P.

#### Action of Sodium Hyposulphite on Diazo-Salts.

EUGÈNE GRANDMOUGIN (*Ber.*, 1907, 40, 858—859. Compare this vol., i, 263).—An alkaline solution of sodium hyposulphite reacts with the solution of a diazo-salt to displace the diazo-group by hydrogen.

C. S.

[Azo-derivative of Anthranilic Acid.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 175828).—Anthranilic acid diazotised and introduced into a solution of sodium  $\beta$ -naphthol-6-sulphonate in sodium carbonate yields a reddish-bronze azo-compound which is soluble in water or concentrated sulphuric acid to a yellowish-red solution. Its lake has a vivid red colour and is extremely fast to light.

G. T. M.

#### Constitution of Azo-derivatives of Ethyl Benzoylacetate.

ANDRÉ WAHL (*Compt. rend.*, 1907, 144, 569—571).—Ethyl benzoylglyoxalate (this vol., i, 217) combines with phenylhydrazine in presence of alcohol or dilute acetic acid to furnish an *additive* product,  $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_2$ , m. p. 89—90°, which crystallises from alcohol in colourless or faintly yellow needles, and rapidly decomposes even in the absence of air, producing a mixture of 4-phenylhydrazo-1:3-diphenyl-

5-pyrazolone,  $\text{N} \begin{smallmatrix} \text{CPh} \\ \text{NPh} \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{NHPh} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}$  (Stierlin, *Abstr.*, 1888, 1089), and

ethyl benzoylglyoxalate-phenylhydrazone. The latter may also be obtained by the action of phenylhydrazine (1 mol.) on the ester dissolved in cold acetic acid. It is identical with Stierlin's (*loc. cit.*) ethyl benzeneazobenzoylacetate and must be represented by the formula  $\text{NHPh} \cdot \text{N} \cdot \text{CBz} \cdot \text{CO}_2\text{Et}$ , since on treatment with acetic anhydride in presence of a drop of sulphuric acid, it yields an acetyl derivative, which on reduction with zinc and sulphuric acid furnishes acetanilide (compare Bülow and Hailer, *Abstr.*, 1902, i, 325). These results indicate that the azo-derivatives of the benzoylacetic series have the phenylhydrazone structure. Bouveault and Wahl have shown (*Abstr.*, 1904, i, 789) that when phenylhydrazine reacts with the acetylglyoxalates condensation takes place with the  $\beta$ - in place of the  $\alpha$ -carbonyl group as in the present instance.

T. A. H.

Preparation of the Sulphonic Acids of 1-Diazo-2-oxy-naphthalene. KALLE & Co. (D.R.-P. 175593).—The orthoaminonaphtholsulphonic acids are not readily diazotised by the ordinary process, but when the normal salt of the sulphonic acid of 1-amino- $\beta$ -naphthol is treated with zinc nitrite the diazo-oxynaphthalene-

sulphonic acid is obtained in the form of its zinc salt. The same result is produced when a mixture of a soluble zinc salt and an alkali nitrite is used, and when the free aminonaphtholsulphonic acids or the acid salts of the aminonaphtholpolysulphonic acids are employed. When treated in this way, 1-amino- $\beta$ -naphthol-4-sulphonic acid gives rise to zinc 1-diazo-2-oxynaphthalene-4-sulphonate,  $\text{Zn}(\text{SO}_3 \cdot \text{C}_{10}\text{H}_5 \text{ < } \overset{\text{N}}{\underset{\text{O}}{\parallel}} )_2$ , which crystallises from hot water in well-defined needles having a bronze lustre. G. T. M.

**Sulphonation of Diazo-oxynaphthalene-4-sulphonic Acids.** KALLE & Co. (D.R.-P. 176618 and 176620).—The diazo-oxynaphthalenesulphonic acids, prepared from the ortho-aminonaphthol-sulphonic acids by the action of the nitrites of zinc, nickel, mercury, and other heavy metals, are remarkably stable diazo-derivatives which may be recrystallised and dried without undergoing any change. It has now been found that these diazo-compounds can actually be sulphonated.

1-Diazo-2-oxynaphthalene-4-sulphonic acid, when treated at 30–50° with fuming sulphuric acid containing about 6% of sulphuric trioxide, yields a soluble sulphonated product which can be salted out from aqueous solution as a pale yellow, crystalline precipitate. Similar sulphonated products are obtained from 1-diazo-2-oxynaphthalene-6-sulphonic acid and 2-diazo-1-oxynaphthalene-5-sulphonic acid.

G. T. M.

**Nitration of Diazo-oxynaphthalenesulphonic Acids.** KALLE & Co. (D.R.-P. 176619).—The diazo-oxynaphthalenesulphonic acids when dissolved or suspended in concentrated sulphuric acid are readily nitrated on the addition of either a nitrate or a mixture of nitric and sulphuric acids.

1-Diazo-2-oxynaphthalene-6-sulphonic acid when nitrated in this way furnishes a soluble, yellow, crystalline *nitro*-derivative which may be salted out from its aqueous solution. 2-Diazo-1-oxynaphthalene-5-sulphonic acid furnishes a similar *nitro*-derivative which may be recrystallised from dilute hydrochloric acid.

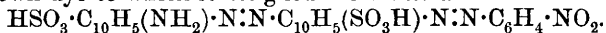
G. T. M.

**Preparation of Azo-derivatives of the Pyrazolone Group.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 176954).—*m*-Xylidine-*o*-sulphonic acid when diazotised and coupled with 1-*p*-sulphophenyl-3-methyl-5-pyrazolone furnishes a yellow dye, and similar compounds are obtained from 1-*p*-sulpho-*o*-tolyl-3-methyl 5-pyrazolone, 1-*p*-sulpho-*o*-tolyl-5-pyrazolone-3-carboxylic acid, and 1-phenyl-3-methyl-5-pyrazolone. These compounds are distinguished by their beautiful yellow colour and their fastness to light.

G. T. M.

**Formation of New Polyazo-dyes According to Hitherto Unknown Law.** LUDWIG PAUL (*Zeitsch. angew. Chem.*, 1907, 20, 268–272).—It has hitherto been supposed that only when a benzene or naphthalene derivative contains so-called primary groups, such as the hydroxyl groups in resorcinol or 1-8-dihydroxynaphthalene, or a

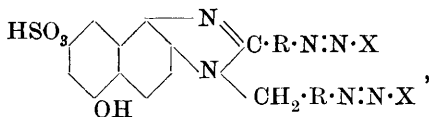
hydroxyl and an amino-group as in aminonaphthol, is it possible for 1 molecule of this compound to combine directly with more than 1 molecule of a diazo-compound to form polyazo-dyes. The author finds, however, that all monoazo-dyes derived from diazonaphthalene, diazonaphthols, or the sulphonic acids of these compounds are capable of combining directly with a further molecule of a diazo- or bisdiazo-compound; for example, 1-naphthionic acid-azonaphthalene-4-sulphonic acid combines with 1 molecule of *p*-nitrodiazobenzene to form a red-dish-brown dye to which is assigned the formula



By adding diazotised benzidine to 1-naphthionic acid-azonaphthalene-4-sulphonic acid, an intermediate condensation product is obtained, which condenses further with phenols, aromatic amines, and derivatives of these compounds to form dyes of various shades of red. In the same way, a considerable number of dyes of various colours have been obtained by coupling phenols, aromatic amines, and derivatives of these substances with the intermediate condensation products obtained by condensing diazotised benzidine with several monoazo-dyes derived from the sulphonic acids of diazonaphthalene and diazonaphthols. No analyses of the compounds obtained are given.

W. H. G.

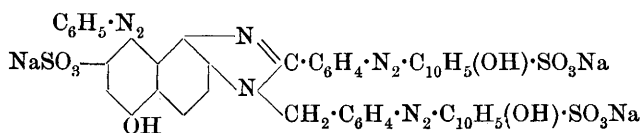
**Preparation of Polyazo-derivatives.** LEOPOLD CASSELLA & Co. (D.R.-P. 175666).—1 : 2-Diamino-5-hydroxynaphthalene-7-sulphonic acid condenses with two molecular proportions of a monoazo-compound containing an aldehydic group to furnish bisazo-colouring matters



having the general formula where R is a bivalent aromatic group and X an aminic or phenolic residue. These compounds when further condensed with a diazo-compound

are substantive dyes for cotton which are extremely fast to light, acid, and scouring agents. The most useful substances from this point of view are those derived from *m*-diazobenzaldehyde and the naphthol-sulphonic acids.

The azo-compound from diazotised *m*-aminobenzaldehyde and  $\beta$ -naphthol-6-sulphonic acid is condensed with 1 : 2-diamino-5-hydroxynaphthalene-7-sulphonic acid in hot dilute acetic acid solution, the ring formation being completed by further boiling with hydrochloric acid. The product is then collected, redissolved in aqueous sodium carbonate, and coupled with diazobenzene chloride; the re-



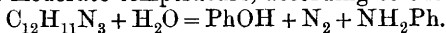
sulting trisazo-compound is a red powder which

dyes unmordanted cotton in yellowish-scarlet shades. In these condensations the  $\beta$ -naphthol-6-sulphonic acid may be replaced by other naphtholsulphonic acids and the aniline by other

aromatic amines. A table of the dyes produced by these various combinations is given in the patent.  
G. T. M.

**Isomeric Diazoaminobenzene.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 587—595).—If a primary aromatic base, such as aniline, is diazotised by means of sodium nitrite in presence of acetic acid instead of a mineral acid, orange-coloured spangles separate and the yellow solution obtained, which contains a nitrosoamine, exhibits the reactions of diazo-solutions, that is, it yields an azo-colouring matter with alkaline phenol or naphthol solution, whilst, when it is treated with cuprous chloride, molecular copper, or potassium iodide, decomposition and evolution of nitrogen occur. The formation of the nitrosoamine takes place according to the equation:  $\text{NH}_2\text{Ph} + \text{HNO}_2 = \text{NHPh}\cdot\text{NO} + \text{H}_2\text{O}$ , its reaction with phenols being expressed by  $\text{NHPh}\cdot\text{NO} + \text{C}_6\text{H}_5\cdot\text{OH} = \text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{H}_2\text{O}$ , and its decomposition by  $\text{NHPh}\cdot\text{NO} = \text{Ph}\cdot\text{OH} + \text{N}_2$ .

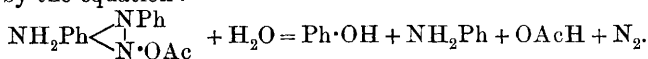
When a solution of 7 grams of sodium nitrite in 30 c.c. of water is added to a mixture of 12 grams of glacial acetic acid, 18 grams of aniline, and 500 grams of water at the ordinary temperature, an *isomeride* of diazoaminobenzene separates as an orange-coloured precipitate, which gradually becomes crystalline and sometimes assumes a dark brown colour. In the latter form it has m. p. 91·5—93°, whilst when crystallised from alcohol it is deposited in leaflets, m. p. 81—94°. It is probably a mixture of substances or of different crystalline forms of the same substance, or possibly isomeric change occurs during the melting. It dissolves in glacial or 80% acetic acid, concentrated sulphuric acid, ether, benzene, chloroform, or alcohol, and partially in dilute hydrochloric (or sulphuric) acid giving a red solution, which, on heating, deposits aminoazobenzene hydrochloride:  $\text{C}_{12}\text{H}_{11}\text{N}_3 + \text{HCl} = \text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$ . With alkaline  $\beta$ -naphthol solutions, its acetic acid solution yields a red azo-colouring matter at the ordinary temperature, whilst ordinary diazoaminobenzene gives a yellow azo-compound only on boiling. When treated in acetic acid solution with cuprous chloride, molecular copper, or potassium iodide, it decomposes completely at a moderate temperature, according to the equation:



Cryoscopic measurements in acetic acid or nitrobenzene and ebullioscopic measurements in ether or carbon disulphide indicate the formula  $\text{C}_{12}\text{H}_{11}\text{N}_3$ . When reduced by means of zinc and hydrochloric acid, the compound is converted into phenylhydrazine and aniline.

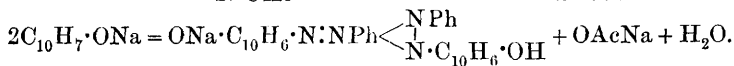
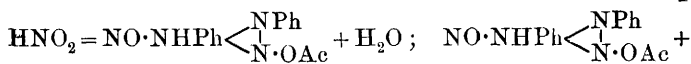
The properties of the isomeric diazoaminobenzene are best represented by the formula  $\text{NHPh}\cdot\text{N}^{\text{NPh}}$ . On dissolving in acetic acid,

a compound,  $\text{NH}_2\text{Ph}\cdot\text{N}^{\text{NPh}}\cdot\text{OAc}$ , is formed. The decomposition in presence of cuprous chloride, molecular copper, or potassium iodide is represented by the equation:



When the isomeric diazoaminobenzene is treated with excess of sodium

nitrite in acid solution and subsequently with alkaline  $\beta$ -naphthol solution, a red colouring matter is obtained:  $\text{NH}_2\text{Ph} \begin{smallmatrix} \text{NPh} \\ | \\ \text{N} \cdot \text{OAc} \end{smallmatrix} +$



In the preparation of the isomeric diazoaminobenzene and in the reactions described above, the acetic acid may be replaced by formic, lactic, tartaric, and other organic acids; but the stronger the acid used, the less the yield of the compound and the greater the instability of its solution in the acid. T. H. P.

**Albumins of the White of Turkeys' Eggs. I. Crystalline Albumin.** WLADIMIR W. WORMS (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 597—607).—The white of turkeys' eggs contains, besides globulin, several albumins, one of which is crystalline, and may be isolated as follows. The egg-white is cut up, neutralised with 4% sulphuric acid solution and filtered through muslin, the solution being mixed with one-half its volume of saturated ammonium sulphate solution and filtered through a paper filter which is renewed from time to time. To the filtrate, sufficient saturated ammonium sulphate is added to render the liquid half saturated with the salt, and the globulin thus precipitated is removed by filtration after twenty-four hours. The filtrate is evaporated at the ordinary temperature and treated with saturated ammonium sulphate solution until a faint turbidity appears. The precipitate which gradually forms is filtered off when the deposition begins to slacken, and to the filtrate ammonium sulphate is again added until a slight turbidity appears. A sticky mass separates, which, when dissolved in one-fifth saturated ammonium sulphate solution and precipitated by a saturated solution of the salt, is deposited in almost colourless, slender needles and leaflets, readily soluble in water, but nearly insoluble in semi-saturated ammonium sulphate solution. Aqueous solutions of the albumin are slightly acid and give all the albumin reactions. It is completely coagulated by heating or by the addition of 95% alcohol. Its composition is represented by  $\text{C}_{258}\text{H}_{422}\text{O}_{83}\text{N}_{63}\text{S}_3$  (compare Panormoff, *Abstr.*, 1899, i, 655), and it has  $[\alpha]_D^{20} = -34.9^\circ$ . With hydrochloric acid, it gives a salt  $\text{Alb} \cdot 4\text{HCl}$ . Although the albumin has the same composition and reactions as that obtained from hens' eggs (Panormoff, *loc. cit.*), it differs from the latter in specific rotation and in its property of being converted into a non-crystalline modification by treatment with water. T. H. P.

**Presence of Phosphorus in Crystalline Egg-albumin.** Miss EDITH G. WILLCOCK and WILLIAM B. HARDY (*Proc. Camb. Phil. Soc.*, 1907, 14, 119—120).—The presence of phosphorus in egg-albumin has only been mentioned by Osborne and Campbell (*Abstr.*, 1900, i, 574), who consider it to be present as associated phosphate and not as a constituent of the protein molecule. The authors find that phos-



phorus is present as "organic" phosphorus, and that it is undoubtedly a constituent of crystalline egg-albumin, which, since it contains 0.13% of phosphorus, contains in 1 molecule 12 atoms of sulphur to each atom of phosphorus, thus giving the value 23,800 as the mol. weight of this protein.

W. H. G.

**Action of Nitrous Acid on Egg-albumin.** ZDENKO H. SKRAUP and KARL KAAS (*Annalen*, 1907, 351, 379—389. Compare Paal, Abstr., 1896, i, 455; Schrötter, Abstr., 1898, i, 610).—In view of the interesting results obtained by treating casein with nitrous acid (Skraup and Hoernes, Abstr., 1906, i, 913), the authors have extended the reaction to other proteins. The present paper deals with the products obtained in this manner from crystalline egg-albumin (Kaas, Abstr., 1906, i, 777).

Deaminoalbumin,  $C_{100}H_{160}O_{33}N_{25}S_{1.6}P_{1.6}$  (Schiff, Abstr., 1896, i, 632), is formed by the action of sodium nitrite and acetic acid on crystalline egg-albumin,  $C_{100}H_{166}O_{33}N_{25}SP_{0.6}$ ; from analytical figures, it is concluded that the molecule of egg-albumin decomposes into two parts, the deaminoalbumin being formed from that which contains the more sulphur and phosphorus. Deaminoalbumin has a feeble acid reaction, gives with aqueous alkalis a yellow to brown, with  $\alpha$ -naphthol and concentrated sulphuric acid a dark violet, or with thymol and sulphuric acid a yellowish-red solution, and behaves towards acids in the same manner as albumin. Whilst hydrolysis of egg-albumin leads to the formation of arginine and lysine, that of deaminoalbumin leads to the formation of arginine only. Histidine is not found in either of the products of hydrolysis. The lysine of egg-albumin is probably in that part of the molecule from which deaminoalbumin is not derived.

G. Y.

**A New Decomposition Product of Gliadin.** THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, 18, 123—126).—A crystalline substance was isolated from the products of acid hydrolysis of gliadin; a crystallographic study of its copper salt is given. It is probably a dipeptide, and yields proline and phenylalanine on further hydrolysis.

W. D. H.

**Ion-protein Compounds. IV. Properties of Caseinogen.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1907, 2, 317—384).—Caseinogen (called casein in the paper) reddens litmus. A volumetric method of estimation is described, and the solubilities of the material in various salts estimated. The bulk of the paper deals with the physical chemistry (velocity of hydrolysis of caseinogen compounds, &c.) of the subject on the lines of the author's previous work. Proteins are regarded as amphoteric electrolytes.

W. D. H.

**Some Phenomena observed in the Peptic Digestion of Caseins.** JOHN H. LONG (*J. Amer. Chem. Soc.*, 1907, 29, 223—230).—In a previous paper (Abstr., 1906, i, 391) it has been shown that the caseins of goat's milk and cow's milk are very similar, that the

equivalent weight of the former is slightly lower than that of the latter, and that solutions of their salts have nearly the same electrical conductivity.

Experiments have now been made on the behaviour of the two caseins with pepsin and dilute hydrochloric acid at 38°. During the digestion, the casein does not dissolve completely, but leaves a light, flocculent residue of "pseudonuclein" which in appearance and quantity is characteristic of each casein. The casein of the goat's milk undergoes change more slowly than that of the cow's milk and the former leaves about 4.4% of "pseudonuclein," whilst the latter yields 12.8%. In the course of the digestion, the electrical conductivity and the total and free acidity vary regularly. Both acidity values are lower for the goat casein than for the cow casein.

After separating the "pseudonuclein," the filtrates were slowly evaporated and the residue dried at 100–105°. On weighing these residues, it was found that a considerable increase in weight had taken place owing to hydrolysis and combination with hydrochloric acid to form complex salts. The increase amounted to 31.5% in the case of the cow casein and to 36.4% in that of the goat casein. On redissolving these residues, the conductivities and total acidities of the solutions, when calculated on unit weight of solid present, were nearly the same for each casein. The chief difference in the two caseins therefore appears to be the amount of "pseudonuclein" obtainable.

E. G.

**Relationship between Chlorophyll and Hæmoglobin.** LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1907, 3, 320–322. Compare Abstr., 1905, i, 399, 500; 1906, i, 779).—Zaleski's hydrogenised hæmin is very like ordinary hæmin; on decomposition with hydrobromic acid in an acetic acid solution, it yields mesoporphyrin, a substance exactly like phylloporphyrin obtained from chlorophyll. The present research shows that by dissolving phylloporphyrin with warm glacial acetic acid saturated with sodium chloride, and warming it with some Mohr's salt dissolved in 50% acetic acid, on the water-bath, a brown pigment is obtained called phyllohæmin which spectroscopically is identical with hæmin.

W. D. H.

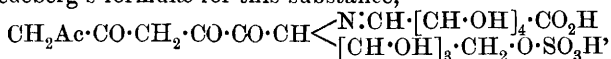
**New Reactions of Hæmatin.** OTTO VON FÜRTH (*Annalen*, 1907, 351, 1–11. Compare Küster, Abstr., 1904, i, 357, 358).—I. *Action of Phenylhydrazine on Hæmin.*—Hæmin reacts with an excess of phenylhydrazine at the laboratory temperature with development of heat, evolution of ammonia, and formation of a *product* of the interaction of hæmin and aniline. This is obtained as a loose, brown powder containing nitrogen and iron in the proportion N : Fe = 7.9 : 1; after reduction with phosphonium iodide and hydriodic acid, D 2.0, in glacial acetic acid solution on the water-bath, it gives the characteristic reactions for hæmopyrrole. Hæmatoporphyrin does not react with phenylhydrazine.

II. *Action of Bromophenylhydrazine on Hæmin.*—*p*-Bromophenylhydrazine acts on hæmin at 50–60° with development of heat, evolution of gas, and formation of a brown, granular *product*, which is soluble in chloroform, and gives analytical results agreeing with the

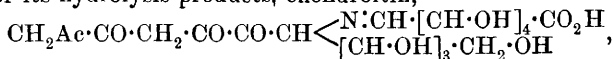
formula  $C_{52}H_{45}O_6N_6Br_3Fe$ . A similar product is formed by the action of *p*-bromophenylhydrazine on hæmatin. When reduced with phosphonium iodide and hydriodic acid in glacial acetic acid solution and distilled in a current of steam, it yields a *product* which gives the reactions characteristic of hæmopyrrole. The action of hydrogen bromide on the additive product of *p*-bromophenylhydrazine and hæmatin leads to the formation of hæmatoporphyrin and of a brown *product* which contains bromine and nitrogen in the proportion  $N:Br = 1:0.52$ , and is almost free from iron. G. Y.

**Oxidation of Nucleic Acid. II.** HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 50, 538—539. Compare Abstr., 1906. i, 915).—In order to obtain some knowledge of the nature of the carbohydrate obtainable from the nucleic acid of fish sperm, oxidation was carried out by means of nitric acid. The barium salt of an acid was obtained which in composition agrees with that of saccharic and mucic acids, but differs in its properties from both. It is suggested it may be Habermann's parasaccharic acid. W. D. H.

**Chondroitin-sulphuric Acid.** SIGMUND FRÄNKEL (*Annalen*, 1907, 351, 344—353. Compare Mörner, Abstr., 1895, i, 254).—The results of an investigation of the products of the hydrolysis of chondroitin-sulphuric acid, with different strengths of sulphuric acid, support Schmiedeberg's formulæ for this substance,



and for its hydrolysis products, chondroitin,



and chondroisin,

$CHO \cdot CH(N:CH \cdot [CH \cdot OH]_4 \cdot CO_2H) \cdot [CH \cdot OH]_3 \cdot CH_2 \cdot OH$  (*Arch. Exp. Pathol.*, 1891, 28, 355), against the criticisms of Orgler and Neuberg (Abstr., 1903, i, 589), who failed to obtain any of the reactions for glycuronic acid.

Hydrolysis of copper chondroitin-sulphate by means of 70% sulphuric acid at the ordinary temperature leads in forty-eight hours to removal of the sulphuric acid and one acetyl group with formation of a substance,  $C_{16}H_{23}O_{13}N \cdot 3H_2O$ , which has an acid reaction, and has reducing properties after, but not before, being boiled with dilute sulphuric acid; the barium salt,  $C_{16}H_{21}O_{13}NBa \cdot 5H_2O$ , was analysed.

The two basic copper salts obtained on hydrolysis of copper chondroitin-sulphate with 10% sulphuric acid for ten hours, contain carbon and nitrogen in the proportion,  $C_{12}:N$ , and are derivatives of chondroisin.

The action of 70% sulphuric acid on copper chondroitin-sulphate at the laboratory temperature for four days, leads to the formation of a substance,  $C_{10}H_{19}O_9N$ , which reduces Fehling's solution, but does not form an insoluble phenylhydrazone.

When hydrolysed with 20% sulphuric acid in a current of hydrogen for twelve hours, copper chondroitin-sulphate yields an *aminoglycuronic acid*,  $C_6H_{11}O_6N$ , which is obtained as a white powder, and gives with

orcinol and concentrated hydrochloric acid a violet coloration, becoming green on addition of ferric chloride; the green substance is extracted by amyl alcohol.

G. Y.

**Iodogorgonic Acid.** MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1907, 51, 64—70).—Iodogorgonic acid,  $C_9H_9O_3NI_2$ , is an iodine compound prepared from Drechsel's gorgonin; it is identical with inactive di-iodotyrosine. Its method of preparation is described.

W. D. H.

**Colloidal Nature of Albumose Solutions.** PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1907, 3, 109—115).—The albumoses contained in Riedel's peptone yield a flocculent precipitate with a mastic emulsion even in the absence of an electrolyte, but the precipitate is not obtained if the peptone solution is previously made slightly alkaline. The amount of mastic required in the case of peptone is much less than with albumins.

The method recommended for removing proteins is to make faintly alkaline, then add the mastic emulsion and finally acidify with acetic acid and add the electrolyte (magnesium sulphate). All the albumoses are not precipitated by this process, some 70% of the total peptone nitrogen is found in the filtrate, and the addition of phosphotungstic acid to the filtrate produces a heavy precipitate. To obtain the albumose from the mastic precipitate, the latter is dried and the mastic removed by extraction in a Soxhlet extractor with chloroform and the mixture of albumose and proteins carefully extracted with hot water. A series of experiments has shown that of 0.296 gram of peptone nitrogen originally present 0.062 gram is precipitated by mastic and 0.211 gram is not. The peptone not precipitated the first time cannot be precipitated by the addition of more protein and mastic to the filtrate. The concentration of the solution does not appear to affect the amount of albumose precipitated. The albumoses precipitated by the mastic are the "higher" albumoses which can be precipitated by ammonium sulphate; but the solution from the mastic precipitate also contains albumoses which can be salted out by means of ammonium sulphate.

J. J. S.

**Preparation of Solid Soluble Silver Salts in Combination with Colloids.** KALLE & Co. (D.R.-P. 175794).—Colloidal silver carbonate is produced by precipitating silver protoalbate or lysalbate by mixing solutions of the sodium salt of one of these organic acids with silver nitrate, dissolving the precipitate in aqueous sodium carbonate, and dialysing the solution. On evaporating the dialysed solutions under reduced pressure at moderate temperatures a residue is obtained consisting of normal silver carbonate mixed with the colloidal alkali salt of the organic acid.

Colloidal silver phosphate is made by adding silver nitrite to a solution of sodium phosphate and sodium protoalbate; the precipitate is dissolved by the addition of sodium phosphate and the clear solution dialysed.

Colloidal preparations containing a high percentage of silver

chloride, bromide, and iodide are prepared similarly, the most stable of the series being the iodide. The preparation of this compound with sodium lysalbinat forms yellowish-brown granules containing 95% of silver iodide.  
G. T. M.

**Plasteins.** I. J. LUKOMNIK (*Beitr. chem. Physiol. Path.*, 1907, 9, 205—214).—Plastein is the name given to the precipitate which is the result of the action of rennet on "peptone" solutions. During dialysis against distilled water, the plastein-yielding material passes partly into the dialysate. Urea has no important action on the course of plastein formation, but it hinders their being "salted out" from solutions. The view taken of the precipitation of plastein is that it is due to a process of "salting out" which occurs during rennet action.

W. D. H.

**Hydrolytic Decomposition Products of Caseoplastein.** L. ROSENFELD (*Beitr. chem. Physiol. Path.*, 1907, 9, 215—231).—Five preparations of plastein from casein-peptone were made, and were found to be very similar in elementary composition. In comparison with caseinogen they have a high carbon and a low nitrogen percentage. Among their hydrolytic products, arginine, histidine, lysine, tyrosine, leucine, pyrrolidine-2-carboxylic acid, phenylalanine, and glutamic acid were identified. The following table contrasts the distribution of nitrogen in caseinogen and caseo-plastein.

	Caseinogen.	Caseoplastein.
Amino-nitrogen .....	9.48	3.12
Diamino-nitrogen .....	20.53	20.09
Nitrogen in unknown combination ...	69.99	76.79

W. D. H.

**The Lecithin-like Substances from the Myocardium and from Striped Muscle.** A. ERLANDSEN (*Zeitsch. physiol. Chem.*, 1907, 51, 71—155).—The wide distribution of phosphatides in the organism is confirmed. These, however, do not merely differ in the kind of fatty acid they contain, and may be classified into mono- and diamino-monophosphatides and diphosphatides. The monoaminomonophosphatides (the lecithin-kephalin group  $N:P=1:1$ ) are the most abundant. The lecithin prepared from ox-flesh has the same formula as that prepared from egg-yolk ( $C_{43}H_{80}O_9NP$ ); the two fatty acid radicles appear to belong to the linoleic acid series. The mono-amino-diphosphatides ( $N:P=1:2$ ) are represented by *cuorin*, which was separated from the ox-heart. It contains two phosphoric acid radicles which are in part united to glycerol, three fatty acid radicles, and a basic substance which is not choline. Its empirical formula is  $C_{71}H_{125}O_{21}NP_2$ . It is characterised by its insolubility in alcohol, its auto-oxidisability, and the insolubility of its metallic compounds. Diamino-monophosphatides ( $N:P=2:1$ ) are not regarded as existing free in the organism, but probably united to protein. After the proteins are coagulated by alcohol, the phosphatides can be extracted with ether. The cadmium compound of one from the heart had the

formula  $C_{40}H_{75}O_2N_2P_2CdCl_2$ ; this contains only one fatty acid radicle and two basic ones; the bases are, in part, different from choline. Thudichem's aminomyelin and sphengomyelin belong to this group. Diaminodiphosphatides ( $N:P=2:2$ ) were isolated by Thudichem, but not found in the present research. No definite conclusions are reached respecting jecorin and protagon. The methods hitherto in use for estimating phosphatides, including the recent one of W. Koch and Woods, are regarded as inaccurate. Precipitation by cadmium chloride also is not quantitative.

W. D. H.

**Inorganic Ferments and Organic Enzymes.** GEORG BREDIG (*Chem. Zeit.*, 1907, 31, 184—185).—A reply to Bokorny's criticisms (this vol., ii, 184); the latter's statement that organic enzymes once poisoned cannot be restored is disproved by the fact that both catalase and zymase which have been poisoned by hydrocyanic acid recover their activity on removal of the acid.

P. H.

**The Use of Antiseptics in Investigations on Enzymes.** ALB. J. J. VANDEVELDE (*Biochem. Zeitschr.*, 1907, 3, 315—319).—The difficulties of investigating enzyme action in the presence of most antiseptics are described. The experiments recorded with milk show that an admixture of iodoform and dimethyl ketone does not interfere with proteolytic and other enzyme activity, but yet ensures complete sterility.

W. D. H.

**Oxidation of Philothionic Hydrogen by Oxydases.** JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1907, [iv], 1, 165—167. Compare Abstr., 1906, i, 999).—When a solution of manganese chloride is mixed with white of egg diffused in water and sodium hydroxide is added, a solution is formed which becomes brown on exposure to air. The protein matter obtained by acidifying and then boiling the solution evolves hydrogen sulphide on the addition of sulphur. This property is still retained after heating the brown solution for two hours at 40—45°, but disappears after heating for four hours at the same temperature, this being due to the oxidation of the philothionic hydrogen. This oxidation does not occur in the absence of either manganese chloride or sodium hydroxide and probably indicates that philothionic hydrogen may be oxidised by the oxydase, which occurs in muscular tissue.

Philothion may be either an isomeride of non-philothionic protein or a hydrogenised product of ordinary protein, the hydrogen being obtained by the decomposition of water.

T. A. H.

## Organic Chemistry.

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**Abnormal Reactions, Especially in the Action of Alkyl Haloids on Salts.** RUDOLF WEGSCHEIDER and ERICH FRANKL (*Monatsh.*, 1907, 28, 79—114).—The formation of esters by the action of metallic salts on alkyl haloids takes place according to the equation:  $MA + AlkX = MX + AlkA$  (A = anion of organic acid, M = metal, X = halogen, Alk = alkyl); on the other hand, it is found frequently that the product obtained is not that of this normal reaction, but is a substance known to be formed by the action of an alcohol on the free organic acid. The normal reaction product is then to be obtained by the exclusion of water and alcohol, or sometimes by carrying out the reaction at low temperatures. Such cases occur in the action of methyl iodide on *o*-aldehydo-carboxylates, when  $\psi$ -esters may be formed (Abstr., 1892, 1208), and in the formation of  $\beta$ -alkyl hydrogen or dialkyl esters instead of  $\alpha$ -alkyl hydrogen esters in the esterification of dibasic acids (Abstr., 1895, i, 520). Alongside of these must be placed the formation of free acids by the action of alkyl iodides on silver salts.

Whilst the formation of the free acid may be ascribed in a few cases to the hydrolysis of the normal reaction product by water or, in the esterification of sulphonic acids, by alcohol, it appears to result more generally from the action of the water or alcohol on the alkyl iodide, since not infrequently the normal product, which can be obtained only on exclusion of alcohol and water, is not hydrolysed by these to any marked extent, and the formation of the free acid is accompanied by that of alkyl ethers. This explanation, although satisfactory when the reacting substances are heated with water or alcohol for a long time at high temperatures, is insufficient when the reaction takes place at the ordinary temperature, as under these conditions alkyl haloids are hydrolysed by alcohol (Burke and Donnan, *Trans.*, 1904, 85, 587) or by water (Cain, *Abstr.*, 1894, ii, 133) only very slowly. Certain results (Abstr., 1904, i, 249) have suggested that the amount of free acid formed is dependent on the nature of the organic acid; the action of methyl iodide on a number of organic silver salts has now been investigated and it is found that with silver acetate, phthalonate, camphorate, or benzoate the amount of free acid obtained is greater in presence of water and methyl alcohol than in that of the alcohol alone. Acetic acid is formed at the ordinary temperature or at 55° only in presence of water. On the other hand, 3-nitrophthalic acid is formed from the silver salt in approximately the same amount in methyl-alcoholic as in aqueous methyl-alcoholic solution. The conclusion is drawn that the action of methyl alcohol or water on methyl iodide is catalytically accelerated by the silver salt, the extent of the acceleration being dependent on the nature of the organic acid.

The formation of the free acid and the abnormal reactions to which it gives rise are discussed from a theoretical point of view. G. Y.

**Identity of the Four Valencies of the Carbon Atom.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 722—731).—The author has compared the physical properties of the four nitromethanes and acetonitriles obtained by the successive replacement of the four atoms of hydrogen, one at a time, in methane by  $\text{NO}_2$  and by CN respectively (compare Abstr., 1887, 711), and confirms his statement that each set of compounds consists of the same substance. The following physical constants are given: nitromethane, b. p.  $101-102^\circ/750-760$  mm.,  $D_4^{20}$   $1.13723-1.13782$ ,  $n_D^{20}$   $1.39345-1.39358$  (compare Brühl, Abstr., 1895, ii, 194), m. p.  $-28.4^\circ$  to  $-28.5^\circ$ . Acetonitrile, b. p.  $82.2-83^\circ/747-764$  mm., m. p.  $-44^\circ$  to  $-46^\circ$  (compare Schneider, Abstr., 1897, ii, 304),  $D_4^{20}$   $0.78614-0.78670$ ,  $n_D^{20}$   $1.34420-1.34426$  (compare Brühl, loc. cit.).

The coefficients of dilatation of the two compounds have been determined by De Heen, who finds for the following relation,  $V_t = V_{10}(1 + a\tau + b\tau^2)$ , where  $\tau = t - 10$ , that in the case of nitromethane between  $10^\circ$  and  $100^\circ$ ,  $a = 0.001147$  and  $b = 0.000002356$ , and for acetonitrile between  $10^\circ$  and  $80^\circ$ ,  $a = 0.0013$  and  $b = 0.000003$ . T. A. H.

**Direct Dehydration of Dimethylisopropylcarbinol.** LOUIS HENRY (*Compt. rend.*, 1907, 144, 552—554).—Dimethylisopropylcarbinol was prepared by treating ethyl isobutyrate with magnesium methyl bromide. When heated with slight excess of acetic anhydride in presence of a little sulphuric acid, it is dehydrated, yielding a mixture of  $\beta\gamma$ -dimethyl- $\Delta^a$ -butylene,  $\text{CH}_2:\text{CMe}:\text{CHMe}_2$ , b. p.  $56-58^\circ/767$  mm., and  $\beta\gamma$ -dimethyl- $\Delta^b$ -butylene,  $\text{CMe}_2:\text{CMe}_2$ , b. p.  $72-73^\circ/767$  mm. The same mixture of hydrocarbons is produced when dimethylisopropyl bromide is heated with potassium acetate in presence of acetic acid, or when the haloid esters of *sec.*-pinacolyl alcohol are treated with alkalis (compare Delacre, Abstr., 1906, i, 476; 1907, i, 7). T. A. H.

**Secondary  $\text{C}_7$  and  $\text{C}_8$  Alcohols.** JOSEPH MUSSET (*Bull. Acad. roy. Belg.*, 1906, 775—789. Compare Abstr., 1906, i, 723).—*Propylisopropylcarbinol*, b. p.  $141-142^\circ/765$  mm.,  $D^{17}$   $0.821$ ,  $n_D$   $1.41493$ , obtained by the action of isobutaldehyde on magnesium *n*-propyl bromide, is a colourless liquid of agreeable odour and bitter burning taste and decolorises bromine in the cold. The corresponding *acetate*, b. p.  $162-163^\circ/765$  mm.,  $D^{20}$   $0.877$ , obtained by the action of acetyl chloride on the alcohol, is a colourless liquid of agreeable odour. The isomeric *tert.*-alcohol, dimethylbutylcarbinol, b. p.  $141-142^\circ/755$  mm., prepared by de Wael, on treatment with acetyl chloride yields the corresponding *chloride*, b. p.  $130-135^\circ$  (decomp.), and only decolorises bromine on warming; thus confirming Henry's suggestion (Abstr., 1907, i, 4) that bromine may be used as a differential reagent for isomeric *sec.*- and *tert.*-alcohols.

*isoPropylbutylcarbinol*,  $\text{C}_4\text{H}_9\cdot\text{CHPr}^i\cdot\text{OH}$ , b. p.  $153-154^\circ$ ,  $D^{20}$   $0.825$ ,  $n_D$   $1.42041$ , is a colourless liquid, less mobile than water, and has a pleasant odour and a burning taste, and is obtained, together with isobutyl alcohol, by the interaction of isobutaldehyde with magnesium butyl bromide; the corresponding *acetate*, b. p.  $172^\circ/760$  mm.,  $D^{20}$   $0.875$ ,  $n_D$   $1.41664$ , is a colourless, mobile liquid with a pleasant odour and bitter taste.  $\gamma$ -Iodo- $\beta$ -methylheptane, b. p.  $160-175^\circ$ , obtained by



the action of red phosphorus and iodine on the alcohol, when distilled over lead hydroxide furnishes dimethylamylcarbinol,  $C_5H_{11} \cdot CMe_2 \cdot OH$  (Masson, Abstr., 1901, i, 250), b. p.  $162^\circ$ ,  $D^{20} 0.819$ ,  $n_D 1.43031$ , which has also been prepared by the action of ethyl *n*-hexoate on magnesium methyl iodide. On treatment with acetyl chloride, this *tert*-alcohol furnishes the corresponding *chloride* (compare Henry, 1906, i, 781), a colourless, mobile, strongly-smelling liquid, which on heating alone, or better, with potassium hydroxide, furnishes the *octylene*,  $CMe_2 \cdot CH \cdot C_4H_9$ , b. p.  $123-125^\circ/755$  mm.,  $D^{20} 0.816$ , a colourless, mobile, feebly-smelling liquid, which burns with a brilliant flame and furnishes a liquid *dibromide*.

*Propylisobutylcarbinol*,  $CH_2Pr^{\beta} \cdot CHPr^{\alpha} \cdot OH$ , b. p.  $160^\circ$ ,  $D^{20} 0.8207$ ,  $n_D 1.42031$ , obtained together with amyl alcohol by the action of *isovaleraldehyde* on magnesium propyl bromide, is a colourless, rather viscid liquid with a pleasant odour and burning taste. The corresponding *acetate*, b. p.  $178^\circ/768$  mm.,  $D^{18} 0.880$ ,  $n_D 1.41554$ , is a colourless liquid of pleasant odour. T. A. H.

**Methyl-*n*-heptylcarbinol.** JOSEPH VAN GYSEGEM (*Bull. Acad. roy. Belg.*, 1906, 692—706).—*Methyl-*n*-heptylcarbinol*,  $C_7H_{15} \cdot CHMe \cdot OH$ , b. p.  $197-198^\circ/747$  mm., m. p.  $-35^\circ$  to  $-36^\circ$ ,  $D^{20} 0.84708$ ,  $n_D 1.43533$ , prepared by the action of acetaldehyde on magnesium *n*-heptyl bromide, is a colourless, rather viscid liquid with a rancid odour and a bitter, nauseous taste. The corresponding *acetate*, b. p.  $214-215^\circ/752$  mm.,  $D^{20} 0.8804$ ,  $n_D 1.42251$ , obtained by the action of the bromide on silver acetate in presence of ether, is a colourless liquid with a slight, fruity odour. The *chloride*, b. p.  $190^\circ/764$  mm.,  $D^{20} 0.8563$ , is a colourless, feebly-smelling liquid which does not solidify at  $-75^\circ$ . The *bromide*, b. p.  $140^\circ/100$  mm., and  $208-209^\circ/767$  mm. (decomp.),  $D^{20} 1.081$ ,  $n_D 1.45357$ , resembles the chloride, and, on treatment with potassium hydroxide or sodium methoxide or ethoxide, yields the corresponding *nonylene*,  $CHMe \cdot CH \cdot C_6H_{13}$ , b. p.  $153-154^\circ/768$  mm.,  $D^{20} 0.8371$ ,  $n_D 1.42031$ , which is a colourless, mobile liquid of penetrating odour and furnishes a liquid *dibromide*. The *methyl ether*,  $C_7H_{15} \cdot CHMe \cdot OMe$ , cannot be obtained by the action of the bromide on sodium methoxide, and was prepared by the action of the compound,  $CHMeCl \cdot OMe$ , on magnesium *n*-heptyl bromide. It is a mobile, pleasant-smelling liquid, b. p.  $188-189^\circ/760$  mm.,  $D^{20} 0.8228$ . The *ethyl ether*, b. p.  $200^\circ/757$  mm.,  $D 0.8193$ ,  $n_D 1.423$ , similarly prepared, resembles its lower homologue.

When methyl-*n*-heptylcarbinol is oxidised with potassium dichromate and sulphuric acid, it furnishes *methyl n-heptyl ketone*, b. p.  $191-192^\circ/760$  mm.,  $D^{20} 0.8281$ ,  $n_D 1.42791$ , a colourless, mobile liquid with a pleasant, fruity odour and a disagreeable taste; it furnishes a crystalline compound with sodium hydrogen sulphite. On oxidation with warm chromic acid mixture the ketone yields acetic and *n*-heptic acids. Methyl *n*-heptyl ketone was prepared synthetically by the interaction of acetonitrile and magnesium *n*-heptyl bromide, but, as Blaise has observed in other cases (Abstr., 1902, i, 164), this method gives a poor yield. T. A. H.

**Ethyl-*n*-hexylcarbinol.** ADHÉMAR GÉRARD (*Bull. Acad. roy. Belg.*, 1906, 790—795. Compare Wagner, *Abstr.*, 1885, 370).—This alcohol may be obtained by the action of magnesium ethyl bromide on heptaldehyde, or by the action of propaldehyde on magnesium hexyl bromide. As Konowaloff has shown, the former reaction gives rise to a mixture of the required alcohol with heptyl alcohol, from which it cannot be separated readily. By employing the second reaction, a yield equivalent to 50% of the theoretical of ethyl-*n*-hexylcarbinol, m. p.  $-20^{\circ}$  to  $-23^{\circ}$ ,  $D^{20}_D$  0.8150,  $n_D$  1.42791, is obtained. This is a colourless, rather viscous liquid with a disagreeable odour and a burning taste; with acetyl chloride it furnishes the corresponding *acetate*, b. p.  $203-204^{\circ}/761$  mm.,  $D^{20}_D$  0.8321, a colourless, pleasant-smelling liquid. T. A. H.

**Propyl-*n*-amylcarbinol.** MARCEL PEXSTERS (*Bull. Acad. roy. Belg.*, 1906, 796—802).—*Propyl-n-amylcarbinol*,  $C_5H_{11}\cdot CHPr\cdot OH$ , b. p.  $192-193^{\circ}/760$  mm.,  $D^{20}_D$  0.8282,  $n_D$  1.41971, prepared by the action of *n*-butaldehyde on magnesium *n*-amyl bromide, is a colourless, somewhat viscid liquid with a faintly ethereal odour and a piquant, slightly bitter taste; it does not yield a phenylurethane. The corresponding *acetate*, b. p.  $199-200^{\circ}/767$  mm.,  $D^{20}_D$  0.8531, obtained by the action of acetyl chloride, is a colourless liquid with a pleasant ethereal odour.

**Primary *n*-amyl nitrite**, b. p.  $104^{\circ}/761$  mm.,  $D^{20}_D$  0.8528,  $n_D$  1.38506, obtained by the addition of dilute sulphuric acid to *n*-amyl alcohol dissolved in an aqueous solution of sodium nitrite, is a mobile, slightly yellow liquid with the characteristic odour of nitrous esters; it is unstable and develops an acid reaction when kept.

**Primary *n*-amyl mercaptan**, b. p.  $126^{\circ}/767$  mm.,  $D^{20}_D$  0.8572,  $n_D$  1.44366, prepared by the action of potassium hydrogen sulphide in alcohol on amyl bromide, is a colourless, mobile liquid with a penetrating and particularly disagreeable odour. T. A. H.

***n*-Dibutylcarbinol.** FERNAND MALENGREAU (*Bull. Acad. roy. Belg.*, 1906, 802—810).—*n*-Dibutylcarbinol,  $CH(C_4H_9)_2\cdot OH$ , may be obtained by the interaction of magnesium *n*-butyl bromide and either ethyl formate or *n*-valeraldehyde (compare Grignard, *Abstr.*, 1901, i, 250). The first of these reactions furnishes *dibutylcarbinyll formate*, b. p.  $194^{\circ}/766$  mm.,  $D^{20}_D$  0.870, which is a colourless, mobile, pleasant-smelling liquid. The second reaction furnishes free *n-dibutylcarbinol*, b. p.  $193^{\circ}/766$  mm.,  $D^{20}_D$  0.823, and mol. refraction 44.8 (calc. 45.05). The corresponding *acetate*, b. p.  $205^{\circ}/770$  mm.,  $D^{20}_D$  0.850, obtained by the action of acetyl chloride, is a mobile, pleasant-smelling liquid.

*Butylisobutylcarbinol* may be prepared by the action of *isovaleraldehyde* on magnesium *n*-butyl bromide, or by the action of *n*-valeraldehyde on magnesium *isobutyl* bromide; the first of these reactions, which also give rise to some *isoamyl* alcohol, was employed in the present instance. This alcohol,  $CH_2Pr\cdot CH(OH)\cdot C_4H_9$ , b. p.  $184^{\circ}/766$  mm.,  $D^{20}_D$  0.815, mol. refraction 44.83 (calc. 45.05), is a colourless, not very mobile liquid of pleasant odour. The *acetate*, b. p.  $195^{\circ}/768$  mm.,

$D^{20}_D$  0.859, mol. refraction 55.2 (calc. 55.14), is a pleasant-smelling liquid.

The *n*-butyl alcohol, used as a starting point in the foregoing reactions, was prepared either by Grignard's method, the action of formaldehyde on magnesium propyl bromide, or by the reduction of ethyl butyrate as described by Bouveault; the former method gave a yield of 70% and the latter of 60% of the theoretical. The *n*-valeraldehyde was prepared by distilling  $\alpha$ -hydroxycaproic acid, as suggested by Blaise, and only a 20% yield was obtained.

T. A. H.

**The Wax from the Palm *Raphia Ruffia* of Madagascar and *Arachyl* Alcohol.** ALBIN HALLER (*Compt. rend.*, 1907, 144, 594—598).—The wax from *Raphia Ruffia*, described by Jumelle (*Compt. rend.*, 1905, 141, 1251), has m. p. 80°, b. p. 280—300°/10 mm. (decomp.), is completely soluble in boiling benzene, but when treated with boiling alcohol leaves 10% (m. p. 77°) undissolved. Analysis of the crude wax, the product of distillation and the portion soluble in alcohol, agree most nearly with the formula  $C_{20}H_{42}O$ . It is not identical with Etard's medicagol (*Abstr.*, 1892, 746), but appears to be a saturated alcohol or mixture of alcohols. It is not attacked by boiling aqueous or alcoholic potash, and does not combine with bromine. It forms an *acetate*,  $C_{20}H_{41}OAc$ , with a grey colour, soft consistency, and m. p. 65°; and a *benzoate*,  $C_{20}H_{41}O \cdot CO \cdot C_6H_5$ , a dark brown, oily mass, m. p. 55°.

The wax when heated with zinc chloride gives a white, greasy substance which crystallises in ill-defined nacreous lamellæ, m. p. 55°. When this is distilled with phosphoric oxide, the melting point is reduced to 40°, and a repetition of the process reduces it to 36° without change in composition. The hydrocarbons so obtained combine with bromine.

The wax resists oxidation by potassium dichromate in glacial acetic acid, or by heating with potash-lime. *Arachyl alcohol*,  $C_{20}H_{42}O$ , a white, waxy substance, m. p. 71°, prepared by reduction of methyl arachidate, is not identical with the preceding substance. E. H.

**Preparation of Ethylene Glycol and Other Alcohols.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 732—740. Compare *Abstr.*, 1897, i, 1; 1899, i, 660; 1901, i, 577; 1902, i, 736).—The author has applied the method of hydrolysis described by Haller (*Abstr.*, 1907, i, 9), which consists in heating the requisite alkyl ester with methyl alcohol containing hydrogen chloride, to the diacetyl derivatives of ethylene and trimethylene glycols, and to pyruvyl acetate, and finds that in each of these three cases better yields of the corresponding alcohols are obtained than can be secured by the processes previously in use for their preparation. Similarly, trimethylene chlorohydrin,  $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot OH$ , may be prepared readily from the corresponding chloroacetate,  $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot OAc$ , by this means.

T. A. H.

**Sodium Ethoxide.** WILLIAM OECHSNER DE CONINCK and EDOUARD CHAUVENET (*Bull. Acad. roy. Belg.*, 1907, 33—34).—At a red heat, sodium ethoxide furnishes ethylene, acetylene, and hydrogen. Nitric

acid yields at first ethyl nitrite and finally carbon dioxide. Other oxidising agents furnish acetaldehyde and acetic acid, but with chlorine a small quantity of monochloroacetic acid is also formed. Formic, acetic, oxalic, benzoic, and hydrochloric acids furnish the corresponding ethyl esters, but with sulphuric acid a mixture of ethyl ether and ethyl hydrogen sulphate is formed, and after prolonged action some ethylene is produced. Ethyl benzoate reacts with the ethoxide to form a number of products, among which ethyl ether and sodium benzoate were recognised.

T. A. H.

**The Substitution of Ethoxy-Groups by Radicles.** ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 8—13).—A reply to Reformatsky's criticism of the author's paper on this subject (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 327, 677).

Z. K.

**Nitrogen Bases Formed in the Decomposition of Cephalin.** H. COUSIN (*J. Pharm. Chim.*, 1907, [vi], 25, 177—180. Compare Abstr., 1906, i, 725).—Thudichum has stated that, on hydrolysis with baryta, cephalin furnishes choline and two other bases yielding platinichlorides having respectively the formulæ  $(C_2H_7ON)_2H_2PtCl_6$  and  $C_3H_4ON_2HClPtCl_4$ . The author finds that on hydrolysis with hydrochloric acid the only base obtained from cephalin is choline and he suggests that the others obtained by Thudichum are probably formed by prolonged ebullition of the choline with baryta.

T. A. H.

**Preparation of Formates from Alkali Hydroxides and Carbon Monoxide at a High Temperature under Pressure.** ELEKTROCHEMISCHE WERKE (D.R.-P. 179515).—Alkali formates are readily produced in theoretical yield when the alkali hydroxide is employed in the form of lumps as large as peas. The reaction is carried out in a closed vessel fitted with a mechanical stirrer, so that the solid materials can be continually agitated. The carbon monoxide, either pure or in the form of producer gas, is introduced under pressure, and the initial temperature is 100—120°. A small amount of moisture, about 4%, may be present, and when two-thirds of the alkali hydroxide is converted into formate, a further 2% of water is introduced.

G. T. M.

**Hydrogenation of Compounds Containing the Carboxyl Group by the Method of Sabatier and Senderens.** JOHAN F. EYKMAN (*Chem. Weekblad*, 1907, 4, 191—193. Compare Darzens, this vol., i, 277).—The application of the method of Sabatier and Senderens to the hydrogenation of various acids, such as undecenoic, erucic, isolauronic, and others, yielded good results, indicating that the presence of the free carboxyl group does not retard the action. At about 210°, camphoric anhydride is reduced almost quantitatively to campholide, m. p. 215° (Haller gives 211°). With benzene and aluminium chloride, campholide yields phenylcampholic acid, m. p. 132°. Reduction of succinic anhydride yields  $\gamma$ -butyrolactone, but part of the anhydride is converted into succinic acid by the water formed. Citraconic acid undergoes partial hydrogenation into pyrotartaric acid, m. p. 112°.

A. J. W.

**Esterification of Castor Oil.** ALBIN HALLER (*Compt. rend.*, 1907, 144, 462—466).—When castor oil is dissolved in methyl alcohol containing 1% hydrochloric acid and heated in a reflux apparatus for several hours, there are obtained a small quantity of oenanthaldehyde, proceeding either from decomposition of the oil itself or of the methyl ricinoleate, methyl stearate, *methyl ricinoleate*, b. p. 225—227°/10 mm.;  $D^{15}_D$  0.927;  $[\alpha]_D + 5.02'$ ;  $n^{15}_D$  1.4645, and methyl dihydroxystearate, m. p. 107—108° (Juillard, *Abstr.*, 1895, i, 500).

Esterification of the oil with ethyl alcohol, under the same conditions, gives *ethyl ricinoleate*, b. p. 227—230°/10 mm.;  $D^{15}_D$  0.918;  $[\alpha]_D + 4.48^\circ$ ;  $n^{15}_D$  1.4630; whilst with *n*-propyl and isobutyl alcohols, *n-propyl ricinoleate*, b. p. 233—236°/10 mm.;  $D^{15}_D$  0.912;  $[\alpha]_D + 4.35^\circ$ ;  $n^{15}_D$  1.4624, and *isobutyl ricinoleate*, b. p. 239—241°/10 mm.;  $D^{15}_D$  0.908;  $[\alpha]_D + 4.22^\circ$ ;  $n^{15}_D$  1.4621, are obtained.

The results confirm the conclusions of previous authors of the presence in castor oil of the glycerides of stearic, ricinoleic, and dihydroxystearic acids, but do not confirm Hazura and Grüssner's discovery (*Abstr.*, 1888, 1270) of two isomeric ricinoleins. As yet, the oxidation of methyl ricinoleate by means of potassium permanganate in acetone solution has only given a methyl trihydroxystearate,  $C_{19}H_{38}O_5$ , m. p. 87°, whilst the authors cited obtained two isomeric trihydroxystearic acids by oxidation of liquid ricinoleic acid.

When methyl or ethyl ricinoleate is distilled under the ordinary pressure, oenanthaldehyde and an ester of undecenoic acid are formed,  $C_{18}H_{33}O_3R = C_7H_{14}O + C_{11}H_{19}O_2R$ .

With methyl ricinoleate the yield of aldehyde is 62% and of methyl undecenoate 40% of the theoretical, whilst with the ethyl ester the corresponding quantities are 50% and 32% respectively.

E. H.

**Action of Mercuric Acetate Dissolved in Acetic Acid on Unsaturated Fatty Acids.** ALEXANDRE LEYS (*Bull. Soc. Chim.*, 1907, [iv], 1, 262—268. Compare *Abstr.*, 1905, i, 433; ii, 655).—When oleic acid or olein is added to a solution of mercuric acetate in acetic acid and the mixture is warmed, it becomes brown and a precipitate of mercurous acetate is formed, which, unless excess of mercuric acetate is present, is further reduced to mercury. Crotonic, elaidic, and linoleic acids behave similarly, but their glyceryl and other esters do not react in this manner. The reaction appears to be confined to the monobasic unsaturated acids, but in the case of maleic acid, although no precipitate is formed, a soluble mercurous salt appears to be produced, and with succinic acid there is a formation of mercurous acetate. The other product (mercurialised olein), formed when olein is treated in this manner, can be isolated as a brown syrup, which, after a time, solidifies to a confused mass of transparent crystals and gives a yellowish-red colour with nitric acid. The mercury may be estimated in this material by dissolving it in chloroform, adding excess of iodine in alcohol, decolorising after an hour with sodium thiosulphate, separating and evaporating to dryness the aqueous layer, treating the residue with *aqua regia*, and applying Deniges's process (*Abstr.*, 1896, ii, 385).

T. A. H.

**Hydrogen Iodide Additive Compounds of Oleic, Elaidic, and Brassidic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 180087).—The unsaturated acids of high molecular weight on treatment with phosphorus, iodine, and water give rise to a mixture of the hydrogen iodide additive compounds and certain products containing phosphorus; the latter are removed only with great loss of the iodo-derivative. The iodation leads to pure products when it is effected with a concentrated glacial acetic acid solution of hydrogen iodide; the latter being prepared from iodine and copaiva oil.

*Iodobehenic acid* is obtained as a colourless solid on shaking erucic acid with rather more than the calculated amount of the hydrogen iodide solution; the operation takes several days and is effected at 60–70°.

Iodostearic acid, a pale yellow oil at the ordinary temperature, is prepared in a precisely similar manner from oleic acid, and brassidic and elaidic acids are also amenable to this process. G. T. M.

**Condensation of Ethyl Acetoacetate and Formaldehyde in the Presence of Sodium Hydroxide.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1200–1204).—From the mass obtained by the action of formaldehyde on a cold solution of ethyl acetoacetate

in sodium hydroxide, a substance, probably 
$$\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{OH} \\ \parallel \quad \quad \parallel \\ \text{OH} \cdot \text{C} - \text{CH} \cdot \text{CMe} \end{array},$$

has been isolated. It is amorphous and does not melt at 118°, is readily soluble in sodium hydroxide and alcohol, sparingly so in many organic solvents. It is of an acidic or phenolic character, has many of the properties of shellac, and with methyl iodide yields the methoxy-derivative,  $\text{C}_9\text{H}_{10}(\text{OMe})_2$ . Z. K.

[**Esters of Citrylidenealkoxyacrylic Acids.**] A. MASCHMEYER (D.R.-P. 178298).—The compound obtained by condensing citral and ethyl acetoacetate has no distinctive odour of violets when warmed with strong acids, and yields a product which furnishes ionone on hydrolysis. It is now found that the condensation products, obtained from citral and the alkyl chloroacetates in the presence of the alkali ethoxides, readily yield yellow, oily substances which, although possessing an intense odour of violets, are nevertheless quite distinct from ionone.

*Methyl citrylidenemethoxyacrylate*,  $\text{C}_9\text{H}_{15} \cdot \text{CH} : \text{C}(\text{OMe}) \cdot \text{CO}_2\text{Me}$ , b. p. 170–200°/20 mm., is prepared by adding a cooled mixture of citral and ethyl chloroacetate to ether containing suspended sodium methoxide.

*Methyl cyclocitrylidenemethoxyacrylate*, b. p. 165–185°/21 mm.,  $D_{25} 0.950$ , is produced by dissolving the foregoing ester in cold concentrated sulphuric acid and pouring the product on to ice; it may also be obtained by boiling with strong aqueous solutions of oxalic or phosphoric acid. G. T. M.

**New Synthesis of Tetronic Acid.** ERICH BENARY (*Ber.*, 1907, 40, 1079—1083).—When ethyl sodiomalonate (2 mols.) and acetyl chloride (1 mol.) in ether are gently warmed, instead of a *cyclopropanedicarboxylate* being produced, there is formed ethyl tetrone-4-carboxylate (Anschütz and Bertram, *Abstr.*, 1903, i, 271), from which tetronic acid can be obtained by digestion with baryta and conversion of the barium tetronecarboxylate into tetronic acid by acidification, carbon dioxide being liberated.

After the removal of the ethyl tetronecarboxylate from the ethereal solution, there remains behind in small quantity a *compound*,  $C_9H_{12}O_5$ , crystallising in needles, m. p. 91—92°, the constitution of which has not yet been determined. Its aqueous solution is neutral, but it quickly changes to ethyl tetronecarboxylate, and this compound is likewise obtained on treatment with bromine. With phenylhydrazine it yields a *phenylhydrazone*,  $C_{13}H_{14}O_4N_2$ , a white powder, m. p. 188—189° (decomp.), giving Bülow's reaction. Dry ammonia gas gives a *compound*,  $C_7H_9O_4N$ , a white powder, m. p. 243° (decomp.). Hydroxylamine gives a monobasic *hydroxamic acid*,  $C_7H_9O_5N$ , m. p. 180° (decomp.), which gives an intense bluish-violet coloration with ferric chloride.

The interaction of *bromoisobutyl bromide* and ethyl malonate results in the formation of 3:3-*dimethyltetronic acid*,  $CH_2 \begin{smallmatrix} \diagup CO \\ \diagdown CO \cdot O \end{smallmatrix} CMe_2$ , crystallising from benzene in colourless leaflets, m. p. 142—143°. The aqueous solution with ferric chloride and sodium nitrite gives the same characteristic colorations as tetronic acid. W. R.

**Mutual Interconversion of Optically Active Bromosuccinic and Aspartic Acids.** EMIL FISCHER and KARL RASKE (*Ber.*, 1907, 40, 1051—1057. Compare this vol., i, 192).—Although Tilden and Marshall (*Trans.*, 1895, 67, 494) converted aspartic into optically active chlorosuccinic acid by means of nitrosyl chloride, the opposite change has not yet been effected; the product described by Walden and Lutz (*Abstr.*, 1898, i, 127), produced by the interaction of methylalcoholic ammonia and *l*-bromosuccinic acid, being possibly a monoamide of malic acid.

*l*-Bromosuccinic acid when treated with aqueous ammonia cooled at first to -40° and subsequently maintained for a day at +3° was converted into an amorphous mass from which *d*-aspartic acid,  $[\alpha]_D^{20} - 25.47^\circ$ , was isolated. A Walden re-arrangement takes place (compare Walden, *Abstr.*, 1896, i, 205; 1898, i, 127, 178; 1899, ii, 538; Fischer, this vol., i, 192), and, similarly, from ethyl *l*-aspartate and nitrosyl bromide, ethyl *d*-bromosuccinate was obtained. The replacement of the amino-group by halogen takes place in two stages, *perbromides* being first formed.

The *dibromide* of ethyl *l*-aspartate *hydrobromide* is obtained as an oil solidifying in the cold to a mass of reddish-yellow crystals which decompose when warmed, but can be kept at 0° in a vacuum for some little time. The *dibromide* of *l*-aspartic acid *hydrobromide* forms glistening, brown needles or prisms which decompose slowly even below 0°. E. F. A.

**$\alpha\gamma$ -Dihydroxyglutaric Acids.** HEINRICH KILIANI and O. MATTHES (*Ber.*, 1907, 40, 1238—1242. Compare Kiliani and Herold, *Abstr.*, 1905, i, 739).—It has been overlooked previously that loss of carbon dioxide from *isosaccharic* acid must lead to the formation of a mixture of two  $\alpha\gamma$ -dihydroxyglutaric acids, consisting of the optically

inactive acid,  $\text{CO}_2\text{H}\cdot\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\cdot\text{CH}_2\cdot\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\cdot\text{CO}_2\text{H}$  and one of the two active acids,

$\text{CO}_2\text{H}\cdot\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\cdot\text{CH}_2\cdot\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\cdot\text{CO}_2\text{H}$ , and  $\text{CO}_2\text{H}\cdot\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\cdot\text{CH}_2\cdot\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\cdot\text{CO}_2\text{H}$ . This is now shown

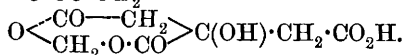
experimentally to be the case; the configuration of the active acid remains to be established. The acids are separated by means of the calcium salts, that of the active acid being much the more soluble.

The lactone of the *i*-acid,  $\text{C}_5\text{H}_6\text{O}_4$ , m. p. 167—168°, is anhydrous; the calcium, zinc, and copper salts have the properties described previously (*loc. cit.*); the *silver*, *brucine hydrogen*,

$(\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2, \text{C}_5\text{H}_8\text{O}_6)_2, \text{H}_2\text{O}$ , m. p. 238° (decomp.),  $[\alpha]_{\text{D}} -29\cdot3^\circ$ , and *brucine*,  $(\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2)_2, \text{C}_5\text{H}_8\text{O}_6$ , m. p. 222—223°, salts are described.

*d*- $\alpha\gamma$ -Dihydroxyglutaric acid,  $\text{C}_5\text{H}_8\text{O}_6$ , crystallises in prisms, m. p. 125°,  $[\alpha]_{\text{D}} + 3\cdot9^\circ$ , and does not form a lactone. The *calcium*, *zinc* ( $+2/7\text{H}_2\text{O}$ ), *copper*, *silver*, *quinine*, m. p. 156°, *brucine hydrogen*, m. p. 151°,  $[\alpha]_{\text{D}} -24\cdot4^\circ$ , and *brucine* ( $+7\text{H}_2\text{O}$ ), m. p. 128—129°, or when anhydrous, 203°, salts are described. G. Y.

**Condensation of Some Hydroxy-Acids and Formaldehyde in the Presence of Picric Acid.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1211—1216).—By the action of formaldehyde on citric acid in the presence of picric acid, a *substance*,  $\text{C}_7\text{H}_8\text{O}_7 + 2\text{H}_2\text{O}$ , m. p. 98—118°, was isolated; when melted, it loses water, forming first  $\text{C}_7\text{H}_8\text{O}_7, \text{H}_2\text{O}$ , and finally, on drying at 118°,  $\text{C}_7\text{H}_8\text{O}_7$ . Its probable structure is  $\text{CH}_2\begin{matrix} \text{O} \cdot \text{CO} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CO} \cdot \text{CH}_2 \end{matrix} > \text{C}(\text{OH}) \cdot \text{CO}_2\text{H}$  or



When tartaric acid is substituted for citric acid, a *substance*, probably  $2\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}, \text{C}_6\text{H}_6\text{O}_6$ , m. p. 115—117°, is formed. It is soluble in water and most organic solvents, but in water and in alcohol it decomposes with liberation of picric acid. The form and colour of the crystals obtained depend on the relative proportions of the reacting substances. As might be expected from the formula, the substance is explosive. Z. K.

**Carbithionic Acids. II. Dithioacetic Acid.** JOSEF HOUBEN and HEINRICH POHL (*Ber.*, 1907, 40, 1303—1307. Compare *Abstr.*, 1906, i, 847).—Whilst the thioacyl disulphides are stable compounds, the carbithionic acids have been characterised only in the form of salts or derivatives. It has been found possible now to isolate carbithionic

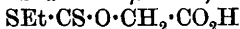


acids of the aliphatic series in a state of purity and, of these, methylcarbithionic acid is described in the present paper.

*Methylcarbithionic acid* [dithioacetic acid],  $\text{CH}_3\cdot\text{CS}\cdot\text{SH}$ , prepared by the action of carbon disulphide on magnesium methyl iodide in cooled absolute ethereal solution and decomposition of the product with ice and cooled hydrochloric acid, is obtained as a reddish-yellow oil, b. p.  $37^\circ/15$  mm.,  $D_{20}^{20}$  1.24, is readily soluble in organic solvents, and displaces acetic and formic acids from their salts. It is readily oxidised, forms thioacetyl disulphide when shaken with water, but inflames only when heated, colours paper reddish-yellow, and produces black spots on the skin. The *alkali*, *alkaline earth*, *aluminium*, and *magnesium* salts are soluble in water; the neutral solutions give coloured precipitates with salts of the heavy metals. The dithio-acid yields a viscid, yellow mass when saturated with hydrogen chloride, forms thioacetyl disulphide when treated with iodine in potassium iodide solution, and is reduced in alkaline solution to a yellow, odourless oil. G. Y.

**Ester-Acids of Sulphur-substituted Carbonic Acids with Aliphatic Hydroxy-Acids.** II. B. HOLMBERG (*J. pr. Chem.*, 1907, [ii], 75, 169—187. Compare Abstr., 1905, i, 323).—One trithio-, three dithio-, and three monothio-carboglycollic acids may be derived from carboglycollic acid,  $\text{OH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , by substitution of sulphur for oxygen atoms. These acids are unstable in the free state. In the present paper, derivatives of the trithio- and of one of the dithio-acids are described. Such ester-acids may be formed by addition of carbon disulphide to glycollic or thioglycollic acid in alkaline solution; by double decomposition of the resulting monoglycollic acids with alkyl haloids or salts or esters of halogen-substituted acids; by oxidation of the higher sulphur acids, the sulphur atoms being substituted partially by oxygen; by the action of carbonyl or thiocarbonyl chloride on hydroxy- or mercapto-acids, and by decomposition of other related compounds.

In the nomenclature of the sulphur derivatives of carboglycollic acid, the author now uses the term " $\Delta$ -thio-" in place of "sulpho-" previously employed to denote a sulphur atom doubly linked to carbon, and distinguishes the other two sulphur atoms of the trithiocarbonic group, when necessary, as  $\alpha$ - and  $\beta$ -thio-, thus



becomes ethyl  $\alpha\Delta$ -dithiocarboglycollic acid,  $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  is ethyl  $\beta\Delta$ -dithiocarboglycollic acid, whilst  $\text{SEt}\cdot\text{CO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  is ethyl dithiocarboglycollic acid.

Dithiocarbodiglycollic acid has the conductivity constant  $K=0.156$  with  $\infty=378$ ; trithiocarbodiglycollic acid, with  $\infty=378$ , has  $K=0.26$ .

*Potassium  $\alpha\Delta$ -dithiocarboglycollate*,  $\text{SK}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ , formed by the action of carbon disulphide on glycollic acid in aqueous potassium hydroxide solution, separates on addition of alcohol as a yellow, crystalline crust. The lead salt was analysed. With potassium chloroacetate, the potassium salt yields  $\alpha\Delta$ -dithiocarbodiglycollic acid (*loc. cit.*). On liberation, the monoglycollic acid forms a yellow oil which decomposes immediately into glycollic acid and carbon disulphide. *Ethyl  $\alpha\Delta$ -dithio-*

*carboglycollic acid*, formed by the action of ethyl bromide on the potassium salt in aqueous solution, crystallises in slightly yellow needles, m. p.  $77-78^{\circ}$ , and, with  $\infty = 378$ , has the conductivity constant  $K = 0.212$ ; the *potassium* ( $+ H_2O$ ), *sodium* ( $+ 3H_2O$ ), and *barium* ( $+ 2H_2O$ ) salts are described. The ethyl-acid is decomposed by alcoholic potassium hydroxide at the ordinary temperature, yielding ethyl mercaptan, potassium glycolate, and potassium ethyl thiocarbonate. When heated in neutral solution, the potassium salt of the ethyl-acid decomposes, forming carbon dioxide, hydrogen sulphide, ethyl mercaptan, and potassium glycolate. The action of aqueous ammonia on the ethyl-acid leads to the formation of ethyl mercaptan and *ammonium thiocarbamylglycolate*,  $NH_2 \cdot CS \cdot O \cdot CH_2 \cdot CO_2NH_4$ , which separates, on evaporation of the aqueous solution, as a white, crystalline mass. The acid crystallises from alcohol in colourless plates, m. p.  $111-112^{\circ}$ , and can be titrated with *N*-sodium hydroxide and phenolphthalein.

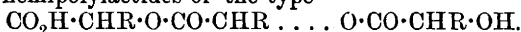
*Potassium trithiocarboglycolate*,  $SK \cdot CS \cdot S \cdot CH_2 \cdot CO_2K$ , formed by the action of carbon disulphide and potassium hydroxide on thioglycollic acid in aqueous solution, crystallises in yellowish-red needles or leaflets, gives coloured *precipitates* with salts of the heavy metals, and with potassium chloroacetate forms potassium trithiocarboglycolate.

The action of a chloroacetate on potassium ethyl trithiocarbonate, in aqueous solution cooled by ice, leads to the formation of ethyl trithiocarbonate, trithiocarboglycollic acid, and *ethyl trithiocarboglycollic acid*,  $SEt \cdot CS \cdot S \cdot CH_2 \cdot CO_2H$ , which is formed also in small amount by the action of ethyl bromide on potassium trithiocarboglycolate. It crystallises in yellow needles or thin prisms, m. p.  $75.5-76^{\circ}$ , is soluble in chloroform, with  $\infty = 378$  in aqueous solution, has the conductivity constant  $K = 0.082$ , and decomposes slowly at the ordinary temperature. The *calcium* salt crystallises in two forms, differing in their water of crystallisation; the more stable ( $+ 3H_2O$ ) was analysed. The *amide*, formed from chloroacetamide and potassium ethyl trithiocarbonate, crystallises in thin, golden leaflets, m. p.  $123.5-124^{\circ}$ . Ethyl trithiocarboglycollic acid is decomposed only slightly by water; in neutral solution it yields ethyl trithiocarbonate and potassium trithiocarboglycolate slowly at the ordinary temperature, quickly at  $50-60^{\circ}$ , whilst at higher temperatures decomposition of the trithiocarboglycollic acid takes place. The partial decomposition takes place rapidly in aqueous alkaline solution at the ordinary temperature, whilst the products of complete decomposition are obtained by the action of alcoholic potassium hydroxide or ammonia. Aqueous ammonia acts partly as an alkali, but forms also a *product* which is probably thiocarbamylthioglycollic acid. The oxidation of ethyl trithiocarboglycollic acid by dilute potassium permanganate does not stop at ethyl dithiocarboglycollic acid, but proceeds to the formation of products such as ethylsulphonic and thioacetic acids.

G. Y.

**Preparation of Acyclic Aldehydes. I.** P. BAGARD (*Bull. Soc. chim.*, 1907, [iv], 1, 307-320. Compare Blaise, *Abstr.*, 1904, i, 369; Le Sueur, *Trans.*, 1904, 85, 827, 1708).—When an  $\alpha$ -hydroxycarboxylic

acid is heated, it loses water and gives rise to the production of a small quantity of the corresponding dilactide,  $\text{CHR} \begin{smallmatrix} \text{O} \cdot \text{CO} \\ \text{CO} \cdot \text{O} \end{smallmatrix} \text{CHR}$ , and a considerable amount of non-volatile acid product, probably constituted of hemipoly lactides of the type



Both these products on further heating furnish an aldehyde containing one carbon atom less than the acid initially employed, and in addition small quantities of unsaturated acids and olefinic hydrocarbons, these two by-products being formed by loss of water and carbon dioxide from the hydroxy-acid or the dilactide. The esters of the  $\alpha$ -hydroxy-acids distil unchanged, but the corresponding alkyloxy-acids and acyloxy-acids when heated decompose, furnishing the corresponding lower aldehydes without any intermediate change, and give a better yield of the aldehydes than is obtained from the parent hydroxy-acids. The  $\alpha$ -hydroxy-acids employed in this investigation have been prepared by the series of reactions already described by Blaise (*loc. cit.*).

*Ethyl- $\alpha$ -hydroxyheptate* has b. p.  $106^\circ/14.5$  mm. The *anilide* of the acid, m. p.  $70^\circ$ , crystallises from a mixture of ethyl acetate and light petroleum. The *toluidide*, m. p.  $103^\circ$ , crystallises from ethyl acetate. When  $\alpha$ -hydroxyheptic acid is heated, it furnishes, in addition to hexaldehyde (Lieben and Janacek, Abstr., 1877, 879) and butylethylene (Schorlemmer, Abstr., 1880, 158), (a)  $\gamma$ -heptolactone, b. p.  $118-120^\circ/15$  mm., which by Blaise and Luttringer's method (Abstr., 1905, i, 329) yields *hydrazino- $\gamma$ -heptolactone*, m. p.  $88-89^\circ$ , crystallising from ethyl acetate in flattened needles; (b) an unsaturated acid, b. p.  $123-124^\circ/20$  mm., which was not obtained pure, and did not give concordant combustion results for heptenoic acid, and (c)  $\alpha$ -hydroxy-

*heptolactide*,  $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{CO} \cdot \text{O} \cdot \text{CH} \cdot [\text{CH}_2]_4 \cdot \text{CH}_3$ , m. p.  $88^\circ$ , which crystallises from light petroleum. The last-mentioned substance, which can only be isolated when the reaction is stopped at an early stage, when heated to  $280-300^\circ$  yields carbon monoxide and hexaldehyde, and leaves an amorphous, viscous residue of acid reaction, which is probably a hemipoly lactide.

When  *$\alpha$ -acetoxyheptic acid*, obtained as an oily product by the action of acetyl chloride on the hydroxy-acid, is heated, it yields carbon monoxide, acetic acid, and hexaldehyde, the yield of the last being 68.7%, that is, 18% higher than is obtained by distilling the hydroxy-acid itself.

*Hexaldehydesemicarbazone*, m. p.  $106^\circ$ , crystallises from a mixture of benzene and light petroleum. The *oxime*, m. p.  $51^\circ$ , separates in long crystals from methyl alcohol. The *azine*,  $(\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} : \text{N})_2$ , b. p.  $132^\circ/13$  mm., is a colourless liquid which is very unstable. 2-n-*Amylnaphthacinchonic acid*, m. p.  $255-260^\circ$ , obtained by the action of pyruvic acid and  $\beta$ -naphthylamine on the aldehyde, is a crystalline powder, and separates from formic acid on the addition of methyl alcohol. The *diethylacetal* of the aldehyde, b. p.  $90^\circ/30$  mm., is a colourless liquid.

T. A. H.

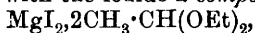
**Molecular Compounds of Magnesium Bromide and Iodide with Aldehydes, Ketones, and Acetals.** BORIS N. MENSCHUTKIN (*Zeitsch. anorg. Chem.*, 1907, 53, 26—33. Compare Abstr., 1904, i, 215; 1906, i, 131, 132, 552).—The molecular compounds described in the paper were obtained by direct action of the organic compounds on the dietherates of the magnesium halides.

The compound,  $\text{MgBr}_2 \cdot 3\text{C}_6\text{H}_5 \cdot \text{CHO}$ , occurs in small, hygroscopic plates, m. p.  $159^\circ$ ;  $\text{MgI}_2 \cdot 6\text{C}_6\text{H}_5 \cdot \text{CHO}$  melts at  $139^\circ$ . The solubility curve of these compounds in benzaldehyde has been determined from  $0^\circ$  to their respective melting points. The compound  $\text{MgBr}_2 \cdot 3\text{CH}_3 \cdot \text{CHO}$  has also been obtained; it undergoes partial decomposition on fusion.

Compounds of the respective formulæ  $\text{MgBr}_2 \cdot 3\text{COMe}_2$  (m. p.  $92^\circ$ ) and  $\text{MgI}_2 \cdot 6\text{COMe}_2$  (m. p.  $106.5^\circ$ ) have also been prepared and the solubility in acetone from  $0^\circ$  to the respective melting points determined.

At low temperatures, magnesium bromide forms a compound with chloral hydrate, probably  $\text{MgBr}_2 \cdot 3\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$ , but at higher temperatures, owing to partial dissociation of chloral hydrate, magnesium bromide hexahydrate is also produced.

With methylal, the compound  $\text{MgBr}_2 \cdot 2\text{CH}_2(\text{OMe})_2$ , m. p.  $112^\circ$ , was obtained. Acetal gives with the iodide a compound,



m. p.  $86^\circ$ . The mutual solubility of these compounds and methylal and acetal respectively is very small. G. S.

**Methylation of Oximino-compounds.** GIACOMO PONZIO and G. CHARBIER (*Rend. Accad. Sci. Torino*, 1907, 42, 328—336).—The ordinary method of preparing methyl derivatives of oximino-compounds by the action of methyl iodide in presence of sodium methoxide is somewhat tedious, and in the case of the aliphatic ketoximes gives very small yields, acetoxime, for example, acting in the two tautomeric forms,  $\text{CMe}_2 \cdot \text{N} \cdot \text{OH}$  and  $\text{CMe}_2 \cdot \text{N} \cdot \text{H}$   $\begin{smallmatrix} \text{O} \\ \diagup \\ \text{N} \end{smallmatrix}$ , and giving rise to both the *O*-methyl ether and the *N*-methyl ether (compare Dunstan and Goulding, *Trans.*, 1901, 79, 628).

The following method for preparing the *O*-methyl ethers of oximino-compounds is simple, and can be applied to compounds of the aromatic series. The oximino-derivative (1 mol.), dissolved in an excess (4 mols.) of 30% sodium hydroxide solution, is agitated with commercial methyl sulphate (1.5 mols.). This reaction, which should be moderated by cooling the mixture, gives a yield of 60—90% of the *O*-methyl ether; the latter, being insoluble in the alkaline liquid, can generally be isolated directly.

*Methylethylketoxime O-methyl ether*,  $\text{CMeEt} \cdot \text{N} \cdot \text{OMe}$ , is a pleasant-smelling liquid, b. p.  $95^\circ/739.3$  mm.; the *platinichloride*,



forms yellow prisms. When the ether is boiled with 10% hydrochloric acid solution in a reflux apparatus it undergoes hydrolysis, yielding methyl ethyl ketone. The semicarbazone of the latter separates immediately if the ketone is shaken with an acetic acid solution of semi-

carbazine (compare Scholtz, Abstr., 1896, i, 343), and crystallises from a mixture of benzene and light petroleum in white prisms, m. p. 143—144°; Scholtz (*loc. cit.*) gave m. p. 135—136°. On evaporating on a water-bath a hydrochloric acid solution of the ether, the latter partly resinifies and is partly converted into ammonium chloride.

Benzophenoneoxime *O*-methyl ether crystallises from light petroleum in white laminæ, m. p. 102°; Spiegler (Abstr., 1884, 1155) gave m. p. 92°.

The *O*-methyl ethers of acetoxime, benzaldoxime, anisaldoxime, camphoroxime, and isonitrosocamphor were also prepared. T. H. P.

**Application of Metallic Calcium to Reductions in the Sugar Series.** CARL NEUBERG and FRITZ MARX (*Zeitsch. Ver. deut. Zucker-ind.*, 1907, 615, 456—461).—The use of sodium amalgam for effecting the reduction of the sugars or their derivatives, such as that of lactones to aldoses, or that of aldoses or ketoses to the corresponding alcohols, involves the subsequent difficulty of separating sodium salts from the carbohydrate derivative. This difficulty is avoided by replacing the sodium amalgam by calcium, which has the further advantage that it can be used either directly, best in the form of coarse turnings, or as calcium amalgam. The authors illustrate the mode of using calcium or its amalgam as a reducing agent by examples, and describe a crystalline alcohol, lactobiotitol, obtained by the reduction of lactose; this compound is the first alcoholic derivative of a disaccharide to be prepared in a crystalline condition.

The preparation of calcium amalgam by the method of Moissan and Chavanne (*Compt. rend.*, 1905, 140, 122—127; Abstr., 1905, ii, 163) is troublesome, as the development of heat during the shaking of the mercury and calcium usually results in the breaking of the flask. Large quantities of the amalgam can be prepared in a single operation as follows. A spacious, thick, porcelain mortar, after being slowly heated to 100° in an oven, is charged with the required amount of mercury, and then with a little of the calcium in the form of grits (Calciumgries), the two metals being then rubbed together with a warm pestle. The formation of amalgam soon begins and, after the remainder of the calcium has been added, is continued at a rapid rate by the heat developed. In the authors' experiments a 3% calcium amalgam was employed.

The reductions of dextrose to *d*-sorbitol, of *d*-galactose to dulcitol, and of dextroseoxime to *d*-glucamine are readily effected by gradually adding calcium turnings to a 2.5% solution of the compound, which is kept cooled and well shaken whilst a current of carbon dioxide is passed through it.

*Lactobiotitol*,  $C_{12}H_{24}O_{11}$ , obtained in small yield by the gradual addition of a large excess of calcium amalgam to an aqueous lactose solution through which a current of carbon dioxide is kept passing, forms colourless crystals, begins to turn brown at about 200° and is not melted even at 280°, although at this temperature small quantities of a white sublimate are formed. It dissolves readily in water and sparingly in alcohol and, when boiled with acid, is apparently

hydrolysed to galactose and sorbitol:  $C_{12}H_{24}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{14}O_6$ .  
T. H. P.

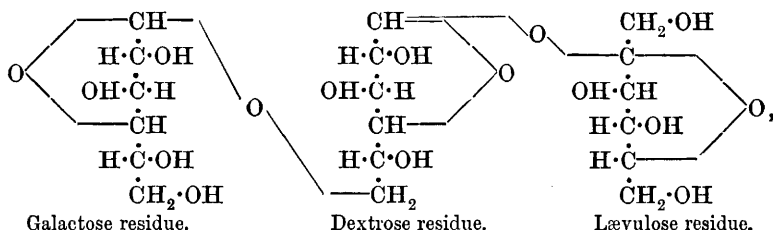
**Viscosity of Solutions of Sucrose and Invert Sugar.** HENRY PELLET and CH. FRIBOURG (*Chem. Zentr.*, 1907, i, 631; from *Bull. Assoc. Chim. Sucr. Dist.*, 24, 666—668. Compare this vol., i, 185).—Experiments have been made with solutions of sucrose and invert sugar which have the same concentration, 65° Brix. The solutions contain the following proportions of sucrose and invert sugar respectively, 100+0, 88+12, 82+18, 77+23, 71+29, 64·5+35·5, 57+43, 49+51, 41+59, and 0+100. The number of seconds required for the flow of 50 cm. are respectively 225, —, 195, 180, 172, 166, 155, —, 146, and 115, and the relative viscosities 1, —, 0·87, 0·80, 0·76, 0·74, 0·69, —, and 0·65. The viscosity of solutions of sucrose and invert sugar is nearly twice as great at 27° as at 40°. E. W. W.

**Kjeldahl's Method: Rapidity of Oxidation of Sucrose by Means of Sulphuric Acid.** JAROSLAV MILBAUER (*Zeitsch. Zuckerind. Böhm.*, 1907, 31, 350—353. Compare Bredig and Brown, *Abstr.*, 1904, ii, 247).—The author has measured the velocity of oxidation of sucrose (0·05 gram) by 94·9% sulphuric acid (50 c.c.) at 213°. A constant current of carbon dioxide was passed through the heated mixture of sugar and acid to expel the sulphur dioxide, which was absorbed and determined iodometrically. During twelve hours the rate of evolution of sulphur dioxide was practically constant, namely, 0·13 mg. per minute. The effects of a number of catalysts on the reaction were determined, the only ones found to increase the velocity appreciably being copper sulphate (1·9614 gram of the crystallised salt) and mercuric sulphate (added in the form of 0·5399 gram of mercuric oxide), the evolution of sulphur dioxide being at the rates of 0·19 and 0·37 mg. per minute in the two cases; with cobalt sulphate (0·6406 gram CoO), the rate was 0·16 mg. per minute. T. H. P.

**Formation of Formaldehyde in the Combustion of Sugar.** AUGUSTE TRILLAT (*Chem. Zentr.*, 1907, i, 630; from *Bull. Assoc. Chim. Sucr. Dist.*, 24, 611—612. Compare *Abstr.*, 1906, i, 401, 476).—In reference to a paper by Herzfeld (*Jahresber. Inst. Zuckerind.*) in which doubt is expressed as to the formation of formaldehyde by the combustion of sugar, the author points out that the blue coloration with magenta paper is also produced by acetaldehyde and propaldehyde. In his opinion the dimethylaniline test is the best; the quantity of tetramethyldiaminodiphenylmethane may be determined gravimetrically. E. W. W.

**Resolution of Raffinose into Sucrose and Galactose:** CARL NEUBERG (*Zeitsch. Ver. deut. Zuckerind.*, 1907, 615, 440—453).—Up to the present all the various means adopted for the resolution of raffinose into simpler sugars have given rise, in the first place, to lævulose and melibiose, and, finally, to lævulose, dextrose, and galactose. The author finds that emulsin is capable of hydrolysing raffinose, the resultant sugars being, however, galactose and sucrose.

This result affords conclusive proof of the existence of a sucrose complex in the raffinose molecule, thus confirming the suspicion based on the observation that raffinose is hydrolysed by invertase. Since emulsin, according to Fischer, only attacks compounds having  $\beta$ -glucoside structures, raffinose must be looked on either as the  $\beta$ -galactoside of sucrose or as the l  vuloside of melibiose. The formula of raffinose is hence :



which is uncertain only as regards the constitutions of the sucrose and melibiose, that is, as regards the mode of the anhydride formation between the hydroxyl groups of the separate monosaccharides.

By the conversion of raffinose into galactose and sucrose, the latter makes its first appearance as a product of the resolution of a more complex, naturally occurring sugar. This change may, indeed, be of interest to vegetable physiology. The principal source of raffinose, the sugar-beet, contains this sugar in amounts varying from mere traces to quantities such that the molasses contains as much as 22% of raffinose. The content of raffinose is often increased abnormally by disturbance of the growth, such as is caused, for example, by the sudden occurrence of frost. It must be assumed that, under these conditions, greatly increased amounts of galactans and pectic substances containing galactose residues undergo hydrolysis, the galactose liberated combining, as the result of abnormal fermentative processes, with sucrose to form raffinose. The action of emulsin on raffinose may find industrial application in the treatment of beet-sugar products containing notable proportions of raffinose. The action also affords a means of detecting small quantities of raffinose (compare Neuberg and Marx, this vol., ii, 408).

The rare sugar stachyose, which is a non-reducing tetrasaccharide of the formula  $C_{24}H_{42}O_{21}$  and yields, on complete hydrolysis, 2 mols. of galactose, 1 mol. of l  vulose, and 1 mol. of dextrose, is also decomposed by emulsin, but, owing to paucity of materials, the products have not yet been characterised.

T. H. P.

**Acetyl Derivatives of Cellobiose.** EMIL R. VON HARDT-STREMYER (*Monatsh.*, 1907, 28, 63—72).—It is found that Skraup and Geinsperger's octa-acetylcellobiose (*Abstr.*, 1906, i, 67), m. p. 198  ,  $[\alpha]_D + 30.51^\circ$ , is identical with Maquenne and Goodwin's second octa-acetylcellobiose (*Abstr.*, 1904, i, 799), the transformation of which into Skraup and K  nig's compound, m. p. 228   (*Abstr.*, 1902, i, 135), is confirmed. Attempts to bring about the reverse transformation were unsuccessful.

G. Y.

**Reducing Properties of Various Celluloses.** CARL G. SCHWALBE (*Ber.*, 1907, 40, 1347—1351).—The author has studied the reducing properties of various celluloses. The percentage of water in the sample is first determined. In a second air-dried specimen the reducing property is then estimated and the result calculated for dry cellulose. The cupric reducing power of cellulose is estimated by mixing 3 grams of the air-dried, finely-divided specimen with 200 c.c. of water and boiling for quarter of an hour with 100 c.c. of Fehling's solution. The amount of copper in the precipitated cuprous oxide is estimated electrolytically, using a rotating electrode.

Pure celluloses exhibit very little reducing property (from 1.1 to 1.8). Hydrocellulose and oxycellulose, on the other hand, had the numbers 5.2 and 7.9 respectively. A specimen of "over-bleached cellulose" gave a value so high as 19.3. A. McK.

**Theory of the Nitration of Cellulose.** A. V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1192—1200. Compare Abstr., 1905, ii, 583).—When sulphuric acid is added to any solution of nitric acid in water, the vapour pressure of the solution increases until the system  $\text{HNO}_3 + n(\text{H}_2\text{SO}_4, \text{H}_2\text{O})$  is reached, when it is a maximum and is equal to the vapour pressure of pure nitric acid mixed with pure sulphuric in this proportion. Concurrently with this change in the vapour pressure, not only does nitric acid of sp. gr. less than that required for the nitration of cellulose acquire the power to react, but the nature of the nitration products formed also vary considerably. Tables and curves are given showing this relation. Sulphuric acid thus has the power of abstracting the water from the nitric acid without itself interfering with the process of nitration, even when it is present in considerably larger quantity than that necessary for fixing all the water, providing only that it does not decompose the nitric acid with formation of higher oxides of nitrogen. The highest nitration product obtained contained 13.4% of nitrogen, and to obtain cellulose nitrates still richer in nitrogen it will be necessary most probably to work with mixtures  $\text{HNO}_3 + n(\text{H}_2\text{SO}_4, \text{H}_2\text{O})$ , where  $n$  has a high value. The lowest nitration product is obtained when the ratio of water to nitric acid is  $\text{HNO}_3, \text{H}_2\text{O}$  or  $\text{H}_3\text{NO}_4$ , the vapour pressure of this mixture, or possibly compound, is only 2 mm.

What must be the nature of the nitric acid which gives rise to nitration products between the higher and lower limit has not yet been elucidated. Z. K.

**Decomposition of Cellulose Nitrate at Temperatures Below that of Ignition.** A. V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1186—1192. Compare Abstr., 1906, i, 68).—The experiments on cellulose nitrate of the formula  $\text{C}_{24}\text{H}_{81}(\text{NO}_{3/9})_{11}\text{O}_{11}$  were performed in a similar manner to those described previously. The temperatures of decomposition can be divided into three zones. Between 160° and 150° all the nitrogen and most of the hydrogen is lost; between 145° and 130° less of both these elements are lost; at 125° and below, very little nitrogen is liberated, but the water formed is still high. Above 160° the substance explodes after thirty to forty minutes' heat-



ing. The substances liberated are carbon dioxide, nitric oxide, carbon monoxide, nitrogen, and water. The appearance of the residue varies considerably with the temperature to which the cellulose nitrate has been subjected. A curve is drawn showing the rate of decomposition at various temperatures, from which it is deduced that the rate of decomposition decreases with the fall in temperature. For the intervals  $125-140^{\circ}$ ,  $(dv/dt)_{\max} = -24.6 + 0.201t$ , and for  $145-155^{\circ}$ ,  $(dv/dt)_{\max} = -136.5 + 0.985t$ . Z. K.

**Acetylation of Some Oxycelluloses.** EMIL R. VON HARDT-STREMAJR (*Monatsh.*, 1907, 28, 73—78).—Skraup and König's octa-acetylcellobiose, m. p.  $228^{\circ}$  (Abstr., 1902, i, 135), is obtained, in almost the same amount as from cellulose, on acetylation by Maquenne and Goodwin's method (Abstr., 1904, i, 799) of hydralcellulose (Bumcke and Wolfenstein, Abstr., 1899, i, 852), or of oxycellulose formed by the action of potassium chlorate and hydrochloric acid on cotton wool (Tollens, Abstr., 1901, i, 453), or of nitric acid on sawdust (Faber and Tollens, Abstr., 1899, i, 854). Only about one-third of the same amount of the octa-acetyl compound is obtained from "acid-cellulose" (Bumcke and Wolfenstein, *loc. cit.*). G. Y.

**Colloidal Properties of Starch.** EUGÈNE FOUARD (*Compt. rend.*, 1907, 144, 501—503).—Fernbach and Wolff's soluble starch was treated five times with acid and washed with water until the electric conductivity of the water remained constant. It was found that the total ash diminished slightly with each treatment, falling from 0.331% to 0.124%, whilst the phosphoric acid was reduced from 0.1915% to 0.1117%. The phosphorus is not present in organic combination as might be supposed from its persistence in remaining. Whilst the acidity of 5% solutions of the five successive preparations using phenolphthalein was found to diminish from 0.212% to 0.172% the results with methyl-orange were 0.162% to 0.010%. The pseudo-solutions which are not absolutely transparent lose a considerable proportion of their acidity when filtered, although coincidently only some milligrams of starch are held back. The undissolved starch grains, therefore, fix the acid withdrawn from the colloidal medium, and the coagulation of the colloidal starch is correlative to fixation of acid. Addition of acid accelerated coagulation especially at low temperatures, whilst heat or alkalis reproduce the pseudo-soluble state. Colloidal starch is the first well-defined organic colloid which exhibits the phenomena of reversibility. N. H. J. M.

**Separation of Ammonia and Methylamine.** MAURICE FRANÇOIS (*Compt. rend.*, 1907, 144, 567—569).—When a current of air charged with a mixture of ammonia and methylamine and dried is passed over yellow mercuric oxide the ammonia is absorbed to form ammonio-mercuric oxide, and the methylamine so purified may be collected in water or hydrochloric acid. The elimination of the ammonia may be more rapidly accomplished by agitating an aqueous solution containing the mixture of ammonia and methylamine with yellow mercuric oxide during one hour. The decanted liquid yields on

distillation a solution of methylamine free from ammonia. The latter may also be separated from dimethylamine, trimethylamine, ethylamine, diethylamine, or triethylamine by these methods, although the dry process is difficult of application in the cases of di- and triethylamine.  
T. A. H.

**Tetramethylammonium Platinocyanide.** JAROSLAV MILBAUER (*Zeitsch. anorg. Chem.*, 1907, 53, 135—136).—This compound,  $\text{Pt}(\text{NMe}_4)_2(\text{CN})_4$ , prepared by neutralising tetramethylammonium hydroxide with hydrogen platinocyanide,  $\text{H}_2\text{Pt}(\text{CN})_4$ , occurs in colourless crystals which are readily soluble in water and completely decomposed on heating; they are not dichroic, and show no triboluminescence. The results of crystallographic measurements are also quoted.  
G. S.

**Influence of Cyclic Linkings on the Degree of Stability of Complex Compounds.** LEO TSCHUGAEFF (*J. pr. Chem.*, 1907, [ii], 75, 153—168. Compare Abstr., 1904, i, 478; 1905, i, 743, 865; 1906, i, 814, 984).—The analogy of complex compounds (metal-alkylamines, -imides, -oximes, -glyoximes, &c.) with carbon compounds is apparent from the expositions of Werner and of Pfeiffer (Abstr., 1905, i, 33). The known cyclic complex compounds are discussed with the object of investigating the influence of cyclic linkings on the degree of stability of such substances. It is concluded that in general and especially in the case of compounds of the metals of group VIII of the periodic system, cyclic complex compounds are more stable than the corresponding acyclic compounds, and that, *ceteris paribus*, there is a marked tendency to the formation of penta-atomic rings. Stable hexa-atomic cyclic complex compounds are also formed, but there appears to be little or no tendency to the formation of tetra-, hepta-, or octa-atomic ring systems.  
G. Y.

**Hexamethylenetetramine and its Salts (Cystopurine).** PETER BERGELL (*Chem. Zentr.*, 1907, i, 487—488; from *Deut. med. Woch.*, 33, 55—56).—A method of preparing hexamethylenetetramine in the form of the hydrochloride by evaporating urine to which ammonia has been added, mixing the residue with dry sodium sulphate, drying, treating with chloroform, extracting the residue with alcohol, and finally precipitating by means of hydrogen chloride is described. In order to estimate the quantity, the sample of urine is acidified with acetic acid, mercuric chloride added, the solution filtered after remaining twenty-four hours, and the precipitate after washing with a solution of mercuric chloride containing acetic acid, treated by Kjeldahl's method. When 50 c.c. of urine are used, the nitrogen is determined in a fifth. It was found that after administering 6 grams of hexamethylenetetramine to a dog, the urine only contained 2 grams.

Hexamethylenetetramine can behave as a mono- or di-basic base, but it has not been proved that it can form a tribasic salt with an inorganic acid, and a triborate cannot be prepared. Bayer's reagent for double linkings is not reduced by the base, and it probably does not contain an asymmetric carbon atom, for although it is partially burnt in the organism, the residue which is formed in the urine is optically

inactive. Monobasicity is the chief objection to Duden and Scharff's constitutional formula.

Besides the compound  $C_6H_{12}N_4 \cdot 6HgCl_2$ , the base also forms other very readily soluble compounds with salts. *Cystopurine*, or the compound with 2 mols. of sodium acetate and six of water, forms long, white, pointed crystals, and is a homogeneous substance which appears to possess certain advantages in respect to medicinal application; 1 part dissolves in 0.9 of cold water and 1.5 parts dissolve in 1 of warm water. *Cystopurine* may also be prepared directly from formalin, ammonia, and sodium acetate. E. W. W.

**Mechanism of the Reaction in the Formation of  $\alpha$ -Amino- and Imino-Acids.** GEORGE STADNIKOFF (*Ber.*, 1907, 40, 1014—1019. Compare Zelinsky and Stadnikoff, *Abstr.*, 1906, i, 425).—If the assumption be made that an imino-nitrile is the product of a reaction between a hydroxy-nitrile (as a weak acid) and an amino-nitrile (as a base), the mechanism of the Strecker synthesis of  $\alpha$ -amino-acids is understood; the formation of an imino-nitrile presupposes the presence of a hydroxy-nitrile as an intermediate product, and the whole process may be represented by the following example:  $CH_3 \cdot CHO \cdot NH_3 + HCN = CH_3 \cdot CHO + NH_4 \cdot CN$ ;  $NH_4 \cdot CN + H_2O \rightleftharpoons NH_4 \cdot OH + HCN$ ;  $CH_3 \cdot CHO + HCN = CH_3 \cdot CH(OH) \cdot CN$ ;  $CH_3 \cdot CH(OH) \cdot CN + NH_3 = CH_3 \cdot CH(NH_2) \cdot CN + H_2O$ ;  $CH_3 \cdot CH(OH) \cdot CN + CH_3 \cdot CH(NH_2) \cdot CN = H_2O + CH_3 \cdot CH(CN) \cdot NH \cdot CH(CN) \cdot CH_3$ .

The author proves that an imino-nitrile can be formed by the interaction of hydroxy-nitrile and amino-nitrile. Further, esters of amino-acids interact with hydroxy-nitriles to form imino-compounds, which, on hydrolysis, yield iminodicarboxylic acids.

*Iminodipropionic acid* was obtained in a 73.5% yield from  $\alpha$ -aminopropionitrile, acetaldehyde, and potassium cyanide, and subsequent hydrolysis of the imino-nitrile thus formed; it is microcrystalline and has m. p. 235—236° (decomp.). The *nickel* and *copper* salts are described.

*Iminodipropionic acid* may also be obtained from ethyl *dl*-alanine hydrochloride, acetaldehyde, and potassium cyanide.

*Iminotricarboxylic acid* may be obtained from glutamic acid in an analogous manner. Its *copper* salt is described. A. McK.

**Optically Active Modifications of Serine, *iso*Serine, and Diaminopropionic Acid.** EMIL FISCHER and WALTER A. JACOBS (*Ber.*, 1907, 40, 1057—1070. Compare *Abstr.*, 1906, i, 807).—The benzoyl compounds of the amino-acids have been resolved by means of alkaloids, the brucine and quinine salts being used for *isoserine* and the quinidine and quinine salts for diaminopropionic acid. Since Neuberg and Silbermann (*Abstr.*, 1905, i, 408) have connected *d*-glyceric acid with tartaric acid and hence with dextrose and so established its configuration, and E. Fischer (this vol., i, 192) has shown that the replacement of the amino-group by hydroxyl by means of nitrous acid is an optically normal reaction, it becomes possible to establish the configuration not only of serine but also of alanine. *d*-Serine yields *l*-glyceric acid and *l*-serine (the natural product) *d*-glyceric acid. Serine is converted by the action of hydrogen iodide into alanine (Fischer and

Leuchs, Abstr., 1902, i, 12), but at the high temperature racemisation takes place.

The *hydrochloride* of serine methyl ester is converted on shaking with acetyl chloride and phosphorus pentachloride into a well characterised, crystalline product, the *hydrochloride* of *ethyl β-chloro-α-amino-propionate*,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{NH}_2\cdot\text{HCl})\cdot\text{CO}_2\text{Et}$ , which renders it possible to couple serine with other amino-acids.

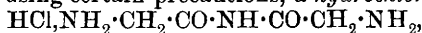
*Benzoyl-dl-isoserine*, m. p.  $151^\circ$  (corr.), crystallises from water in pointed prisms aggregated in bunches, or from alcohol in microscopic needles; the *barium* salt forms aggregates of prisms and the sparingly soluble *copper* salt bunches of almost colourless plates. The *brucine* salt of *benzoyl-l-isoserine* separates slowly from a mixture of *brucine* and the above compound at  $0^\circ$ ; *benzoyl-l-isoserine*, m. p.  $107-109^\circ$  (corr.),  $[\alpha]_D^{20} + 10.5^\circ$ , crystallises in right-angled, colourless prisms; the *barium* salt is characteristic and in acid solution has  $[\alpha]_D^{20} + 11.2^\circ$ . *l-isoserine*, m. p.  $199-201^\circ$  (decomp.),  $[\alpha]_D^{20} - 32.58^\circ$ , forms large, colourless crystals.

*Benzoyl-d-isoserine*,  $[\alpha]_D^{20} - 10.12^\circ$ , and *d-isoserine*,  $[\alpha]_D^{20} + 32.44^\circ$ , are similar to the *l-isomerides*.

*Dibenzoyl-dl-diaminopropionic acid* was resolved by means of the *quinidine* salts, that of the *d*-compound being least soluble and crystallising in colourless, glistening needles. *Dibenzoyl-d-diaminopropionic acid*, m. p.  $171-172^\circ$  (corr.),  $[\alpha]_D^{20} - 35.76^\circ$ , crystallises from water in minute, rhombic plates and from ethyl acetate in stellate aggregates of prisms. *d-Diaminopropionic acid hydrochloride* becomes brown at  $230^\circ$ , m. p.  $245^\circ$  (corr.) (decomp.),  $[\alpha]_D^{20} + 25^\circ$ , and forms bunches of long crystals. *Dibenzoyl l-diaminopropionic acid*,  $[\alpha]_D^{20} + 35.89^\circ$ , and *l-diaminopropionic acid*,  $[\alpha]_D^{20} - 24.98^\circ$ , have similar properties to the *d-isomerides*.

*d-Serine* was converted by the action of nitrous acid into the calcium salt of *l-glyceric acid*,  $[\alpha]_D^{20} + 12.94^\circ$ , crystallising in pointed prisms, whereas Frankland and Appleyard (Trans., 1893, 63, 296) found  $[\alpha]_D^{17} - 11.66^\circ$  for *d-glyceric acid*. E. F. A.

**New Compounds of Amino-Acids and Ammonia.** PETER BERGELL (*Zeitsch. physiol. Chem.*, 1907, 51, 207-212).—Several types of compounds of ammonia and amino-acids are known, but until the present research no compound has been described in which two amino-acid groups are united in an anhydride-like manner with their carboxyl groups linked by an ammonia group. The simplest representation of this would be *diglycinimide*,  $\text{NH}(\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2)_2$ , and it was prepared as follows. Chloroacetamide is converted by heating with phosphoric oxide into the corresponding nitrile. This reacts with chloroacetic acid to form dichlorodiacetimide in which two chloroacetyl groups are united by an imino-group. By treatment with ammonia, using certain precautions, a *hydrochloride*,



is obtained in crystalline form, m. p.  $234-238^\circ$ , and by careful treatment of this with silver oxide, the free base is obtained as a crystalline mass, m. p.  $138^\circ$ . W. D. H.

**Action of Absolute Nitric Acid on Heterocyclic Compounds.**

ANTOINE P. N. FRANCHIMONT (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 600—606).—Previous work by the author on this subject led to the formulation of the following rule. The hydrogen atom of the NH group is not attacked by absolute nitric acid when this group is situated between either two carbonyl groups or two saturated hydrocarbon residues, which, however, need not be  $\text{CH}_2$  groups as stated wrongly by Harries (*Abstr.*, 1903, i, 738), but when placed between two dissimilar groups, the hydrogen atom of the NH group is replaced by a nitro-group. It has now been found necessary to modify this rule, in that the direct nitration of heterocyclic compounds containing the NH group between a CO group and a saturated hydrocarbon residue depends on the configuration of the ring; for example, glycine anhydride, alanine anhydride, and ethyleneoxamide, all of which contain NH groups in the para-position in regard to each other, when treated with nitric acid yield not nitro-derivatives but nitrates.

W. H. G.

**Compounds of Magnesium Bromide and Iodide with Derivatives of the Acids.**

BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, i, 102—118. Compare *Abstr.*, 1906, i, 552; this vol., i, 19, 386).—Walker and Johnson's compound,  $\text{KI}_2\cdot 6\text{COMe}\cdot\text{NH}_2$  (*Trans.*, 1905, 87, 1597), is probably a eutectic mixture, m. p.  $54^\circ$ , of potassium iodide and acetamide; amongst other reasons the existence of such a compound is very unlikely, owing to the fact that potassium iodide does not form hydrates or compounds with methyl alcohol.

Magnesium iodide forms with acetamide compounds similar to those formed by magnesium bromide, but they are less stable. The eutectic point of the system lies at  $49^\circ$  at the composition  $\text{MgI}_2\cdot 15\cdot 1\text{COMe}\cdot\text{NH}_2$ ; on further addition of magnesium iodide, the temperature rises until the compound,  $\text{MgI}_2\cdot 6\text{COMe}\cdot\text{NH}_2$ , m. p.  $177^\circ$ , separates. With acetonitrile, magnesium iodide forms the compound  $\text{MgI}_2\cdot 6\text{MeCN}$ , which crystallises from acetonitrile in long, colourless plates or stars, very hygroscopic and easily decomposed by water. It does not melt, but decomposes when the system contains 87%  $\text{MgI}_2\cdot 6\text{MeCN}$  at  $88^\circ$ , after which the curve indicates the formation of a new substance, possibly  $\text{MgI}_2\cdot 2\text{MeCN}$  or  $\text{MgI}_2\cdot 4\text{MeCN}$ . Magnesium bromide does not combine so readily with acetonitrile, but forms opaque solutions from which crystals of the compound  $\text{MgBr}_2\cdot 3\text{MeCN}$ , m. p.  $132^\circ$ , commence to separate above  $88^\circ$ . At the ordinary temperature another substance, probably  $\text{MgBr}_2\cdot 4\text{MeCN}$ , separates. With acetic anhydride, magnesium bromide yields the compound  $\text{MgBr}_2\cdot 6\text{OAc}_2$ , m. p.  $136$ — $137^\circ$ . Acetyl chloride and magnesium bromide yield a compound, probably  $\text{MgBr}_2\cdot \text{AcCl}$ , which decomposes without melting at low temperatures and does not dissolve in acetyl chloride. The compound  $\text{MgBr}_2\cdot \text{BzCl}$ , with benzoyl chloride, crystallises better, but does not melt even at  $200^\circ$ . The solubility curves of all the compounds  $\text{MgX}_2\cdot 6\text{R}$ , in R (where R stands for acetamide, &c.), very much resemble the curves for  $\text{MgX}_2\cdot 6\text{H}_2\text{O}$  in water, but the substances must be quite dry, as the least amount of moisture greatly increases the solubility. Composition-

temperature curves for the substances investigated in this and previous papers are given. Z. K.

**Reactions at Low Temperatures. II. Sulphides and Carbamates.** WALTER PETERS (*Ber.*, 1907, 40, 1478—1482. Compare Abstr., 1906, i, 817).—The reactions between various bases and hydrogen sulphide or carbon dioxide in absolute ethereal solution at  $-70^{\circ}$  have been studied. The results are similar to those previously obtained with hydrogen cyanide. Hydrogen sulphide yields compounds with propylamine, diethylamine, triethylamine, tripropylamine, *as*-dimethylhydrazine, pentamethylenediamine, piperidine, and coniine. These compounds contain 2 molecules of base combined with 1 of hydrogen sulphide.

Carbon dioxide yields compounds with propylamine and *as*-dimethylhydrazine at the ordinary temperature, with piperidine at about  $-15^{\circ}$ , and with diethylamine, propylenediamine, and pentamethylenediamine at  $-70^{\circ}$ . The products are carbamates formed by the union of the dioxide (1 mol.) with 2 molecules of a monoamine or 1 molecule of a diamine,  $2\text{NH}_2\text{R} + \text{CO}_2 = \text{NHR}\cdot\text{CO}\cdot\text{ONH}_3\text{R}$ . Carbon dioxide does not combine with tertiary amines.

Ethyl glutaconate does not combine with iodine at  $-70^{\circ}$ , and at the same temperature trithioaldehyde and trithioacetone do not appear to combine with bromine. Phosphorus tri-iodide combines with iodine in carbon disulphide solution at  $-70^{\circ}$ , yielding the penta-iodide which is, however, excessively hygroscopic. J. J. S.

**Preparation of Diurethane Derivatives of Dialkylmalonic Acids.** WILHELM TRAUBE (D.R.-P. 179946).—The chlorides of the dialkylmalonic acids react with urethane only at temperatures above  $100^{\circ}$  to furnish diurethane derivatives in accordance with the following equation:  $\text{CET}_2(\text{COCl})_2 + 2\text{NH}_2\cdot\text{CO}_2\text{Et} = 2\text{HCl} + \text{CET}_2(\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$ .

This condensation is effected by heating the reagents either alone or in boiling xylene or cumene. G. T. M.

**Calcium Cyanamide.** GEORG BREDIG, W. FRAENKEL, and E. WILKE (*Zeitsch. Elektrochem.*, 1907, 13, 69—75).—Powdered calcium carbide is heated with or without an admixture of 10% of other substances in an atmosphere of nitrogen, and the rate of absorption of nitrogen and also the quantity taken up after two hours are observed. At  $800^{\circ}$  the carbide alone absorbs about 3% of nitrogen in two hours; admixture of 10% of calcium chloride increases the absorption to 22%; 10% of barium chloride gives 12.5%. Lithium, sodium, and potassium chlorides give absorptions of about 17%, 12%, and 11% respectively, so that it appears that the acceleration of the reaction is greater the lower the atomic weight of the metal. Calcium fluoride, sulphate, oxide, and hydroxide cause little or no acceleration of the reaction; magnesia, coke-powder and sand do not accelerate, but sodium carbonate and sugar charcoal gave absorptions of 6% to 8% and 8% to 9% respectively.

Absorption begins at  $750^{\circ}$  with calcium carbide alone, whilst the mixtures with sodium or calcium chloride begin to take up nitrogen at  $650^{\circ}$ .

A set of experiments at 700° gave similar results ; lithium chloride, however, gave a greater acceleration than calcium chloride.

The results show that the acceleration is not due (1) to the presence of oxygen salts of calcium, (2) to an initial rise of temperature, or (3) to an increase in the porosity of the mass. T. E.

**Formation of Calcium Cyanamide.** FRITZ FOERSTER and HANS JACOBY (*Zeitsch. Elektrochem.*, 1907, 13, 101—107).—Curves are given showing the influence of time and temperature on the quantity of nitrogen absorbed by calcium carbide, both alone and mixed with calcium chloride or fluoride. With the commercial carbide (containing when powdered about 10% of calcium hydroxide) the absorption is slow and incomplete at temperatures below 1000°. Calcium fluoride accelerates the absorption, so that fairly complete conversion is attained in two hours at 900°. The effect of the quantity of the catalyst added is remarkable. The quantity of nitrogen absorbed in two hours at 800° increases with the quantity of calcium chloride added, the conversion being almost complete with 30% calcium chloride. With calcium fluoride, a maximum absorption of about 8% in two hours is reached with 5% of added fluoride at 800°, or 29% with 3% of fluoride at 900°; the addition of larger quantities of the fluoride diminishes the quantity of nitrogen absorbed.

The authors consider that the acceleration is due to partial fusion, owing to which any protective skin of calcium cyanamide is broken up and the unchanged carbide so exposed to the action of the nitrogen.

T. E.

**Violent Explosions of Hydrocyanic Acid and the Nature of the Products formed thereby.** EGIDIO POLLACCI (*Boll. Chim. Farm.*, 1907, 46, 237—244).—The author describes several violent explosions of concentrated hydrocyanic acid solutions which have come under his notice. The explosions are accompanied by the formation of a black substance, which, when heated in a tube closed at one end, yields ammonia and hydrogen cyanide. This substance is apparently condensed or polymerised hydrogen cyanide, the ammonia evolved on heating being the result of the decomposition of part of the acid. When the substance is heated gradually in a test-tube, a sublimate of ammonium carbonate appears on the sides of the tube. The formation of this salt during the explosion is easily explained by assuming that cyanuric acid (or some other xanthic compound) is first formed. This acid would then decompose, giving cyanic acid, which, in presence of aqueous vapour, is rapidly transformed into ammonia and carbon dioxide:  $\text{HCNO} + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2$ .

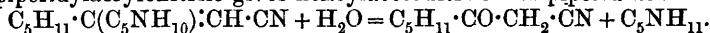
T. H. P.

**Method of Synthesis of Non-substituted  $\beta$ -Ketonic Nitriles.** CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1907, 144, 491—493).—When hydrolysed by sulphuric acid, phenylpropionitrile gives benzoylacetamide,  $\text{CH}_2\text{Bz}\cdot\text{CO}\cdot\text{NH}_2$ , whilst amylpropionitrile and hexylpropionitrile give amyl- and hexyl-propionamides respectively.

In the former case, both the  $\cdot\text{CN}$  group and the acetylenic linking are attacked, whilst in the latter only the  $\cdot\text{CN}$  group is hydrolysed

(*Bull. Soc. chim.*, 1906, [iii], 35, 526). On the other hand, the hydrolysis of the condensation products of acetylenic nitriles with alcohols or phenols cannot easily be limited to the formation of  $\beta$ -ketonic nitriles (*loc. cit.*, p. 531).

The condensation products of acetylenic nitriles with amines (Abstr., 1906, i, 956), however, are easily hydrolysed by oxalic acid in ethereal solution with the formation of the corresponding  $\beta$ -ketonic nitrile and regeneration of the original amine. Thus  $\beta$ -amyl- $\beta$ -piperidylacrylonitrile gives hexoylacetonitrile and piperidine:



As the yields in this reaction and in the formation of the initial condensation derivative are nearly theoretical, the two processes form an excellent method of passing from acetylenic to  $\beta$ -ketonic nitriles. The latter are completely soluble in alkali hydroxide or carbonate solutions, from which they are reprecipitated by acids. The following are described.

*Hexoylacetonitrile*,  $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 126—128°/14 mm.,  $D^{15}_D$  0.9414; *heptoylacetonitrile*,  $\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 137—141°/15 mm.,  $D^{15}_D$  0.9375. Benzoylacetonitrile,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CN}$ , first prepared by Haller, was obtained similarly. E. H.

**Constitution of Organo-Magnesium Compounds.** VICTOR GRIGNARD (*Bull. Soc. chim.*, 1907, [iv], 1, 256—262).—In reply to Tschelinzeff (this vol., i, 199), who adopts Baeyer and Villiger's formula for organo-magnesium compounds (Abstr., 1902, i, 355), mainly on the ground that it permits of the representation of the two isomeric forms of these compounds he has obtained, namely,  $\text{OR}_2\text{X}\cdot\text{MgR}'$  and  $\text{ORR}'\text{X}\cdot\text{MgR}$ , the author points out that the formula proposed by himself (Abstr., 1903, i, 552) equally well accounts for the existence of isomerides, since it may be assumed that the two additional valencies of oxygen in oxonium compounds and of nitrogen in quinquivalent nitrogen derivatives have not the same value as the normal valencies, so that  $\text{R}_2\text{OR}'\cdot\text{MgX}$  is not necessarily identical with  $\text{RR}'\text{O}\cdot\text{R}\cdot\text{MgX}$ , as has been supposed by Blaise (Abstr., 1906, i, 153), and instances are quoted in which interchanges of alkyl radicles of the type suggested have occurred (Blaise, Abstr., 1905, i, 111; Schmidlin, Abstr., 1906, i, 392; this vol., i, 26; and Grignard, Abstr., 1904, i, 494).

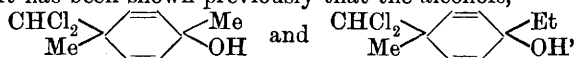
Blaise has asserted that in the case of amino-magnesium compounds the addition of water should lead to the production of an amine hydroxide and not to a hydrocarbon if Grignard's formula were correct. This view, it is suggested, is based on a misconception of the usual method of hydrolysis of organo-magnesium derivatives, which in this particular case may be represented as follows:  $\text{R}_2\text{R}'\text{R}''\text{N}\cdot\text{MgX} + \text{HO}\cdot\text{H} = \text{MgX}\cdot\text{OH} + \text{R}_2\text{R}'\text{R}''\text{N}\cdot\text{H}$ , the unstable substituted ammonium hydride thus formed decomposing immediately, forming the amine and hydrocarbon. The further objection of Blaise that the substituted ammonium iodides do not react with magnesium, has, in the author's opinion, little weight, since the quaternary ammonium radicle has little in common with an alkyl radicle. Incidentally it is pointed out that this non-reactivity of the substituted ammonium iodides with magnesium contradicts Tschelinzeff's view that in the formation of



organo-magnesium compounds the ether or the tertiary amine dissociates the alkyl haloid, forming substances of the type  $R'OR_2X$  and  $RR'R''N \cdot X$ , with which the magnesium then reacts (Abstr., 1905, i, 40). Tschelinzeff's suggestion that by analogy with other oxonium and ammonium compounds organo-magnesium derivatives should be regarded as having the haloid atom attached directly to the oxygen or nitrogen is regarded as unlikely, since they decompose with the production of a magnesium haloid salt, whence there is reason to believe, with Abegg (Abstr., 1906, i, 57), that the radicle  $MgX$  behaves as the positive portion of the molecule; the organic residue being the negative portion. With regard to the constitution of the organo-magnesium compounds containing a second molecule of ether the author thinks there is less objection to the formula proposed by Tschelinzeff (Abstr., 1906, i, 241) than to that used by Zelinsky (Abstr., 1903, i, 802) and by Blaise (Abstr., 1905, i, 111).

T. A. H.

**Alkylidenedihydrobenzenes.** KARL AUWERS (*Annalen*, 1907, 352, 219–272. Compare Abstr., 1903, i, 100, 620; 1904, i, 26; 1905, i, 434).—It has been shown previously that the alcohols,



formed from 4-keto-1-methyl-1-dichloromethylcyclohexadiene by Grignard's reaction, readily lose water and yield unstable products which undergo transformation into the benzene derivatives,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH}_2 \cdot \text{CHCl}_2$  and  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CHMe} \cdot \text{CHCl}_2$  respectively. The work described in the two following papers, to which this is a general introduction, was undertaken to determine the constitution of the intermediate products, and by applying Grignard's reaction to the condensation products of chloroform and *as-m*-xyleneol, *as-o*-xyleneol, and  $\psi$ -cumenol to ascertain if the loss of water takes place with hydroaromatic alcohols derived from homologues of *p*-cresol.

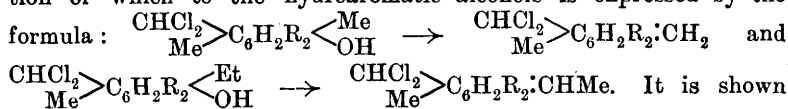
The configuration of the condensation product of chloroform with *p*-cresol, as 4-keto-1-methyl-1-dichloromethylcyclohexadiene is confirmed by the formation of  $\beta$ -chloromethylacrylic acid, a decomposition product of methyl-dichloromethylmalonic acid, on oxidation of the ketone with potassium permanganate.

The constitutions of the unstable compounds formed by loss of water from the hydroaromatic alcohols,  $\text{CHCl}_2 \cdot \text{C}_6\text{H}_2\text{R}_2\text{R}'\text{Me} \cdot \text{OH}$  ( $\text{R}=\text{H}$  or  $\text{Me}$ ;  $\text{R}'=\text{Me}$  or  $\text{Et}$ ), derived from the above three homologues of *p*-cresol, and of the benzene transformation products are discussed. By identification of the aldehydes and ketones formed by elimination of hydrogen chloride and oxidation of the resulting chlorostyrenes,  $\text{C}_6\text{H}_2\text{R}_2\text{Me} \cdot \text{CH} \cdot \text{CHCl}$  and  $\text{C}_6\text{H}_2\text{R}_2\text{Me} \cdot \text{CMe} \cdot \text{CHCl}$  ( $\text{R}=\text{H}$  or  $\text{Me}$ ), the transformation products are shown to be homologues of *p*- $\beta\beta$ -dichloroethyltoluene,  $\text{C}_6\text{H}_2\text{R}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CHCl}_2$ , and of *p*-dichloroisopropyltoluene,  $\text{C}_6\text{H}_2\text{R}_2\text{Me} \cdot \text{CHMe} \cdot \text{CHCl}_2$ , respectively.

Of the hydroaromatic alcohols described, those derived from *p*-cresol, *as-o*-xyleneol, and  $\psi$ -cumenol, having  $\text{R}'=\text{Et}$ , lose water most easily, whilst the alcohols derived from *as-m*-xyleneol, having  $\text{R}'=\text{Et}$ , and from *as-o*-xyleneol, with  $\text{R}'=\text{Me}$ , are the most stable. Most, if not all, of these hydroaromatic alcohols occur in two modifications which

differ in melting point and solubility, and are probably *cis*- and *trans*-forms.

The formation of the unstable intermediate products and their transformation into the stable benzene derivatives can be followed by observation of the change in the angle of refraction which is least for the intermediate compounds. It was shown previously (Abstr., 1905, i, 445) that successive action of phosphorus pentachloride and water on 4-keto-1-methyl-1-dichloromethylcyclohexadiene leads to the formation of *p*-chloro-*o*-tolualdehyde; it is found now that the unstable products derived from *p*-cresol and  $\psi$ -cumenol are converted analogously by the action of sulphuric acid into 2:4-dimethyl- and 2:3:4:5-tetramethyl-benzaldehydes respectively. From this it is argued that the intermediate compounds must be alkylidenecyclohexadienes, the relation of which to the hydroaromatic alcohols is expressed by the formula:



It is shown that the molecular refractions of the intermediate compounds are in agreement with those calculated from these alkylidene formulæ.

The general chemical and physical properties of the alkylidenecyclohexadienes are discussed, compared with those of other analogous and closely related compounds, and shown to support the above conclusions as to the constitution of the compounds in question.

In the following two papers a large number of refractive indices are given, of which only the limiting values of  $n_D$  are quoted.

G. Y.

**Derivatives of Alkylidenedihydrobenzenes from *p*-Cresol.** KARL AUWERS and M. HESSENLAND (*Annalen*, 1907, 352, 273—287. Compare Auwers and Keil, Abstr., 1903, i, 100, 620; 1905, i, 445; and preceding abstract).—On extraction with light petroleum, the resin insoluble in aqueous alkalis, formed in the preparation of 4-keto-1-methyl-1-dichloromethylcyclohexadiene, yields *p*-tolyl orthoformate,  $\text{CH}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_3$ , crystallising in colourless prisms, m. p. 112°.

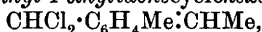
1-Hydroxy-1:4-dimethyl-4-dichloromethylcyclohexadiene is found now to exist in two stereoisomeric modifications, one of which has been described (Abstr., 1903, i, 620); the second form separates from light petroleum in stout, transparent crystals, m. p. 65°. No difference could be observed in the stabilities of the two modifications. When heated with light petroleum at 45° in a current of hydrogen, this hydroaromatic alcohol yields 4-methyl-4-dichloromethyl-1-methylenecyclohexadiene,  $\text{CHCl}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{CH}_2$ , which is obtained as a yellow oil,  $D_4^{14.2}$  1.1800,  $n_D^{14.1}$  1.55844,  $n_D^{18.5}$  1.56109, commences to polymerise after one to two days at the ordinary temperature, and at 70—80° is transformed into *p*- $\beta\beta$ -dichloroethyltoluene, b. p. 114—116°/14 mm. or 129—132°/23 mm.,  $D_4^{14}$  1.1734,  $D_4^{22.4}$  1.1638,  $n_D^{14}$  1.53940,  $n_D^{21.6}$  1.53610. This is converted by boiling alcoholic potassium hydroxide into  $\beta$ -chloro-*p*-methylstyrene (Abstr., 1904, i, 27), b. p. 99—102°/14 mm. or 129—132°/39 mm.,  $D_4^{28.7}$  1.0565,  $n_D^{26.8}$  1.56635.

The action of chlorine on 4-methyl-4-dichloromethyl-1-methylenecyclohexadiene

*cyclohexadiene* in carbon tetrachloride solution cooled by ice, leads to the formation of a mixture of tri- and di-chloro-compounds. The *trichloro*-compound,  $C_6H_4Me \cdot CH_2 \cdot CCl_3$ ?, forms a colourless oil, b. p.  $135-142^\circ/8-9$  mm., and when boiled with alcoholic potassium hydroxide yields a light yellow oil, which contains chlorine, and is volatile with steam, together with *p*-tolylacetic acid.

2 : 4-Dimethylbenzaldehyde, formed by heating 4-methyl-4-dichloromethyl-1-methylenecyclohexadiene with 80% sulphuric acid at  $80-90^\circ$ , is obtained as a yellow oil; it yields a *semicarbazone* crystallising in small prisms, m. p.  $225-227^\circ$ , and is oxidised by permanganate to 2 : 4-dimethylbenzoic acid.

4-Methyl-4-dichloromethyl-1-ethylidenecyclohexadiene,



formed by carefully heating 1-hydroxy-4-methyl-4-dichloromethyl-1-ethylcyclohexadiene (Abstr., 1905, i, 434), or by shaking it with anhydrous formic acid, is obtained as a yellow oil,  $D_4^{25.3}$  1.1669—1.1696,  $n_D^{15.3}$  1.56343. *p*-Dichloroisopropyltoluene, b. p.  $123-125^\circ/13$  mm.,  $D_4^{14.6}$  1.1534,  $D_4^{23}$  1.1519,  $n_D^{14.6}$  1.53732,  $n_D^{27}$  1.53441.  $\beta$ -Chloro- $\alpha$ -*p*-dimethylstyrene, b. p.  $106-108^\circ/10$  mm.,  $D_4^{20}$  1.0580,  $n_D^{19}$  1.55714,  $n_D^{23}$  1.55494. G. Y.

**Alkylidenedihydrobenzenes from *as-m*-Xylenol, *as-o*-Xylenol, and  $\psi$ -Cumenol.** KARL AUWERS and A. KÖCKRITZ (*Annalen*, 1907, 352, 288—321. Compare Abstr., 1900, i, 160; 1902, i, 218; 1903, i, 100; and preceding abstract).—*Derivatives of as-m-xylenol*.—4-Hydroxy-1 : 3 : 4-trimethyl-1-dichloromethylcyclohexadiene,  $C_{10}H_{14}OCl_2$ , formed by the action of magnesium methyl iodide on 4-keto-1 : 3-dimethyl-1-dichloromethylcyclohexadiene, crystallises in transparent, monoclinic prisms, m. p.  $82-83^\circ$ , and decomposes gradually at the ordinary temperature, forming a resinous mass. When heated with ether at  $45^\circ$ , or shaken with formic acid at the laboratory temperature, it yields 1 : 3-dimethyl-1-dichloromethyl-4-methylenecyclohexadiene, which is transformed at  $80-90^\circ$  into 1 : 3-dimethyl-4- $\beta$ -dichloroethylbenzene,  $C_{10}H_{12}Cl_2$ , b. p.  $124-126^\circ/12$  mm. or  $136-138^\circ/17$  mm.,  $D_4^{14.2}$  1.1507,  $D_4^{19}$  1.1574,  $n_D^{15}$  1.54457,  $n_D^{19.5}$  1.53927. On prolonged boiling with alcoholic potassium hydroxide, this is converted into  $\beta$ -chloro-1 : 3-dimethylstyrene,  $C_6H_3Me_2 \cdot CH : CHCl$ , which is obtained as a colourless oil, b. p.  $117-120^\circ/14$  mm.,  $D_4^{23.9}$  1.0466,  $n_D^{23.9}$  1.56351, and on oxidation with permanganate in aqueous acetone solution yields 2 : 4-dimethylbenzaldehyde, formed also by Gattermann's method from *m*-xylene. It forms a *semicarbazone*, crystallising in leaflets, m. p.  $226^\circ$ , and is oxidised to 2 : 4-dimethylbenzoic acid.

4-Hydroxy-1 : 3-dimethyl-1-dichloromethyl-4-ethylcyclohexadiene,  $C_{11}H_{16}OCl_2$ , formed by the action of magnesium ethyl iodide on 4-keto-1 : 3-dimethyl-1-dichloromethylcyclohexadiene, crystallises in slender needles or stout, transparent prisms, m. p.  $85-85.5^\circ$ ; a urethane could not be obtained with phenylcarbimide, diphenylcarbamide being formed. 1 : 3-Dimethyl-1-dichloromethyl-4-ethylidenecyclohexadiene,  $C_{11}H_{14}Cl_2$ , is obtained as a mobile, colourless oil,  $D_4^{21}$  1.1393,  $n_D^{20}$  1.56605,  $n_D^{22.9}$  1.55917. 1 : 3-Dimethyl-4-dichloroisopropylbenzene, formed from the preceding substance at  $120^\circ$ , is a colourless oil, b. p.  $135-137^\circ/$

11 mm. or 143—144°/16 mm.,  $D_4^{149}$  1.1396,  $D_4^{228}$  1.1345,  $n_D^{25}$  1.54212,  $n_D^{22.6}$  1.53619.  $\beta$ -Chloro- $\alpha$ -2 : 4-trimethylstyrene,  $C_9H_9Me_3 \cdot CMe \cdot CHCl$ , is a colourless oil, b. p. 112—114°/16 mm. or 124—125°/24 mm. Reduction of the dichloro-compound with sodium and alcohol leads to the formation of 1 : 3-dimethyl-4-isopropylbenzene, which on bromination is converted into tetrabromo-*m*-xylene, m. p. 248° (241° : Fittig and Bieber, *Annalen*, 1870, 156, 236).

A *polymeric modification* of 1 : 3-dimethyl-1-dichloromethyl-4-ethylidenecyclohexadiene, crystallising in nacreous leaflets, m. p. 183—184°, is formed from the corresponding hydroaromatic alcohol in four months at the winter temperature, or more rapidly from the unimolecular ethylidene compound.

*Derivatives of as-o-xenol.*—4-Hydroxy-1 : 2 : 4-trimethyl-1-dichloromethylcyclohexadiene,  $C_{10}H_{14}OCl_2$ , crystallises in transparent, monoclinic prisms, m. p. 79.5°. 1 : 2-Dimethyl-4- $\beta\beta$ -dichloroethylbenzene is a colourless oil, b. p. 126—128°/9 mm. or 134—136°/11 mm.,  $D_4^{142}$  1.1513,  $D_4^{21}$  1.1428,  $n_D^{14.2}$  1.54144,  $n_D^{21}$  1.53789. The intermediate methylene compound could not be isolated.  $\beta$ -Chloro-3 : 4-dimethylstyrene is an aromatic, colourless oil, b. p. 126—128°/14 mm., and on oxidation with permanganate in aqueous acetone solution yields 3 : 4-dimethylbenzaldehyde, which is formed also directly from *o*-xylene; the semicarbazone,  $C_{10}H_{13}ON_3$ , crystallises in needles, m. p. 224° or, when quickly heated, 227—228°. On further oxidation, the aldehyde yields 3 : 4-dimethylbenzoic acid. The *polymeride* of the methylene compound crystallises from alcohol in flat prisms, m. p. 153—154°; the melting point sinks with repeated recrystallisations.

4-Hydroxy-1 : 2-dimethyl-1-dichloromethyl-4-ethylcyclohexadiene commences to decompose immediately at the laboratory temperature. 1 : 2-Dimethyl-1-dichloro-4-ethylidenecyclohexadiene,  $C_{11}H_{14}Cl_2$ , was obtained as an impure oil,  $D_4^{19}$  1.1761. 1 : 2-Dimethyl-4- $\beta\beta$ -dichloroisopropylbenzene is a transparent oil, b. p. 135—140°/14 mm.,  $D_4^{20.3}$  1.1352,  $n_D^{21}$  1.53837.  $\beta$ -Chloro- $\alpha$ -3 : 4-trimethylstyrene solidifies in a freezing mixture; m. p. 22°, b. p. 128°/14 mm.,  $D_4^{23}$  1.0490,  $n_D^{22.8}$  1.55745, and on oxidation yields 3 : 4-dimethylacetophenone, which forms a *semicarbazone*,  $C_{11}H_{15}ON_3$ , stout, white needles, m. p. 233—234°.

*Derivatives of  $\psi$ -cumenol.*—4-Hydroxy-1 : 2 : 4 : 5-tetramethyl-1-dichloromethylcyclohexadiene crystallises from light petroleum in long needles, m. p. 76—78°, decomposes gradually, forming a yellow oil; and gives with fuming nitric acid a dark blue coloration changing to carmine. 1 : 2 : 5-Trimethyl-1-dichloromethyl-4-methylidenecyclohexadiene,  $D_4^{14}$  1.1484,  $D_4^{19}$  1.1446,  $n_D^{14}$  1.56096,  $n_D^{18.8}$  1.55920. 1 : 2 : 5-Trimethyl-4- $\beta\beta$ -chloroethylbenzene, a colourless oil, solidifying at low temperatures, m. p. 22°, b. p. 134—136°/10 mm. or 143—145°/13 mm.,  $D_4^{17}$  1.1357,  $n_D^{16}$  1.54252.  $\beta$ -Chloro-2 : 4 : 5-trimethylstyrene, a colourless oil, b. p. 133—134°,  $D_4^{21.8}$  1.0429,  $n_D^{21.8}$  1.56680; on oxidation, this yields 2 : 4 : 5-trimethylbenzaldehyde and 2 : 4 : 5-trimethylbenzoic acid. The *semicarbazone* of the aldehyde,  $C_{11}H_{15}ON_3$ , crystallises in flat prisms, m. p. 243—244°.

4-Hydroxy-1 : 2 : 5-trimethyl-1-dichloromethyl-4-ethylcyclohexadiene and 1 : 2 : 5-trimethyl-1-dichloromethyl-4-ethylidenecyclohexadiene were not isolated in a state of purity. 1 : 2 : 5-Trimethyl-4-dichloroisopropylbenzene, a colourless oil, solidifying at low temperatures, m. p. 22°, b. p. 134—136°/10 mm. or 143—145°/13 mm.,  $D_4^{17}$  1.1357,  $n_D^{16}$  1.54252.

*propylbenzene* crystallises from light petroleum or methyl alcohol in slender needles, m. p. 43—44°, b. p. 135—137°/10 mm. or 155—157°/16 mm.,  $D_4^{16}$  1·1321,  $D_4^{21.9}$  1·1263,  $n_D^{21.9}$  1·53812.  $\beta$ -*Chloro- $\alpha$ -2:4:5-tetramethylstyrene* is a colourless oil, b. p. 126—127°/16 mm. or 131—133°/24 mm.,  $D_4^{20}$  1·0341,  $n_D^{20}$  1·54182, and after oxidation yields a *semicarbazone*,  $C_{12}H_{17}ON_3$ , rectangular plates, m. p. 204°, identical with that formed from 2:4:5-trimethylacetophenone prepared from  $\psi$ -cumene and acetyl chloride. 1:2:5-*Trimethyl-4-isopropylbenzene*, prepared by reduction of the dichloro-compound with sodium and alcohol, b. p. 221·5—223·5°,  $D_4^{21}$  0·8795,  $n_D^{21}$  1·50648. The *polymeric modification* of the methylene compound,  $(C_{11}H_{14}Cl_2)_2$ , is formed from the unimolecular compound in the course of some days at the ordinary temperature; it crystallises in small needles, m. p. 132—138°, or after partial oxidation with permanganate, 151—157°. When reduced with sodium and alcohol, it yields durenene. The action of cooled, concentrated sulphuric acid on the uni- or bi-molecular methylene compound leads to the formation of an *aldehyde* which is oxidised rapidly by air, forming durenecarboxylic [prehnitenecarboxylic] acid (Meyer and Molz, Abstr., 1897, i, 476). The *semicarbazide*,  $C_{12}H_{17}ON_3$ , crystallises in long, white needles, m. p. 229—230°. Dinitroprehnitene, m. p. 176°, is formed by the action of fuming nitric acid on prehnitene or prehnitenecarboxylic acid, G. Y.

**Derivatives of *o*- and *p*-tert.-Butyltoluenes.** J. KOZAK (*Bull. Acad. Sci. Cracow*, 1906, 407—417).—This is a study of the dyes obtained by the action of dehydrating agents on the condensation products of maleic anhydride with *o*- and *p*-tert.-butyltoluenes (v. Pechmann, Abstr., 1882, 1074; Marchlewski, Abstr., 1903, i, 667).

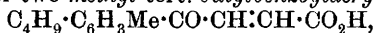
The action of bromine on *tert*.-butylbenzene in presence of iodine leads to the formation of a mixture of *o*- and *p*-bromo-derivatives which are converted by Fittig's reaction into *o*- and *p*-tert.-butyltoluenes; these are separated by fractional distillation.

*o*-tert.-Butyltoluene, b. p. 170—170·5°/743·1 mm.,  $n_D^{17}$  1·49423.

*p*-tert.-Butyltoluene, b. p. 192—192·5°/742 mm.,  $n_D^{17}$  1·493565.

4-Methyl-3-tert.-butylbenzoyl- or 3-methyl-4-tert.-butylbenzoyl-acrylic acid,  $C_4H_9 \cdot C_6H_3Me \cdot CO \cdot CH : CH \cdot CO_2H$ , formed by the action of aluminium chloride and maleic anhydride on *o*-tert.-butyltoluene, cooled by ice-water, crystallises in yellow, monoclinic needles, m. p. 123—124°, and when heated with acetic anhydride yields a *dye*,  $C_{15}H_{16}O_2$ , which forms dark bronze crystals, m. p. 320—326°, sublimes below its melting point, has a yellowish-red fluorescence when dissolved in organic solvents, and dissolves in concentrated sulphuric acid to a blue solution becoming red and then yellowish-brown when heated. The absorption spectrum of the solution in toluene shows two dark bands in the yellow and green,  $\lambda$  559—541 and  $\lambda$  518—502 respectively.

The condensation of maleic anhydride with *p*-tert.-butyltoluene leads to the formation of two methyl-tert.-butylbenzoylacrylic acids,



of which the one crystallising first from water, termed the  *$\alpha$ -acid*, forms yellow needles or prisms, m. p. 133—134°. The more soluble

$\beta$ -acid crystallises in more intensely yellow needles or prisms, m. p. 115—117°.

The dye, obtained by the action of acetic anhydride on the  $\alpha$ -acid, crystallises in almost black needles, m. p. 198—208°, is fluorescent in dilute solution, and dissolves to a blue solution in concentrated sulphuric acid.

The dye,  $C_{15}H_{16}O_2$ , formed from the  $\beta$ -acid, crystallises in reddish-brown needles, m. p. 202—206°, is fluorescent in dilute solution, and forms a violet solution in concentrated sulphuric acid.

The absorption spectra of the two dyes derived from *p*-tert.-butyltoluene show the same two bands as observed in that of the dye derived from *o*-tert.-butyltoluene. G. Y.

**Benzene Hydrocarbons containing a  $\psi$ -Allyl Side-Chains: Methoethenylbenzene and its Homologues. Studies in Molecular Migration. II. Molecular Transpositions Accompanying the Transformation of  $\alpha$ -Glycols and their Derivatives into Aldehydes and Ketones.** MARC TIFFENEAU (*Ann. Chim. Phys.*, 1907, [viii], 10, 322—378. Compare Abstr., 1906, i, 724, 965; this vol., i, 130).—This paper opens with a long theoretical introduction and concludes with a general review of the experimental results described in Parts I (this vol., i, 304) and II. It was found previously (*loc. cit.*) that the halohydrins, formed by addition of hydrogen oxyhaloids to  $\psi$ -allylbenzenes, lose the hydrogen haloid when treated with alkalis, forming ethylene oxides which on distillation undergo simple change into aldehydes:  $OH \cdot CArMe \cdot CH_2X \rightarrow CArMe \begin{smallmatrix} CH_2 \\ \diagup \\ O \end{smallmatrix}$

$\rightarrow CHArMe \cdot CHO$ , whereas when treated with certain metallic oxides or salts, such as mercuric oxide or silver nitrate, the substance obtained is a product of intramolecular change:  $OH \cdot CArMe \cdot CH_2X \rightarrow CH_3Ar \cdot COMe$ . As such intramolecular wandering of groups has been described only in isolated cases, the phenomenon has been studied now systematically in that of the  $\alpha$ -glycols and their derivatives, the halohydrins, the magnesium derivatives of the halohydrins, and the ethylene oxides.

With regard to the manner in which they are transformed into aldehydes or ketones,  $\alpha$ -glycols and their derivatives fall into two classes: (a) these in which the transformation is accompanied by a change in the position of a hydrogen atom, and (b) those in which the transformation is accompanied by a change in the structure of the carbon nucleus resulting from a wandering of a carbon radicle. It is considered that the first stage in the transformation of an  $\alpha$ -glycol or derivative of an  $\alpha$ -glycol into an aldehyde or ketone leads always to the formation of an unstable intermediate form of the type



the further change of which depends on the nature and position of the substituting groups.

Class (b) includes all tetra-substituted  $\alpha$ -glycols, halohydrins, magnesium derivatives of the halohydrins which are formed by addition of organo-magnesium compounds to  $\alpha$ -chloroketones, and ethylene oxides,

and all polysubstituted aromatic  $\alpha$ -glycols, halohydrins, and magnesium derivatives of halohydrins which have an aromatic substituting group attached to the carbon atom carrying the oxygen atom of the hypothetical unstable intermediate substance.

All other  $\alpha$ -glycols, halohydrins, and magnesium derivatives, as also all mono-, di-, and tri-substituted ethylene oxides, are included in class (a).

The transformation of tetrasubstituted  $\alpha$ -glycols, the pinacolin transformation, differs from the formation of aldehydes or ketones from mono-, di- or tri-substituted  $\alpha$ -glycols in that it can take place only if accompanied by intramolecular change in the position of one of the substituting groups, and that all the groups present are capable of undergoing the intramolecular transposition, which takes place, however, more readily with an aromatic group than with an aliphatic group and more readily with methyl than with ethyl.

The experimental part of this paper is chiefly a detailed account of work published previously.

$\beta$ -Phenylpropylene  $\alpha\beta$ -glycol,  $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{OH}$ , formed by the action of baryta on  $\psi$ -allylbenzene dibromide, crystallises in needles, m. p.  $42-43^\circ$ , b. p.  $160-162^\circ/26$  mm., and when boiled with dilute sulphuric acid yields hydratropaldehyde together with small amounts of Stöermer's anhydride (Abstr., 1906, i, 581).

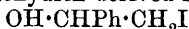
$\beta$ -*p*-Tolylpropylene  $\alpha\beta$ -glycol,  $\text{C}_7\text{H}_7\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , prepared by the action of baryta on *p*- $\psi$ -allyltoluene dibromide, or on *p*-toluoylcarbinol or its acetate, crystallises in needles, m. p.  $36^\circ$ , b. p.  $175-180^\circ/15$  mm., and when boiled with dilute sulphuric acid yields *p*-methylhydratropaldehyde, which forms a semicarbazone, m. p.  $152^\circ$  ( $159-160^\circ$ : Darzens, Abstr., 1905, i, 116).

*aa*-Diphenylethylene glycol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{OH}$ , m. p.  $122^\circ$ , formed by the action of magnesium phenyl bromide on ethyl glycolate, when boiled with sulphuric acid yields diphenylacetaldehyde.

$\alpha$ -Phenylpropylene  $\alpha\beta$ -glycol, formed by the action of potassium carbonate on phenylene dibromide, is converted by boiling sulphuric acid into phenylacetone.

Styrene oxide is very stable towards hydrolysing agents.  $\psi$ -Allylphenyl oxide, when boiled with sulphuric acid, yields  $\alpha$ -phenylpropaldehyde, but is stable towards silver nitrate.

The structure of the iodohydrin derived from styrene,

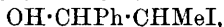


(Bougault, Abstr., 1900, i, 641), is established by its conversion into *sec*-phenylethyl alcohol by successive acetylation, reduction, and hydrolysis, or into dimethylphenacylamine by the action of dimethylamine. The isomeric *iodohydrin*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHPhI}$ , formed by the action of hydrogen iodide on styrene oxide, crystallises in spangles, m. p.  $79^\circ$ .

*p*-Methoxystyrene,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}_3$ , prepared by dehydration by Klage's method of *p*-methoxyphenylmethylcarbinol (Abstr., 1904, i, 1001), is converted by the action of mercuric oxide and iodine into *p*-methoxyphenylacetaldehyde,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHO}$ , b. p.  $255-256^\circ$ ,  $D_0^{20}$  1.140, which yields an oxime, m. p.  $121^\circ$  ( $112^\circ$ : Bouveault, *loc. cit.*), and a semicarbazone, m. p.  $181-182^\circ$ . Reduction of this aldehyde

with zinc and acetic acid leads to the formation of *p*-methoxyphenylethyl acetate, b. p. 156—157°/11 mm. or 277—278°/760 mm.,  $D_0^{20}$  1.101.

Hydratropaldehyde is formed by the successive action of mercuric oxide and iodine and potassium iodide and sodium hydrogen sulphite on phenylpropylene; it reacts with magnesium phenyl bromide forming the alcohol,  $\text{CHPhMe} \cdot \text{CHPh} \cdot \text{OH}$ . The constitution,



has been established for the iodohydrin obtained from phenylpropylene, by its conversion into phenylethylcarbinyl acetate, and into  $\beta$ -dimethylamino- $\alpha$ -phenylpropane- $\alpha$ -ol,  $\text{OH} \cdot \text{CHPh} \cdot \text{CHMe} \cdot \text{NMe}_2$ .

$\alpha$ -Phenylisovaleraldehyde forms a semicarbazone, m. p. 140°.

$\alpha\beta$ -Diphenylpropylene (Klages, Abstr., 1902, i, 668) is formed by the action of magnesium phenyl bromide on phenylacetone.

$\beta$ -n-Propylcinnamic acid,  $\text{CPhPr} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , b. p. 198—201°/18 mm., obtained on hydrolysis of its ethyl ester, prepared by condensation of phenylbutanone with ethyl iodoacetate, and distillation under the ordinary pressure, loses carbon dioxide when boiled, yielding  $\beta$ -phenyl- $\Delta^8$ -amylene, which forms a liquid dibromide.

$\alpha\alpha$ -Diphenylethyl alcohol,  $\text{CPh}_2\text{Me} \cdot \text{OH}$ , m. p. 80—81°, b. p. 175—180°/20 mm., is obtained from  $\alpha\alpha$ -diphenylethylene, and, by way of the iodohydrin, yields deoxybenzoin.

$\alpha$ -Phenyl- $\alpha$ -p-tolylethylene,  $\text{C}_7\text{H}_7 \cdot \text{CPh} \cdot \text{CH}_2$ , b. p. 145—146°/6 mm. or 160—161°/11 mm., formed by repeated distillation under the ordinary pressure of the corresponding carbinol, yields *p*-tolylacetophenone.  $\gamma$ -Phenyl- $\Delta^8$ -amylene,  $\text{CPhEt} \cdot \text{CHMe}$ , b. p. 197—199°,  $D_0^{20}$  0.9321, formed by the action of oxalic acid on phenyldiethylcarbinol prepared by treating ethyl benzoate with magnesium ethyl bromide, yields methylbenzyl ethyl ketone,  $\text{CHPhMe} \cdot \text{COEt}$ , b. p. 222—225°,  $D_0^{20}$  0.982; the semicarbazone, m. p. 172°.

Benzyl ethyl ketone, formed from the additive compound of magnesium phenyl bromide and chloroacetophenone, yields a semicarbazone,  $\text{C}_{11}\text{H}_{15}\text{ON}_3$ , m. p. 146°. G. Y.

**Iodation of Phenol in a Borax Solution, and the Production of  $\psi$ -Iodosiodobenzene.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1204—1210).—The iodine compounds of phenol,  $\beta$ - and  $\alpha$ -naphthol, thymol, pyrogallol, and sodium salicylate form precipitates insoluble in borax. The iodation product of phenol crystallising from chloroform in pink needles, m. p. 144—145°, has none of the properties of idosiodobenzene, and is most probably  $\psi$ -idosiodobenzene,  $\text{C}_6\text{H}_4\text{I} \cdot \text{O} \cdot \text{I} < \begin{smallmatrix} \text{I} \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{I} \\ \text{I} \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{I} \end{smallmatrix}$ . In concentrated sodium hydroxide it

forms a turbid solution, probably due to the formation of the elementary molecule  $\text{OI} \cdot \text{C}_6\text{H}_4\text{I}$ , but in attempting to isolate the latter, the original substance is again obtained. With nitrodiazobenzene chloride in alkaline solution it forms a yellow azo-compound,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{I} \cdot \text{ONa}$ , sodium iodide and iodate being liberated, but on attempting to estimate the quantity of iodate in the solution by means of hydrazine sulphate, only half the theoretical volume of nitrogen is liberated; the reason for this is not clear, possibly the iodate reacts further with the azo-compound in solution. Iodine in borax



solution behaves with sodium thiosulphate differently from ordinary free iodine, also when such a solution is acted on by hydrazine sulphate the nitrogen liberated is the theoretical quantity which would be necessary if all the iodine formed the compound  $\text{ONa} \cdot \text{I} \begin{smallmatrix} \text{I} \cdot \text{ONa} \\ | \\ \text{I} \cdot \text{ONa} \end{smallmatrix}$

Z. K.

**Oxidation of *o*-Nitrotoluene in the Side-Chain with Manganese Dioxide and Sulphuric Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 179589).—The extent to which manganese dioxide and sulphuric acid oxidise *o*-nitrotoluene depends on the concentration of the acid. *o*-Nitrotoluene, when heated in an autoclave with 2 parts of finely-powdered manganese dioxide and 10 parts of sulphuric acid of 30–40° Be'. at 140–165° for two to three hours, is converted mainly into *o*-nitrobenzaldehyde, only a small proportion of *o*-nitrobenzoic acid being formed. The pressure is regulated so as not to exceed 10 atmospheres. When acid of 50–60° Be'. is employed and the temperature is maintained at 135–145°, *o*-nitrobenzoic acid becomes the chief product. These oxidations may be performed under the ordinary pressure, but more concentrated acid is required.

G. T. M.

**Oxidation of Naphthalene to Phthalonic Acid by Alkaline Solutions of Permanganate.** R. ARTHUR DALY (*J. Physical Chem.*, 1907, 11, 93–106).—Experiments have been made to ascertain which of the numerous possible intermediate compounds may be regarded as actual stages in the oxidation of naphthalene to phthalonic by alkaline permanganate solutions. For this purpose the rates of oxidation of naphthalene, homophthalic acid, *o*-carboxymandelic acid, *o*-carboxybenzoylacetic acid, and of  $\alpha$ - and  $\beta$ -naphthaquinones by decinormal permanganate solution containing sodium hydrogen carbonate have been measured at 40°. From the slow rate of oxidation of homophthalic and *o*-carboxymandelic acids, the conclusion is drawn that these cannot be intermediate products in the formation of phthalonic acid from naphthalene, *o*-carboxybenzoylacetic acid, or the naphthaquinones.

In a similar manner it seems probable that  $\beta$ -naphthaquinone does not represent a stage in the oxidation of naphthalene, whereas *o*-carboxybenzoylacetic acid and  $\alpha$ -naphthaquinone are possible intermediate substances.

H. M. D.

**Course of the Oxidation of  $\beta$ -Naphthaquinone to Phthalic Acid.** MAITLAND C. BOSWELL (*J. Physical Chem.*, 1907, 11, 119–131. Compare Daly, preceding abstract).—Information in regard to the intermediate products formed in the oxidation of  $\beta$ -naphthaquinone to phthalic acid by acid dichromate solutions has been sought by a comparative study of the rates of oxidation of the quinone and several possible intermediate substances. The experiments were carried out at 100°. The results indicate that neither *o*-carboxycinnamic, *o*-carboxyphenylglyceric, phthalylacetic, homophthalic, nor phthalidecarbonic acid can be formed as essential intermediate products in the oxidation

of  $\beta$ -naphthaquinone, for the last-mentioned substance is more rapidly attacked than any of the preceding acids. Phthalonic acid is formed in the oxidation of all the acids mentioned, as well as by the oxidation of naphthaquinone. It is also considered that homophthalic acid cannot be an intermediate product in the oxidation of either *o*-carboxycinnamic, *o*-carboxyphenylglyceric, or phthalylacetic acid to phthalonic acid. From similar comparative experiments with  $\alpha$ -naphthaquinone and  $\alpha$ -naphthol, the author further considers that neither homophthalic, *o*-carboxycinnamic, nor phthalylacetic acid is an intermediate stage in the oxidation of  $\alpha$ -naphthaquinone, and that homophthalic acid is not formed when  $\alpha$ -naphthol is the original substance acted on.

Experiments made to ascertain the course of the oxidation of naphthalene by nitric acid permit of no definite conclusions on account of the formation of very considerable quantities of nitrated products. The yields of phthalic acid obtained in six hours at  $100^\circ$  with nitric acid of D 1.15 from naphthalene,  $\alpha$ - and  $\beta$ -naphthaquinones, homophthalic, and phthalidecarboxylic acids are compared. H. M. D.

*o*-Nitroaniline. FRIEDRICH LEUCHS (*Ber.*, 1907, 40, 1083—1087).

—The author has prepared *o*-nitrosoacetanilide by a different method from that of Brand and Stohr (this vol., i, 100) with the object of studying the action of potassium cyanide and metallic salts on it (compare Piloty and Schwerin, *Abstr.*, 1901, i, 516).

A 50% yield of the monoacetylphenylenediamine was obtained by the reduction of *o*-nitroacetanilide with tin foil and hydrochloric acid between  $5^\circ$  and  $10^\circ$ . The tin is best removed from the tin double salt by electrolysis. The m. p. is  $132^\circ$  (Manuelli and Galloni, *Abstr.*, 1901, i, 413, give  $145^\circ$ ). By oxidation with Caro's acid, the acetyl-*o*-phenylenediamine is converted into nitrosoacetanilide, yield 75—80%; this with potassium cyanide yields a substance crystallising in white, prismatic needles, m. p.  $224^\circ$ . W. R.

[Acetyl Derivatives of the Highly Chlorinated Alkylanilines.]

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 176474).—The following acyl compounds combine with nitrocellulose to furnish products of the celluloid type, which are, however, much less inflammable than the material obtained from nitrocellulose and camphor. 2:4:6-*Trichloroacetomethylanilide*, m. p.  $89-90^\circ$ ; 2:3:4:6-*tetrachloroacetomethylanilide*, m. p.  $94-97^\circ$ ; *pentachloroacetomethylanilide*, m. p.  $136-137^\circ$ ; 2:4:6-*trichloroacetoethylanilide*, m. p.  $50-51^\circ$ ; 2:3:4:6-*tetrachloroacetoethylanilide*, m. p.  $73-74^\circ$ ; 2:3:5:6-*tetrachloroacetoethylanilide*, m. p.  $84-85^\circ$ ; *pentachloroacetomethylanilide*, m. p.  $99-100^\circ$ ; 2:4:6-*trichloroacetobenzylanilide*, m. p.  $61^\circ$ ; 2:3:4:6-*tetrachloroacetobenzylanilide*, m. p.  $80-81^\circ$ ; 2:3:5:6-*tetrachloroacetobenzylanilide*, m. p.  $97^\circ$ .

Owing to their high melting points and sparing solubility the two following compounds are not suitable for the production of celluloid:

2:3:5:6-*Tetrachloroacetomethylanilide*, m. p.  $175^\circ$ ; *pentachloroacetobenzylanilide*, m. p.  $140^\circ$ .

*Pentachloroaniline*, m. p.  $245-246^\circ$ , and the other chlorinated primary bases also yield acetyl derivatives which are too insoluble to be of use in this connexion. G. T. M.

**Anilide of isoSuccinic Acid.** EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Nat. Napoli*, 1906, [iii], 12, 463—465. Compare Comanducci and Lobello, *Abstr.*, 1905, i, 271).—The author confirms the results previously obtained (*loc. cit.*) concerning the formation of isosuccinoanilide and isosuccinodianilide by the action of aniline on ethyl isosuccinate. The statement made by Meyer and Bock (*Abstr.*, 1906, i, 726) that the dianilide is the only product of this reaction is hence inaccurate; the analytical results given by these authors are also erroneous, the proportions of carbon and hydrogen obtained corresponding with those for the monoanilide, whilst the percentage of nitrogen is equal to the calculated value for the dianilide. T. H. P.

**$\beta$ -o-Tolylethylamine.** E. BLUMENFELD (*Bull. Acad. Sci., Cracow*, 1906, 274—276).— $\beta$ -o-Tolylethylamine, formed together with o-xylene and o-tolylacetic acid by reduction of o-xylyl cyanide with sodium and alcohol, is obtained as a colourless oil, b. p. 215.5—217°,  $D^{18}$  0.9615,  $n_D$  1.527; the hydrochloride, m. p. 227—228°, platinichloride, and hydrogen sulphate were analysed. The acetyl derivative crystallises in white needles, m. p. 53°; the s-thiocarbamide,  

$$CS(NH \cdot CH_2 \cdot CH_2 \cdot C_6H_4Me)_2,$$
m. p. 113.5°, crystallises from alcohol. G. Y.

**Derivatives of p-Xylyl Cyanide.** K. CIESIELSKI (*Bull. Acad. Sci., Cracow*, 1906, 270—274. Compare Radziszewski and Wispek, *Abstr.*, 1885, 889).—Two by-products, b. p. 250—260° and 260—270°, soluble in ether, are obtained in the preparation of p-xylyl cyanide from p-xylyl bromide and potassium cyanide.

p-Tolylthioacetamide,  $C_6H_4Me \cdot CH_2 \cdot CS \cdot NH_2$ , formed by the action of hydrogen sulphide on the cyanide in alcoholic-ammoniacal solution, separates in colourless crystals, m. p. 113—114°.

$\beta$ -p-Tolylethylamine,  $C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot NH_2$ , prepared by reduction of the cyanide with sodium and alcohol, is obtained as an oil, b. p. 214.5°,  $D^{14}$  0.9342,  $n_D^{18}$  1.5240; the hydrochloride,  $C_9H_{14}NCl$ , glistening leaflets, m. p. 216—217°; the platinichloride,

$(C_9H_{13}N)_2, H_2PtCl_6,$   
small, yellow leaflets decomposing at 230°; the hydrogen sulphate,  
 $C_9H_{13}N, H_2SO_4,$

needles or leaflets.

The action of nitrous acid on the amide leads to the formation of two alcohols, of which one, b. p. 217—218°,  $D^{22}$  0.9972,  $n_D^{22.5}$  1.5253, gives the reactions of a secondary alcohol, whilst the other, b. p. 220—221°,  $D^{22}$  0.99928,  $n_D^{22.5}$  1.5232, gives with potassium nitrite, potassium hydroxide, water, and sulphuric acid the red coloration characteristic of a primary alcohol. G. Y.

**Asymmetric Nitrogen. XXVII. Asymmetric Ammonium Salts of the p-Phenetidine Series and the Resolution of p-Ethoxyphenylbenzylmethylallylammonium into its Optical Isomerides.** EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1907, 40, 1001—1009. Compare *Abstr.*, 1906, i, 162).—Quaternary ammonium bromides and iodides of the p-phenetidine series have been

prepared each by three methods: by the action of the benzyl haloid on methylallyl-*p*-phenetidine; of the allyl haloid on benzylmethyl-*p*-phenetidine, and of the methyl haloid on benzylallyl-*p*-phenetidine. The results obtained differ from those in the *o*-anisidine series (*loc. cit.*) in that the three reactions yield identical products.

*Methylallyl-p-phenetidine*, prepared from methyl-*p*-phenetidine, b. p.  $164^{\circ}/40$  mm., and allyl iodide, is a yellow oil, b. p.  $191^{\circ}/95$  mm.

*Benzylmethyl-p-phenetidine*, prepared from methyl-*p*-phenetidine and benzyl bromide, is a viscid oil, b. p.  $215-217^{\circ}/25$  mm.

*Benzylallyl-p-phenetidine*, prepared from benzyl-*p*-phenetidine, m. p.  $45-46^{\circ}$ , and allyl iodide, is a viscid, yellow oil, b. p.  $238-240^{\circ}/35$  mm. The *picrate*,  $C_{24}H_{24}O_8N_4$ , forms yellow leaflets, m. p.  $141^{\circ}$ .

*p-Ethoxyphenylbenzylmethylallylammonium iodide* forms microscopic prisms, m. p.  $128^{\circ}$ . The *bromide* crystallises in microscopic, tetragonal plates, m. p.  $139-140^{\circ}$ . 1-*p-Ethoxyphenylbenzylmethylallylammonium d-camphorsulphonate*, formed by the action of the inactive iodide or bromide on silver *d*-camphorsulphonate, crystallises in small prisms, m. p.  $164^{\circ}$ ,  $[\alpha]_D + 7.95^{\circ}$ ,  $[M]_D + 40.66^{\circ}$ , equivalent to  $[M]_D - 11.1^{\circ}$  for the *p*-ethoxyphenylbenzylmethylallylammonium cation. The *iodide* of the *l*-base crystallises from a mixture of alcohol and ether,  $[\alpha]_D - 1.63^{\circ}$ ,  $[M]_D - 6.65^{\circ}$ , in chloroform solution. The *d-bromocamphorsulphonate*, m. p.  $146^{\circ}$ ,  $[\alpha]_D + 45.86^{\circ}$ ;  $[M]_D + 271^{\circ}$ ; this salt could not be resolved by fractional crystallisation.

*o-Methoxyphenylbenzylmethylallylammonium bromide*, prepared from methylallyl-*o*-anisidine and benzyl bromide or from methylbenzyl-*o*-anisidine and allyl bromide, crystallises in hexagonal prisms, m. p.  $106-107^{\circ}$ . This base could not be resolved by fractional crystallisation of its *d-camphorsulphonate*, m. p.  $108-109^{\circ}$ ,  $[\alpha]_D + 10.32$ ,  $[M]_D + 51.50^{\circ}$ . G. Y.

**Asymmetric Nitrogen. XXVIII. Asymmetric Ammonium Salts of *p*-Anisidine.** EMIL FRÖHLICH and EDGAR WEDEKIND (*Ber.*, 1907, 40, 1009—1013. Compare preceding abstract).—The resolution of *p*-anisylbenzylmethylallylammonium bases into optically active components is rendered difficult on account of the sparing solubility of the *d*-bromocamphorsulphonates and the *d*-camphorsulphonates. The active cation,  $\cdot NMe(C_3H_5)(C_7H_7) \cdot C_6H_4 \cdot OMe(p)$ , has  $[M]_D + 17.45^{\circ}$ .

*Formyl-p-anisidine*,  $C_8H_9O_2N$ , obtained by boiling a mixture of *p*-anisidine and 90% formic acid for two hours, separates from alcohol in prisms, m. p.  $80-81^{\circ}$ . Its alcoholic solution was acted on by sodium ethoxide and methyl iodide and the product then boiled with concentrated hydrochloric acid; the base obtained after the addition of sodium hydroxide was dissolved in dilute hydrochloric acid, converted by nitrous acid into a solid nitroso-compound, which on reduction and subsequent acidification yielded *methyl-p-anisidine*,  $C_8H_{11}ON$ , separating from light petroleum in microscopic crystals, m. p.  $37^{\circ}$ , b. p.  $135-136^{\circ}/19$  mm.

*Benzyl-p-anisidine*,  $C_{14}H_{15}ON$ , obtained from *p*-anisidine (2 mol.)

and benzyl chloride (1 mol.), has b. p. 236—238°/32 mm., and separates from light petroleum in leaflets, m. p. 52°.

*Methylallyl-p-anisidine*,  $C_{11}H_{15}ON$ , obtained from methyl-*p*-anisidine and allyl iodide, is an oil, b. p. 172—173°/60 mm.

*Benzylmethyl-p-anisidine*,  $C_{15}H_{17}ON$ , obtained from methyl-*p*-anisidine and benzyl bromide, is a yellow oil, b. p. 220—222°/30 mm.

*p-Methoxyphenylbenzylmethylallyl ammonium iodide*,  $C_{18}H_{22}ONI$ , obtained either by the addition of benzyl iodide to methylallyl-*p*-anisidine or by the addition of allyl iodide to benzylmethyl-*p*-anisidine, separates from alcohol in prisms, m. p. 132—133°. The corresponding *bromide*, obtained by analogous methods, separates from alcohol in prisms, m. p. 147—148°.

A partial resolution of the base into its optically active components was accomplished by means of *d*-bromocamphorsulphonic acid, the fractionation of the camphorsulphonates having been conducted from a mixture of chloroform and ether. The most sparingly soluble fraction obtained gave a feebly active iodide with  $\alpha_D - 0.05^\circ$  ( $c = 0.776$ ,  $l = 2.5$ ) in chloroform solution. A better result was obtained by the use of *d*-camphorsulphonic acid, the iodide obtained in this case from the most sparingly soluble fraction having  $[\alpha]_D + 6.39^\circ$  in chloroform solution. The tendency of this chloroform solution to autoracemise was slight.

A. MCK.

**Hydroanethole.** J. TH. HENRARD (*Chem. Zentr.*, 1907, i, 343; from *Chem. Weekblad*, 3, 761—764).—When anethole and chavicol methyl ether are reduced with nickel and hydrogen, *p-propylanisole*, b. p. 213.5—214.5°/761 mm., is readily obtained in theoretical quantity. By the action of nitric acid on the product, a *nitro*-compound which crystallises in small yellow needles is formed. The *sulphonic acid*,  $OMe \cdot C_6H_3Pr \cdot SO_3H, H_2O$ , m. p. 94°, is readily soluble in water or alcohol, and soluble in warm benzene, toluene, or chloroform, but insoluble in cold ether.

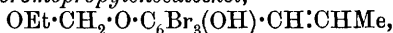
E. W. W.

**Dibromides of Aromatic Propenyl Compounds. VI. Tri-bromo-isosafrole Dibromide.** PAUL HOERING (*Ber.*, 1907, 40, 1096—1110. Compare *Abstr.*, 1905, i, 902, 903, 592; 1904, i, 577).—Anethole and isosafrole are similar in most of their properties, but anethole with bromine gives a tetrabromide, whereas isosafrole yields a pentabromo-derivative, the constitution and properties of which are now described. *isoSafrole* and bromine interact, giving rise to a tetra- or penta-bromide according to the conditions; the pentabromide is formed when the *isosafrole* is dropped into excess of bromine, the temperature being kept at 32—35°; on the other hand, the tetrabromide is obtained free from pentabromide if the *isosafrole* is added quickly. *Tribromoisosafrole  $\alpha\beta$ -dibromide*,  $CH_2O_2 \cdot C_6Br_3 \cdot CHBr \cdot CHMeBr$ , crystallises from a mixture of alcohol and benzene in small aggregates, m. p. 196.5—197°. It is stable towards aqueous acetone, hydrogen bromide, and alcoholic or molten potassium hydroxide. By oxidising agents, such as chromic acid and potassium permanganate, it is only slightly attacked, but it is easily reduced by zinc dust in a mixture of alcohol and benzene to *tribromoisosafrole*,  $CH_2O_2 \cdot C_6Br_3 \cdot CH \cdot CHMe$ , m. p.

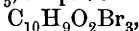
110—111°. Excess of zinc has little action on the latter, but if the heating is continued for ten hours it yields a *dibromo*-derivative,  $C_{10}H_8O_2Br_2$ , m. p. 98·5—100°, and a small amount of a substance, m. p. 147—150°. Reduction with hydriodic acid, D 1·7, however, gives *tribromodihydroisosafole*,  $CH_2O_2 \cdot C_6Br_3 \cdot CH_2 \cdot CH_2Me$ , crystallising from light petroleum in needles, m. p. 72—74°, insoluble in alkali. *Tribromoisosafole* is thus shown to contain an ethylenic linking, which is also proved by its re-forming the original pentabromide when placed with bromine in sunlight; in diffused light, however, a new stereoisomeric *isosafole* pentabromide is formed.

*isoSafrole* tetrabromide on reduction with zinc dust yields *dibromoisosafole*,  $C_{10}H_8O_2Br_2$ , crystallising in needles, m. p. 149—150°, and, under similar conditions, *bromoisosafole* dibromide yields *bromoisosafole*, m. p. 30—33°, b. p. 165—170°/16 mm.

*Tribromoisosafole*, when heated under pressure for five to six hours at 145—150° with alcoholic potassium hydroxide, yields the *ethoxy-methyl ether* of *tribromopropylencatechol*,

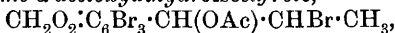


m. p. 96—99°, which is easily hydrolysed by acid to *tribromopropylencatechol*,  $C_6Br_3(OH)_2 \cdot C_3H_5$ , m. p. 111—113°. The *dimethyl ether*,  $C_{11}H_{11}O_2Br_3$ , has m. p. 98—99·5°; the *methyl ethoxymethyl ether*,  $OEt \cdot CH_2 \cdot O \cdot C_6Br_3(OMe) \cdot C_3H_5$ , m. p. 78—80°; the *methyl ether*,



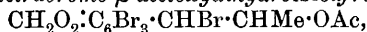
m. p. 135—137°, and the *diacetate*,  $C_{13}H_{11}O_4Br_3$ , m. p. 128—130°.

*Tribromo-isosafole* dibromide, when heated with silver acetate, gives 4 : 5 : 6-*tetrabromo- $\alpha$ -acetoxydihydroisosafole*,



m. p. 178—180°; the reaction is not complete when sodium acetate is used. *Tribromoisosafole oxide*,  $CH_2O_2 \cdot C_6Br_3 \cdot CH < \begin{smallmatrix} CHMe \\ O \end{smallmatrix}$ , obtained

when the above acetoxy-compound is heated with alcoholic potassium hydroxide, has m. p. 201—202°, forms an additive compound with acetyl bromide, 2 : 4 : 6-*tetrabromo- $\beta$ -acetoxydihydroisosafole*,



m. p. 179—181°; a melting point determination of the mixture of the  $\alpha$ -bromo- and  $\beta$ -bromo-derivatives gives 150—155°. *Tribromo- $\alpha$ -hydroxy- $\beta$ -acetoxydihydroisosafole*,  $C_{12}H_{11}O_5Br_3$ , m. p. 174—175°, is obtained by heating the  $\alpha$ -bromo- $\beta$ -acetoxy-compound in toluene with excess of silver nitrate, and on hydrolysis with alcoholic potassium hydroxide yields *tribromoisosafole glycol*,  $CH_2O_2 \cdot C_6Br_3 \cdot CH(OH) \cdot CHMe \cdot OH$ , of m. p. 159—161°, sintering at 110°. The *diacetate*,  $C_{14}H_{13}O_6Br_3$ , has m. p. 154—156°. On oxidising this glycol with potassium permanganate on the water-bath, *tribromopiperonal*,  $CH_2O_2 \cdot C_6Br_3 \cdot CHO$ , crystallising in needles, m. p. 197—201°, is obtained. The *semicarbazone*,  $C_9H_6O_3N_3Br_3$ , does not melt at 240°. *Tribromopiperonylic acid*,  $C_8H_3O_4Br_3$ , from the corresponding aldehyde, is a crystalline powder, m. p. 233°.

*Tribromopropylencatechol dibromide*,  $C_6Br_3(OH)_2 \cdot CHBr \cdot CHMeBr$ , is obtained from *tribromopropylencatechol* and bromine in sunlight, m. p. 85—90°. W. R.

**Action of Phenols on Trichloroacetic Acid.** OTTO ANSELMINO (*Chem. Zentr.*, 1907, i, 339; from *Ber. deut. Pharm. Ges.*, 16, 390—393).—Lossen and Eichloff have found that when trichloroacetic acid is heated with water or with 1 mol. of alkali hydroxide, chloroform and carbon dioxide are formed, whilst by the action of 6 mols. of hydroxide, formic acid and carbon dioxide are obtained, and with less than 6 mols. of hydroxide, both reactions occur. The fact that in the reaction given by the German Pharmacopœia IV the odour of chloroform is not always produced, is to be ascribed therefore to the use of too great an excess of alkali. Chloroform and carbon dioxide are also obtained when trichloroacetic acid is heated with resorcinol or cresol, but the decomposition is much slower in the latter case. By the action of phenol or thymol, trichloroacetic acid forms hydrogen chloride, carbon oxychloride, and carbon monoxide; hence the alleged formation of the so-called *Thymylum trichloroaceticum* (*Pharm. Centr.-h.*, 46, 684) by heating trichloroacetic acid with thymol is incorrect. *Thymol trichloroacetate*,  $C_{12}H_{13}O_2Cl_3$ , b. p. 110—111°/12 mm., which can only be prepared by the action of sodium-thymol on trichloroacetyl chloride, forms a clear liquid, but gradually becomes bluish-green on exposure to air; it is insoluble in alkalis, and is readily hydrolysed, but cannot be distilled under the ordinary pressure without decomposition.

E. W. W.

**Condensation of Resorcinol.** RICHARD MEYER and KARL MARX (*Ber.*, 1907, 40, 1450—1453).—When resorcinol is heated, alone at 200—220° or with zinc chloride at 160—180°, a brown, fluorescent condensation product is obtained, from which a small quantity of a substance,  $C_{14}H_{12}O_8$ , m. p. 263°, can be isolated; this crystallises in slender, colourless needles, and dissolves in alkalis without fluorescence; the *acetate*,  $C_{14}H_{10}O(OAc)_2$ , has m. p. 150—151°, and the *benzoate*,  $C_{14}H_{10}O(OBz)_2$ , m. p. 180° (compare Grimaux, *Abstr.*, 1895, i, 655).

C. S.

**Condensation of Aromatic Hydrocarbons with the Carbohydrates, Cellulose, and Dextrose.** ALEXANDER M. NASTUKOFF (*Zeitsch. Farb. Ind.*, 1907, 6, 70—71. Compare *Abstr.*, 1902, i, 362 and 747).—The method of treating cellulose with benzene in presence of sulphuric acid, formerly described, has been slightly modified, the product obtained under the new conditions containing only a small proportion (0.43%) of sulphur; the substance obtained, termed *β-phenyl-desoxyn* to distinguish it from the former material to which the name of *α-phenyl-desoxyn* is given, appears to have the composition  $C_6H_7O_2Ph_3$ , derived from cellulose by the replacement of three hydroxyl by three phenyl groups. The homologues of benzene (toluene, xylene, *ψ*-cumene) give *desoxyns* with cellulose similar to that obtained with benzene. The oxidation of *β-phenyl-desoxyn* by permanganate gives 45% of benzoic acid, that of *tolyl-desoxyn* giving 20% of terephthalic acid; *xylyl-desoxyn*, prepared from commercial xylene, gives 4% of terephthalic acid and 25% of trimellitic acid; *ψ-cumyl-desoxyn* gives pyromellitic acid. In all these cases carbonic acid and oxalic acid (about 15%) are also formed. The cellulose residue appears in all cases to enter the benzene nucleus in the para position relative to methyl.

Dextrose, like cellulose, also combines with benzene, forming apparently a compound in which three hydroxyl groups have been replaced by three phenyl radicles. W. A. D.

**Action of *pp*-Tetramethyldiaminobenzhydrol on Certain Methylenic Compounds.** ROBERT FOSSE (*Compt. rend.*, 1907, 144, 643—644).—*pp*-Tetramethyldiaminobenzhydrol condenses with  $\beta$ -ketonic esters and diketones, with elimination of  $H_2O$ , and formation of a new class of compounds of which the constitution is at present undetermined. *Ethyl pp-tetramethyldiaminobenzhydrylicetylacetate*,  $C_{23}H_{30}O_3N_2$ , m. p. 128—129°, dissolves in cold acetic acid to a colourless solution which becomes blue on heating, and the coloration persists on cooling. Its *dimethiodide*,  $C_{25}H_{36}O_3N_2I_2$ , m. p. 180—181°, forms small, greyish-yellow crystals which become green in the capillary tube at 175°; the acetic acid solution is colourless both when hot and cold. The acetate forms a *dihydrochloride*,  $C_{23}H_{30}O_3N_2 \cdot 2HCl$  and a *platinichloride*,  $C_{23}H_{30}O_3N_2 \cdot H_2PtCl_6$ .

*Ethyl pp-tetramethyldiaminobenzhydrylicbenzoylacetate*,  $C_{28}H_{32}O_3N_2$ , m. p. 181—182°, dissolves in cold acetic acid to a colourless solution which becomes blue on heating; it forms a *platinichloride*,  $C_{28}H_{32}O_3N_2 \cdot H_2PtCl_6$ .

*pp*-Tetramethyldiaminobenzhydrylicetylacetone,  $C_{22}H_{28}O_2N_2$ , m. p. 148—149°, and *pp*-tetramethyldiaminobenzhydrylicbenzoylacetone,  $C_{27}H_{30}O_2N_2$ ,

m. p. 160°, both give acetic acid solutions behaving as with the above bases. *Ethyl pp-tetramethyldiaminobenzhydrylicmalonate*,  $C_{24}H_{32}O_4N_2$ , forms long, silky needles, m. p. 128—130°, which give a *platinichloride*,  $C_{24}H_{32}O_4N_2 \cdot H_2PtCl_6$ ; the *acid*,  $C_{18}H_{22}N_2(CO_2H)_2$ , is obtained by saponifying the ester with potash and treating the solution obtained with sulphuric acid; when boiled with 30% sulphuric acid it is converted into *pp*-tetramethyldiaminodiphenyl- $\beta\beta$ -propionic acid,

$CH(C_6H_4 \cdot NMe_2)_2 \cdot CH_2 \cdot CO_2H$ , already described (*Abstr.*, 1906, i, 975). *pp*-Tetramethyldiaminobenzhydrylicmalonic acid has not a definite melting point, but when thrown on to a mercury-bath at 200—205° it turns a light green, melts, intumescs, and solidifies to a rust-coloured substance, m. p. 225—230°; if kept for ten minutes at 188° it becomes light green, then, without melting, rust-coloured with m. p. 225°. The *potassium salt*,

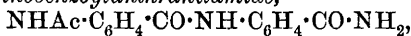
$C_{18}H_{22}N_2(CO_2K)_2$ , forms small, brilliant needles, and the *sodium salt* forms brilliant, silvery scales, both containing alcohol of crystallisation; the hydrated *barium salt* forms colourless spangles; the hydrated *calcium salt* small, silvery crystals, and the *lead salt* a white precipitate. The acid and its alkali salts form colourless acetic acid solutions which become blue on heating, and in the case of the potassium salt even on keeping in the dark. E. H.

**Acetylation of Anthranoylanthranilic [*o*-Aminobenzoyl-anthranilic] Acid.** ERNST MOHR and FRIEDRICH KÖHLER (*Ber.*, 1907, 40, 997—999. Compare *Abstr.*, 1906, i, 359; Anschütz, Schmidt, and Greiffenberg, *Abstr.*, 1903 i, 57).—The action of an excess of acetic



anhydride on *o*-aminobenzoylanthranilic acid leads to the formation of the *lactimone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc} \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ , so termed because contain-

ing the lactime,  $\cdot\text{O} \cdot \text{C} \cdot \text{N} \cdot$ , as also the lactone group  $\cdot\text{C} \cdot \text{CO} \cdot \text{O} \cdot \text{C} \cdot$ . It separates from benzene in white crystals, m. p.  $211^\circ$ , is insoluble in cold aqueous ammonia, and is an analogue of the anhydride of *o*-acetoxybenzoylanthranilic acid (Meyer, this vol., i, 317) and of the acylanthranils. When heated with alcoholic ammonia, the lactimone yields *o*-acetylaminobenzoylanthranilamide,



which crystallises in thin, white prisms, m. p.  $226^\circ$ , evolving gas.

G. Y.

**Spacial Isomerism in the Phenylnitrocinnamic Acids (Anhydrides, Indones, Chlorides, Phenylhydrazides, Hydrazones, and Oximes).**—MARUSSIA BAKUNIN and L. PARLATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 503—515. Compare Abstr., 1895, i, 531; 1897, i, 622, and 1906, i, 664).—The authors have investigated various derivatives of the stereoisomeric forms of phenyl-*m*- and *p*-nitrocinnamic acids. Of each of the two pairs of stereoisomerides, one (the *allo*-isomeride) forms a salt with phenylhydrazine more readily than the other, which, in its turn, is more easily converted into an acid-chloride by reaction with phosphorus pentachloride in a neutral solvent. With phenylhydrazine, the anhydrides of the acids behave like anhydrides of other monobasic acids, giving rise to phenylhydrazides. The two *m*-acids yield the same indone, as also do the two *p*-acids; the presence of the carbonyl group in the indones is shown by the products they give with phenylhydrazine and hydroxylamine. The esters of these acids are best prepared by boiling the acids with phosphoric oxide in a neutral solvent and boiling the crude anhydrides so obtained with the corresponding alcohols.

In the preparation of phenyl-*m*- and *p*-nitrocinnamic acids by Perkin's synthesis, these acids are accompanied by *m*-nitrobenzylidene diacetate, m. p.  $72^\circ$ , and *p*-nitrobenzylidene diacetate, m. p.  $127^\circ$ , both of which are insoluble in sodium carbonate solution.

Phenyl-*m*-nitrocinnamic acid is obtained in two isomeric forms: (1) the *allo*-isomeride, m. p.  $195^\circ$ ; the *phenylhydrazine* salt,  $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}_2\text{NHPh} \cdot \text{NH}_2$ , separates in yellowish-white, silky plates, m. p.  $142^\circ$ ; the corresponding *phenyl-m-nitrocinnamoyl chloride*,  $\text{C}_{15}\text{H}_{10}\text{O}_3\text{NCl}$ , is deposited from benzene in granules or glassy crystals, m. p.  $89-90^\circ$ ; the *anhydride*,  $(\text{C}_{15}\text{H}_{10}\text{O}_3\text{N})_2\text{O}$ , has m. p.  $139^\circ$ . (2) The *ordinary* form, m. p.  $181^\circ$ ; the *phenylhydrazine* salt,  $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}_2\text{NHPh} \cdot \text{NH}_2$ , crystallises from benzene or alcohol in silky needles, m. p.  $118-120^\circ$ ; the corresponding *phenyl-m-nitrocinnamoyl chloride*,  $\text{C}_{15}\text{H}_{10}\text{O}_3\text{NCl}$ , crystallises from benzene in shining, glassy prisms, m. p.  $90-92^\circ$ ; the *anhydride* has m. p.  $151^\circ$ .

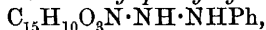
Phenyl-*p*-nitrocinnamic acid also occurs in two forms: (1) the *allo*-isomeride, m. p.  $147^\circ$  or, in the hydrated condition,  $105^\circ$ ; the *phenylhydrazine* salt,  $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}_2\text{NHPh} \cdot \text{NH}_2$ , separates in canary-yellow needles, m. p.  $172^\circ$ ; the corresponding *phenyl-p-nitrocinnamoyl chloride*,

$C_{15}H_{10}O_3NCl$ , crystallises in slender, straw-yellow needles, m. p.  $90-91^\circ$ ; the *anhydride* has m. p.  $182^\circ$ . (2) The *ordinary* form, m. p.  $214^\circ$ ; the corresponding *phenylhydrazine* salt crystallises from alcohol in tufts of slender, golden-yellow needles, m. p.  $136-137^\circ$ ; the corresponding *phenyl-p-nitrocinnamoyl chloride* crystallises from light petroleum in straw-yellow needles, m. p.  $95-97^\circ$ ; the *anhydride* has m. p.  $162^\circ$ .

*Phenyl-p-nitroindone*,  $C_{15}H_9O_3N$ , crystallises in monoclinic, rhomboidal plates, m. p.  $217^\circ$ ; its *phenylhydrazone*,  $C_{15}H_9O_2N:N \cdot N \cdot HPh$ , separates from alcohol as a vermilion-red powder, m. p.  $196^\circ$ ; the *oxime*,  $C_{15}H_9O_2N:N \cdot OH$ , crystallises from alcohol or benzene in orange-yellow needles, m. p.  $235^\circ$ .

*Phenyl-m-nitroindone* has m. p.  $218^\circ$ ; its *phenylhydrazone* crystallises from alcohol or benzene in blood-red clots, m. p.  $182.5^\circ$ ; the *oxime* crystallises from alcohol or benzene in cadmium-yellow needles, m. p.  $246^\circ$ .

Ordinary *phenyl-p-nitrocinnamoyl phenylhydrazide*,



prepared by the action of phenylhydrazine on the anhydride or chloride of the corresponding acid, crystallises from alcohol or benzene in flocks of straw-yellow needles, m. p.  $141^\circ$ .

allo*Phenyl-p-nitrocinnamoyl phenylhydrazide*, prepared similarly to the preceding compound, crystallises from alcohol in plates composed of straw-yellow needles, m. p.  $220-221^\circ$ .

Ordinary *phenyl-m-nitrocinnamoyl phenylhydrazide* separates from alcohol in small, rhombohedral crystals, m. p.  $143^\circ$ , or from benzene in long, silky needles, m. p.  $80^\circ$ , which, after losing their benzene of crystallisation and resolififying, have m. p.  $143^\circ$ .

allo*Phenyl-m-nitrocinnamoylphenylhydrazide* crystallises from alcohol or benzene in flocks of white needles, m. p.  $186-187^\circ$ .

All these phenylhydrazides are moderately stable and are insoluble in sodium carbonate solution.

*Methyl phenyl-m-nitrocinnamate*,  $C_{15}H_{10}O_4NMe$ , crystallises in long, straw-yellow, monoclinic prisms, m. p.  $83-84^\circ$ ; the corresponding *ethyl* ester crystallises from alcohol in tufts of elongated prisms, or from light petroleum in elongated, monoclinic prisms with an irregular, polygonal section, m. p.  $80^\circ$ .

*Methyl phenyl-p-nitrocinnamate* crystallises from alcohol in monoclinic needles, m. p.  $141^\circ$ , and the corresponding *ethyl* ester is deposited from alcohol in tufts of needles, or from light petroleum in short, apparently monoclinic prisms, m. p.  $100-102^\circ$ .

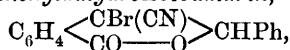
*Methyl phenyl-o-nitrocinnamate* has m. p.  $75-76^\circ$ .

T. H. P.

**Condensation of Benzylcyanide-o-carboxylic Acid with Aldehydes.** JOSEPH GYR (*Ber.*, 1907, 40, 1201-1214. Compare Bistrzycki and Stelling, *Abstr.*, 1901, i, 718).—*α-Cyanostilbene-2-carboxylic acid*,  $CHPh:C(CN) \cdot C_6H_4 \cdot CO_2H$ , m. p.  $163^\circ$  (decomp.), resulting from the condensation of equal molecular quantities of benzylcyanide-o-carboxylic acid and benzaldehyde in the presence of 30% sodium hydroxide, forms white prisms or needles; the *silver* salt,

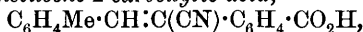
$C_{16}H_{10}O_2Na$ , is fairly stable to light; the *ethyl* ester, m. p.  $62.5^\circ$ , crystallises in well-defined, monoclinic needles, [ $a:b:c = 1.6066:1:2.3310$ ].

4-Bromo-4-cyano-3-phenyldihydroisocoumarin,



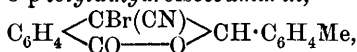
m. p.  $165^\circ$  (decomp.), is obtained by the action of bromine on the preceding ester dissolved in chloroform or by treating the acid with bromine in 50% sodium carbonate solution and acidifying the mixture with dilute sulphuric acid. The lactone crystallises in white needles, is decomposed by warm *N/1* potassium hydroxide, yielding benzaldehyde, and is converted at its melting point into Gabriel and Neumann's 4-cyano-3-phenylisocoumarin (Abstr., 1893, i, 228).

$\alpha$ -Cyano-4'-methylstilbene-2-carboxylic acid,



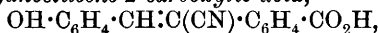
m. p.  $151^\circ$ , derived from *p*-tolualdehyde, forms white needles; the *silver* and *sodium* salts are mentioned. Heated at  $20^\circ$  above its m. p., the acid changes into the isomeric *lactone*, m. p.  $157^\circ$ , the constitution of which is not settled.

4-Bromo-4-cyano-3-*p*-tolylidihydroisocoumarin,



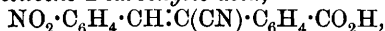
m. p.  $173^\circ$  (decomp.), obtained from the preceding acid and bromine in chloroform or in sodium carbonate solution, crystallises in needles, and at its m. p. changes into Harper's 4-cyano-3-*p*-tolylisocoumarin (Abstr., 1897, i, 106).

3'-Hydroxy- $\alpha$ -cyanostilbene-2-carboxylic acid,



m. p.  $159-161^\circ$ , derived from *m*-hydroxybenzaldehyde, crystallises in needles and is soluble in sodium carbonate to a yellow solution.

2'-Nitro- $\alpha$ -cyanostilbene-2-carboxylic acid,



m. p.  $194^\circ$ , derived from *o*-nitrobenzaldehyde in the presence of 30% sodium hydroxide, crystallises in needles; the *sodium* salt,



and the *barium* salt,  $(C_{16}H_9O_4N_2)_2Ba, 5H_2O$ , form yellow needles. Reduction of the acid by alcoholic ammonium sulphide yields a *substance*, m. p.  $245^\circ$  (decomp.), which appears to be an internal salt of

2'-amino- $\alpha$ -cyanostilbene-2-carboxylic acid,  $C_6H_4 \begin{array}{c} \text{C(CN):CH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \cdot \text{NH}_3 \end{array} C_6H_4$ .

The following condensation products have been also obtained: 2'-chloro- $\alpha$ -cyanostilbene-2-carboxylic acid, m. p.  $182^\circ$ ; 3'-chloro- $\alpha$ -cyanostilbene-2-carboxylic acid, m. p.  $148^\circ$ ; 4'-chloro- $\alpha$ -cyanostilbene-2-carboxylic acid, m. p.  $181-182^\circ$ ;  $\alpha$ -cyano-3':4'-dimethoxystilbene-2:2'-dicarboxylic acid, m. p.  $194^\circ$  (decomp.), derived from opianic acid.

isoNitrosobenzyl-cyanide-*o*-carboxylic acid,  $CO_2H \cdot C_6H_4 \cdot C(CN):N \cdot OH$ , m. p.  $235^\circ$  (decomp.), is obtained as the sodium salt from benzylcyanide-*o*-carboxylic acid, amyl nitrite, and sodium ethoxide in alcoholic solution; it separates from dilute alcohol in greyish-white, micro-crystalline needles.

C. S.

**Occurrence of Abietic Acid in Resin-Oil.** ALEXANDER TSCHIRCH and MAX WOLFF (*Arch. Pharm.*, 1907, 245, 1—4).—From a solution of resin-essence in ether, 5% aqueous sodium carbonate extracted about 30% of acids which, when crystallised first from a mixture of methyl and ethyl alcohols and then from acetic acid, yielded an abietic acid with m. p. 166—167°, composition  $C_{19}H_{28}O_2$  or  $C_{20}H_{30}O_2$ , and acid number 194, corresponding with monobasicity. One % aqueous potassium hydroxide then extracted a small quantity of phenolic substances, and the bulk of the residue distilled between 315 and 385°. The yield of acid varies; it is greatest when the essence or oil has been obtained by distillation under diminished pressure.

C. F. B.

**Derivatives of Methylcyclohexane.** WLADIMIR B. MARKOWNIKOFF and V. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, i, 1—6. Compare Abstr., 1905, i, 760).—Methyl-3-cyclohexanol was employed as a starting point for the preparation of methylcyclohexane-3-carboxylic acid. When treated with potassium cyanide the former yields a crystalline mass, which, when acted on by weak acids, forms an oily liquid yielding *crystals*, m. p. 63—64°,  $\alpha_D - 12^\circ$ , and corresponding with the formula  $C_8H_{13}ON$ . With hydrochloric acid, little of the corresponding hydroxy-acid is obtained, most of it being converted into crystalline condensation products free from nitrogen. With sulphuric acid, the cyanohydrin yields the corresponding *amide*, m. p. 120—121°, which, with dilute acid, forms 3-hydroxymethylcyclohexane-3-carboxylic acid,  $OH \cdot C_6H_9Me \cdot CO_2H$ , b. p. 260—270°/723 mm. (slight decomp.). This acid must be a mixture of the *cis*- and *trans*-modifications, for when heated with aniline it yields two *anilides*,  $C_{14}H_{19}ON_2$ , m. p. 90—91°,  $\alpha_D - 17.93^\circ$ , and m. p. 118.5—119.5°,  $\alpha_D - 13.87^\circ$ . Both anilides yield the acid when treated with alkalis. A crystalline *sodium* salt of the acid has also been obtained, but it was found impossible to convert it to methylcyclohexane-3-carboxylic acid; with hydriodic acid and red phosphorus, it yields condensation products containing iodine, and carbon monoxide and dioxide.

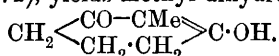
Z. K.

**$\beta$ -Chloroethyl Ketones and Alkyl Vinyl Ketones. Fixation of Sodio-derivatives.** EDMOND E. BLAISE and M. MAIRE (*Compt. rend.*, 1907, 144, 572—574. Compare Abstr., 1906, i, 142).—It has been shown (this vol., i, 241) that the alkyl vinyl ketones readily condense with organic sodium compounds, but, since these ketones readily polymerise in the presence of alkalis, the yields are small and the investigation has been extended to the  $\beta$ -chloroethyl ketones.

Ethyl  $\beta$ -chloroethyl ketone condenses with ethyl sodioacetoacetate to yield the *diketone*,  $COMe \cdot CH(CO_2Et) \cdot CH_2 \cdot COEt$ , which cannot be distilled without decomposing, even under a pressure of 4 mm., and gives a bluish-violet coloration with ferric chloride. On treatment with hydrogen chloride in presence of benzene it furnishes 3-ethyl- $\Delta^2$ -cyclohexenone-6-carboxylate,  $CEt \cdot \begin{matrix} CH_2 \cdot CH_2 \\ \diagdown \quad \diagup \\ CH - CO \end{matrix} \cdot CH \cdot CO_2Et$ , which on hydrolysis furnishes 3-ethyl- $\Delta^2$ -cyclohexenone. In an analogous manner, with the sodium derivative of acetylacetone, ethyl- $\beta$ -chloroethyl ketone

yields the *triketone*,  $\text{CH}(\text{COMe})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COEt}$ , which in the manner already indicated may be converted into 6-acetyl-3-ethyl- $\Delta^2$ -cyclohexenone.

From the sodium derivative of ethyl malonate by the general reaction, the *ketonic ester*,  $\text{COEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$ , is produced, and the dibasic acid corresponding with this decomposes when heated, yielding  $\gamma$ -propionylbutyric acid, which, by Vorländer's method (Abstr., 1896, i, 20; 1897, i, 272), yields methyl dihydroresorcinol,



The last-mentioned substance differs from its next lower homologue in being insoluble in ether, almost insoluble in water, and slightly soluble in cold alcohol, but the value of its molecular refraction indicates that, like the latter, it possesses the keto-enolic structure. T. A. H.

**Salts of cycloGallipharic Acid.** HERMANN KUNZ-KRAUSE and RUDOLF RICHTER (*Arch. Pharm.*, 1907, 245, 28—42. Compare Abstr., 1904, i, 587).—The new salts prepared are enumerated below with their melting points; often the salts softened several degrees before they actually melted, and at the high temperature at which two of the lead salts melted, decomposition occurred ( $\text{A} = \text{C}_{21}\text{H}_{35}\text{O}_3 = \text{OH} \cdot \text{C}_{20}\text{H}_{34} \cdot \text{CO} \cdot \text{O}$ ). Like the higher fatty acids, cyclogallipharic acid dissolves readily when warmed with a concentrated solution of an alkali carbonate, but hardly at an appreciable rate in a dilute solution; moreover, the alkali cyclogallipharates undergo hydrolysis when their aqueous solution is much diluted, the acid being precipitated. The salts, other than those of the alkali metals, were prepared by precipitation by means of a solution of the acid in the equivalent amount of normal potassium hydroxide solution. In the preparation of the ferric salt, no oxidation of the acid took place.

KA, 73·5°, crystalline.  $\text{BaA}_2 \cdot 2\text{H}_2\text{O}$ , 121°; water not lost even at this temperature.  $\text{CdA}_2$ , 135·5°.  $\text{CuA}_2 \cdot \text{H}_2\text{O}$ , 81°; water lost at 100°, but not at the ordinary temperature under diminished pressure.  $\text{HgA}_2 \cdot 3\text{H}_2\text{O}$ , 139·5°; water not lost at 100°.  $4\text{PbA}_2 \cdot \text{Pb}(\text{OH})_2$ , 185—187°;  $3\text{PbA}_2 \cdot \text{Pb}(\text{OH})_2$ , 225—230°; also a crystalline salt, m. p. 88°, containing 2·5% of lead, that is, one-tenth of the amount required by  $\text{PbA}_2$ . The basic salt,  $\text{OH} \cdot \text{FeA}_3$ , was the only ferric salt obtainable. C. F. B.

**Hydrophthalic Acids. IV.  $\Delta^{2:5}$ -cycloHexadiene-1:2-dicarboxylic Acid.** Constitution of the  $\Delta^{2:5}$  and  $\Delta^{1:3}$ -Acids. GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 466—473. Compare Abstr., 1906, i, 959).—The author describes his further investigations on the anhydride obtained by heating  $\Delta^{1:3}$ -cyclohexadiene-1:2-dicarboxylic anhydride for about two hours at 210—230° (*loc cit.*), and shows it to be the  $\Delta^{2:5}$ -anhydride.

$\Delta^{2:5}$ -cycloHexadiene-1:2-dicarboxylic anhydride,  $\text{C}_8\text{H}_6\text{O}_3$ , crystallises from light petroleum in white, nacreous scales, m. p. 73—74°, and from benzene in shining prisms, m. p. 120°, containing  $\frac{1}{2}\text{C}_6\text{H}_6$ . For the corresponding acid, conductivity measurements give the values  $\mu_\infty = 377$  and  $K = 0\cdot0544$ . After the anhydride has been boiled with

10% sodium hydroxide solution, it can be recovered unchanged by the addition of hydrochloric acid, so that  $\Delta^{2:5}$ -cyclohexadiene-1:2-dicarboxylic acid does not exhibit the lability attributed to acids unsaturated in the  $\beta\gamma$ -position (*loc. cit.*, and Baeyer, Abstr., 1892, 1211). On reduction with sodium amalgam, the  $\Delta^{2:5}$ -acid is converted into  $\Delta^1$ -cyclohexene-1:2-dicarboxylic acid. Treatment of the  $\Delta^{2:5}$ -anhydride with bromine vapour, and subsequently with aqueous alcohol, converts it into the *dibromo-acid*,  $C_6H_6Br_2(CO_2H)_2$ , m. p. 197—198° (decomp.).

Support is lent to the  $\Delta^{1:3}$ - and  $\Delta^{2:5}$ -constitutions attributed to the dihydrophthalic acids described by the author (*loc. cit.*) by (1) the values of their affinity constants, and (2) the fact that the first, although it possesses two double linkings, does not form an additive compound with either bromine or hydrogen bromide, whilst the second combines with two atoms of bromine (compare Baeyer, *loc. cit.*).

T. H. P.

**Hydrophthalic Acids; Reduction of Phthalic Acid by Means of Sodium Amalgam.** V. GINO ABATI and SALVATORE MINERVA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 473—498. Compare von Baeyer, Abstr., 1892, 1211; Abati and de Bernardinis, Abstr., 1905, i, 599).—The authors have reduced a large quantity of phthalic acid by means of sodium amalgam and have subjected the resultant mixture to a very thorough fractionation.

Besides the acids obtained by von Baeyer (*loc. cit.*) and the  $\Delta^{1:3}$ -cyclohexadiene-1:2-dicarboxylic and *cis*- $\Delta^3$ -cyclohexene-1:2-dicarboxylic anhydrides obtained by Abati and de Bernardinis (*loc. cit.*), the authors have isolated  $\Delta^{1:4}$ -cyclohexadiene-1:2-dicarboxylic anhydride and have confirmed the formation of *cis*- $\Delta^{3:5}$ -cyclohexadiene-1:2-dicarboxylic acid. The  $\Delta^{2:4}$ - and  $\Delta^{2:5}$ -cyclohexadiene-1:2-dicarboxylic, the  $\Delta^1$ - and *cis*- $\Delta^4$ -cyclohexene-1:2-dicarboxylic, and the two cyclohexane-1:2-dicarboxylic acids could not be traced. The  $\Delta^{2:4}$ -dihydro-acid is reduced by sodium amalgam into the *cis*- $\Delta^4$ -tetrahydro-acid and this, when boiled with sodium hydroxide solution, is transformed into a mixture of the *trans*- $\Delta^4$ - and the  $\Delta^2$ -tetrahydro-acids; the  $\Delta^{2:5}$ -dihydro-acid is converted by sodium amalgam into the  $\Delta^1$ -tetrahydro-acid. The *cis*- and *trans*-cyclohexane-1:2-dicarboxylic acids are formed with some degree of readiness only from the  $\Delta^1$ -tetrahydro-acid. But the latter acid, although stable, is not found among the products of the reduction of phthalic acid by sodium amalgam, and it is this fact alone which prevents the conclusion that this reduction gives rise to all the hydrophthalic acids compatible with the conditions of experiment.

$\Delta^{1:4}$ -cycloHexadiene-1:2-dicarboxylic acid has m. p. 153° and the corresponding anhydride, m. p. 134—135°.

*cis*- $\Delta^{3:5}$ -cycloHexadiene-1:2-dicarboxylic acid has m. p. 174° (compare Abati and de Bernardinis, *loc. cit.*) and the corresponding anhydride, m. p. 100°.

T. H. P.

**$\beta$ -Methylcyclohexanyl Hydrogen Phthalate.** V. TSCHECHEWITSCH (*J. Russ. Phys. Chem. Soc.*, 1907, 39, i, 6—8. Compare Abstr., 1904, i, 383).— $\beta$ -Methylcyclohexanyl hydrogen phthalate,  $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_7H_{11}$ , has been isolated as one of the intermediate

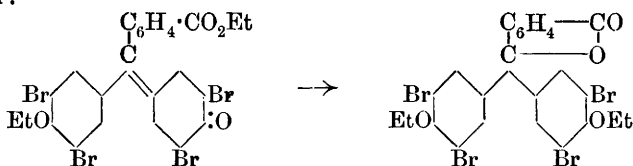
products in the conversion of methylcyclohexane into heptanaphthene by means of phthalic anhydride. It forms prismatic crystals soluble in alcohol, ether, or benzene, m. p.  $89.5-90.5^\circ$ ,  $[\alpha]_D + 8.68-8.41^\circ$ .

Z. K.

**Bromination of Santonin.** JOSEPH KLEIN (*Ber.*, 1907, 40, 939-942. Compare Klein, *Abstr.*, 1893, i, 112; Wedekind and Koch, *ibid.*, 1905, i, 212).—Contrary to the statements of Wedekind and Koch, and in agreement with the author's earlier experiments, it is shown that the compound termed santonin acetate dibromide is obtained when bromine reacts with an acetic acid solution of santonin. It is essential, however, that the acetic acid should contain water (some 5%), as otherwise Wedekind and Koch's compound is formed. It has the composition  $C_{15}H_{18}O_3Br_2$ . When a small amount of santonin is dissolved in 1 c.c. of concentrated sulphuric acid, then mixed with an equal volume of water and a drop of ferric chloride solution, a characteristic violet coloration is obtained. Bromosantonin does not give this coloration unless previously boiled with sodium hydroxide solution. The dibromide gives a coloration which is somewhat more reddish-yellow in colour.

J. J. S.

**Constitution of Phthalein Salts.** RICHARD MEYER and KARL MARX (*Ber.*, 1907, 40, 1437-1441. Compare Green and King, *Abstr.*, 1906, i, 670).—The action of ethyl iodide on the dry silver salt of tetrabromophenolphthalein suspended in benzene gives Nietzki and Burckhardt's intensely yellow diethyl quinonoid derivative; m. p.  $160-163^\circ$  (*Abstr.*, 1897, i, 225, m. p. given  $150-151^\circ$ ); when recrystallised from carbon tetrachloride it gives sulphur-yellow needles, m. p.  $63-65^\circ$ , containing one molecule of carbon tetrachloride of crystallisation. This is the first time a quinonoid derivative of phenolphthalein has been obtained from a salt; the colourless diethoxy-lactoid derivative is obtained from the quinonoid compound either by solution in alcohol, light petroleum, or by fusion:



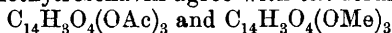
W. R.

**Resoflavin and Galloflavin.** JOSEF HERZIG and RUDOLF TSCHERNE (*Annalen*, 1907, 351, 24-37. Compare *Abstr.*, 1904, i, 814).—A study of the derivatives of resoflavin has established for this substance the formula  $C_{14}H_8O_4(OH)_2$ , and has shown that it must contain two anhydride groupings, and is a derivative of diphenylmethyloolid (compare Graebe, *Abstr.*, 1903, i, 262; Perkin and Nierenstein, *Trans.*, 1904, 87, 1412).

Methylresoflavin, m. p.  $286-288^\circ$  ( $282-283^\circ$ . *loc. cit.*), dissolves in potassium hydroxide, and on acidification is deposited only slowly and on heating. When heated with methyl iodide and potassium hydroxide,

it forms an *ether ester*,  $C_{14}H_3O_2(OMe)_7$ , separating in white crystals, m. p. 132—134°; on hydrolysis this yields the crystalline *ether acid*,  $C_{14}H_4O_3(OMe)_6$ , m. p. 197—199°, which when heated with hydriodic acid is converted into resoflavin.

The analytical results obtained with acetylresoflavin, m. p. 275—279°, and methylresoflavin agree with the formulæ

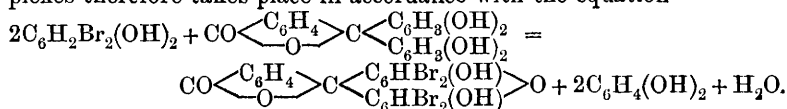


respectively.

The dye formed by the action of ammonium persulphate on ethyl 3:5-dihydroxybenzoate is probably impure resoflavin. The product obtained by the action of ammonium persulphate on gallic acid yields with methyl iodide and potassium hydroxide a white, crystalline product,  $C_{14}HO_3(OMe)_9$ , m. p. 84—87°. The interrelations of these substances require further investigation. G. Y.

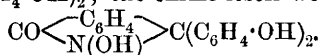
**Catecholphthalein.** RICHARD MEYER and HERMANN PFOTENHAUER (*Ber.*, 1907, 40, 1442—1445).—On condensing catechol with phthalic anhydride in the presence of zinc chloride, Baeyer and Kochendörfer (*Abstr.*, 1889, 1153) obtained catecholphthalein as a brown, uncrystallisable mass. This phthalein has been obtained crystalline by digestion with water and animal charcoal twice and afterwards purifying the yellowish-white needles so obtained by boiling with benzene which dissolves the catechol. It has no definite m.p., but sinters at 80—90°, dissolves more easily in water than other phthaleins, and is volatile in steam. The fact that catechol yields a phthalein, whereas resorcinol and quinol form dihydroxy-fluorans is thus confirmed. The *acetate*,  $C_{20}H_{10}O_2(OAc)_4$ , crystallises in white needles, m. p. 155—156°. W. R.

**Mutual Exchange of Aromatic Complexes.** RICHARD MEYER and HERMANN PFOTENHAUER (*Ber.*, 1907, 40, 1445—1450).—Eosin is obtained when dibromoresorcinol in the form of dibromo- $\beta$ -resorcylic acid is heated with catecholphthalein and zinc chloride at 170° for two to three hours (compare *Abstr.*, 1906, i, 23); the exchange of complexes therefore takes place in accordance with the equation



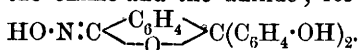
When heated for a week at 180°, Michler's ketone and resorcinol yield dimethylaniline, and, in the place of the expected 3:6-dihydroxy-xanthone, a *substance*,  $C_{16}H_{20}O_3N_2$ , m. p. 238—239°, which is a by-product, resulting probably by the action of the dimethylaniline on the dihydroxyxanthone; the latter, however, cannot be isolated. C. S.

**Reduction Product of Phenolphthaleinoxime.** RICHARD MEYER and J. GLIKIN (*Ber.*, 1907, 40, 1454—1458).—The behaviour of the reduction product of phenolphthaleinoxime (compare Friedländer, *Abstr.*, 1893, i, 273) is in agreement with the formula  $NH_2 \cdot CO \cdot C_6H_4 \cdot CH(C_6H_4 \cdot OH)_2$ ; the oxime itself would be

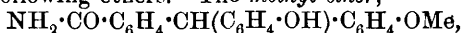




The unexpected stability of phthaleinanilides to reducing agents (following abstract), however, speaks against analogous formulæ for the oxime and the anilide; for the former is suggested the formula



The reduction product of phenolphthaleinoxime does not form an ester by treatment with alcohol and hydrogen chloride; it does yield, however, the following ethers. The *methyl ether*,



obtained by the action of sodium methoxide and excess of methyl iodide in methyl-alcoholic solution, has m. p. 236—237°; the *dimethyl ether*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , m. p. 130—131°, is obtained by the action of sodium hydroxide and methyl sulphate; the *diethyl ether*, prepared in a similar manner to the methyl ether, has m. p. 125—126°; the *dibenzyl ether* has m. p. 158°. The diacetate and the dibenzoate have been prepared by Herzig and Meyer (Abstr., 1897, i, 69).

Attempts to prepare the reduced oxime by replacing OEt by  $\text{NH}_2$  in the ester of phthalin,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OH})_2$ , were unsuccessful.

C. S.

**Behaviour of Phthaleinanilides to Reducing Agents.** RICHARD MEYER and KURT LANGE (*Ber.*, 1907, 40, 1459—1462).—The anilides of diphenylphthalide, fluoran, phenolphthalein, and fluorescein are practically unattacked by potassium hydroxide and zinc dust in boiling alcoholic solution.

C. S.

**Quinic Acid.** GUSTAV KNÖPFER (*Arch. Pharm.*, 1907, 245, 77—80).—Unlike Echtermeyer (Abstr., 1906, i, 367, 368), the author succeeded in preparing a crystalline ammonium salt, amide, and anilide (m. p. 183°; already prepared by Hesse, with m. p. 174°) of quinic acid. *Ammonium quinate*,  $\text{C}_7\text{H}_{15}\text{O}_6\text{N}$ , m. p. 179°, was obtained by triturating quinic acid with solid ammonium carbonate and volatilising the excess of carbonate on the water-bath. *Quinamide*,  $\text{C}_7\text{H}_{13}\text{O}_5\text{N}$ , m. p. 132°, was obtained by heating ethyl quinate with alcoholic ammonia at 125° for six hours.

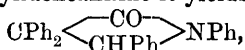
*Methyl methylquinate* and *ethyl ethylquinate*,  $\text{C}_{11}\text{H}_{20}\text{O}_6$ , were obtained by heating lead quinate with methyl or ethyl iodide respectively at 125° for six hours; both are viscid liquids which decompose when distilled even under diminished pressure.

C. F. B.

**Condensation of Aldehydes with Phenolcarboxylic Acids.** E. HÖST MADSEN (*Arch. Pharm.*, 1907, 245, 42—48).—Formaldehyde and benzaldehyde condense with salicylic acid in the presence of hydrogen chloride in accordance with the equation  $\text{CHRO} + 2\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} = \text{CHR}[\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}]_2 + \text{H}_2\text{O}$  [R = H and Ph respectively]; the condensation appears to take place in the para position to the OH group. In the first case the reacting substances were boiled in aqueous solution, in the second they were heated at 160° in a sealed tube without water; in both cases special precautions had to be taken in order to obtain a crystalline product.

*Methanedisalicyclic* (methylenedisalicyclic) acid,  $C_{15}H_{12}O_6$ , melts at 243—244° and loses carbon dioxide at 180°. *Phenylmethanedisalicyclic acid*,  $C_{21}H_{16}O_6$ , melts at 242—245° and loses carbon dioxide at 130—150°; its *diacetyl* derivative,  $C_{25}H_{20}O_8 \cdot H_2O$ , melts at 124° and begins to decompose at 101°. C. F. B.

**Ketens. IV. Reactions of Diphenylketen.** HERMANN STAUDINGER (*Ber.*, 1907, 40, 1145—1148. Compare Abstr., 1905, i, 444; 1906, i, 234, 861).—A solution of diphenylketen in ether or light petroleum reacts with water, alcohol, or amines, yielding diphenylacetic acid, its esters, or amides. The keten forms additive compounds with tertiary amines; the only one isolated was the *quinoline* compound,  $2C_{14}H_{10}O \cdot C_9H_7N$ , m. p. 121—122°, which is completely dissociated in chloroform solution. It also combines with unsaturated compounds, for example, with *cyclopentadiene*, yielding a *product*,  $C_{14}H_{10} \cdot C_5H_6$ , m. p. 89—90°, and with *quinone*, forming a compound,  $C_{14}H_{10}O \cdot C_6H_4O_2$ , which crystallises from acetone in colourless prisms, m. p. 143°. With benzylideneaniline it yields the  $\beta$ -lactam,

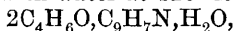


m. p. 159—160°, which on hydrolysis with aqueous alcoholic potassium hydroxide yields the  $\beta$ -anilino-acid,  $NHPh \cdot CHPh \cdot CPh_2 \cdot CO_2H$ , m. p. 122—123°.

The keten does not polymerise, and with magnesium phenyl bromide yields triphenylvinyl alcohol.

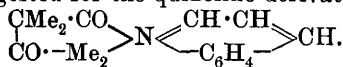
The keten may be prepared by the action of tertiary bases on diphenylacetyl chloride. J. J. S.

**Ketens. V. Dimethylketen.** HERMANN STAUDINGER and H. W. KLEVER (*Ber.*, 1907, 40, 1149—1153. Compare Abstr., 1906, i, 234).—Among the products formed during the preparation of dimethylketen is a liquid bimolecular polymeric compound,  $(C_4H_6O)_2$ , b. p. 170—171°. It has an odour of peppermint, and with sodium hydroxide solution yields an acid readily soluble in water. The *phenylhydrazone*,  $C_{14}H_{18}ON_2$ , melts at 66—67°. The keten forms additive compounds with tertiary bases; these are extremely stable, do not give the characteristic reaction of the keten, and are not affected by oxygen. *Dimethylketen-quinoline*,  $C_9H_7N \cdot 2C_4H_6O$ , forms colourless crystals from light petroleum, m. p. 81—82°, and when boiled for a short time with mineral acids or heated with water at 120° it yields an acid,



m. p. 152—153°, which is completely hydrolysed to quinoline and isobutyric acid with hot hydrochloric acid. The *ethyl* ester has m. p. 60·5—61·5°; *methyl* ester, 58—59°, and the *anilide* 109—110°. *Dimethylketen-quinaldine*,  $2C_4H_6O \cdot C_{10}H_9N$ , has m. p. 119·5—120·5°, and di-*methylketen-p-toluquinaldine*, 129—130°. Both are less stable than the quinoline derivative. When carefully boiled with dilute acetic acid the quinaldine derivative yields an *acid*,  $2C_4H_6O \cdot C_{10}H_9N \cdot H_2O$ , m. p. 137—138°. *Dimethylketen-acridine*,  $2C_4H_6O \cdot C_{13}H_9N$ , melts at 127—128° and is very stable. *Dimethylketen-pyridine* is an unstable oil and readily yields the corresponding *acid*, m. p. 84—96°.

The formula suggested for the quinoline derivative is



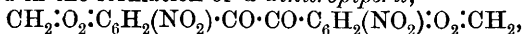
With benzylideneaniline the keten yields an additive compound, namely, a  $\beta$ -lactam,  $\text{CMe}_2 \begin{array}{c} \text{CO} \\ \text{CHPh} \end{array} \text{NPh}$ , m. p. 148—149°.

J. J. S.

### Condensation of Piperil with Benzaldehyde and Ammonia.

T. NOWOSIELSKI (*Bull. Acad. Sci., Cracow*, 1906, 276—278).—The formation of a glyoxaline derivative by condensation of piperil with benzaldehyde and ammonia, according to the general reaction of  $\alpha$ -diketones, offered some points of interest, as in many respects piperil differs from its analogue benzil.

An attempt to prepare piperil by oxidation of piperoin with nitric acid resulted in the formation of a *dinitropiperil*,



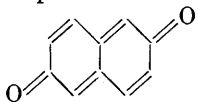
which separates as a yellow crust.

The *glyoxaline* derivative (*piperilbenzoline*),  $\text{C}_8\text{N}_2\text{HPh}(\text{C}_6\text{H}_3:\text{O}_2:\text{CH}_2)_2$ , formed by the action of ammonia on piperil and benzaldehyde in alcoholic solution at 60—70°, crystallises in microscopic plates or long needles, m. p. 251—253°, and, on exposure to air in alcoholic potassium hydroxide solution, yields benzoic and piperonylic acids and ammonia. The *hydrochloride*,  $\text{C}_{23}\text{H}_{16}\text{O}_4\text{N}_2 \cdot \text{HCl}$ , forms small, white needles; the *platinichloride*,  $(\text{C}_{23}\text{H}_{16}\text{O}_4\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , is obtained as a crystalline precipitate.

G. Y.

### Quinonoid Compounds. XI. 2:6-Naphthaquinone.

RICHARD WILLSTÄTTER and JAKOB PARNAS (*Ber.*, 1907, 40, 1406—1415).—*amphi- or 2:6-Naphthaquinone*, prepared by the oxidation of the corresponding quinol in dry benzene solution with lead peroxide in large excess, crystallises from a mixture of benzene and petroleum in small, reddish-yellow prisms changing colour suddenly at 130—135°. The quinone is stable in air, odourless, and non-volatile, thus resembling *o*-quinones. In its chemical behaviour, it resembles *p*-benzoquinone rather than the 1:2- or 1:4-naphthaquinones in the ease with which it passes back into an aromatic substance. A table is given demonstrating this, comparing these quinones with regard to their oxidising action on cold very dilute hydriodic acid, hydrocærulignone, hæmatoxylin, sulphurous acid, ferrous ferrocyanide, and guaiacol resin solution. That the substance is 2:6-naphthaquinone and not a dinaphthalene derivative is shown by its reduction to 2:6-dihydroxynaphthalene by cold dilute hydriodic acid; and the conclusion is supported by a molecular weight determination in benzene by the boiling point method. The small reactivity of the  $\alpha$ - and  $\beta$ -naphthaquinones as compared with this substance is, perhaps, due to the *amphi*-derivative being a true naphthaquinone, the other two affecting only one ring of the naphthalene and therefore being “incomplete.” *as-a*-Tetrahydronaphthaquinone (Bamberger and Lengfeld, *Abstr.*, 1890, 1305) is analogous to *p*-benzoquinone in its behaviour towards hydriodic acid and hydrocærulignone.

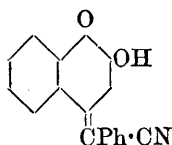


amphi-Naphthaquinonehydron,  $C_{20}H_{14}O_4$ , the additive product obtained by mixing the benzene solution of quinone and corresponding quinol in ether, crystallises in dark bluish-green, microscopic needles which suddenly decolorise at  $124-125^\circ$  without melting. It is more unstable than the quinone.

1.08 Gram of 2:6-dihydroxynaphthalene, m. p.  $218^\circ$  (corr.) (Emmert, Abstr., 1888, 57; m. p.  $215-216^\circ$ ), dissolves in 1 litre of water at  $14^\circ$ . 2:6-Dimethoxynaphthalene,  $C_{12}H_{12}O_2$ , m. p.  $150^\circ$ , crystallises in rhombic plates from benzene. W. R.

### Condensations with 1:2-Naphthaquinone-4-sulphonic Acid.

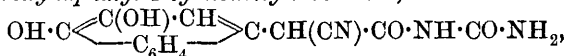
II. FRANZ SACHS, ERICH BERTHOLD, and BRUNO ZAAH (*Zeitsch. Farb.-Ind.*, 1907, 6, 62—68 and 81—84. Compare Abstr., 1905, i, 909).—1:2-Naphthaquinone-4-sulphonic acid is an extraordinarily active substance, condensing not only with amino-compounds but also with



compounds containing a methyl or methylene group (compare Ehrlich and Herter, Abstr., 1904, i, 598). In all cases the sulphonic radicle is displaced and a derivative of 2 hydroxy- $\alpha$ -naphthaquinone obtained; thus, for example, benzyl cyanide gives the annexed compound. The condensation of 1:2-naphthaquinone-4-sulphonic acid (in the form of

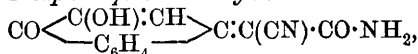
its potassium salt) with different substances gives rise to the compounds described below.

2-Hydroxy-1:4-naphthaquinone-4-carboxycyanomethide carbamide,  $CO \left\langle \begin{array}{c} C(OH):CH \\ \text{---} C_6H_4 \text{---} \end{array} \right\rangle C:C(CN) \cdot CO \cdot NH \cdot CO \cdot NH_2$ , prepared from cyanoacetylcarbamide, crystallises from acetic acid in orange-red needles, m. p.  $303^\circ$ , and on reduction with zinc dust and acetic acid gives 1:2-dihydroxynaphthyl-4-cyanoacetylcarbamide,



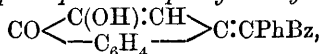
which forms colourless crystals, m. p.  $223^\circ$  (decomp.).

2-Hydroxy-1:4-naphthaquinone-4-cyanomethide carboxylamide,



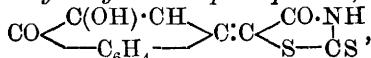
prepared from cyanoacetamide, crystallises from alcohol or acetic acid in yellow needles, m. p.  $227-228^\circ$ .

2-Hydroxy-1:4-naphthaquinone-4-phenylbenzoylmethide,



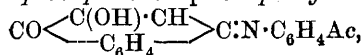
prepared from deoxybenzoin, crystallises from acetic acid in orange-red prisms, m. p.  $179^\circ$ .

4-Rhodanylidene-2-hydroxy-1:4-naphthaquinone,



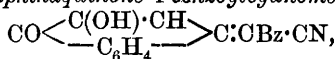
prepared from rhodanic acid, crystallises from glacial acetic acid in dark red needles, m. p.  $290^\circ$ .

2-Hydroxy-1:4-naphthaquinone-4-p-acetophenylimide,



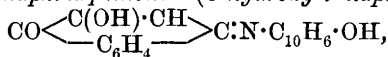
prepared from *p*-aminoacetophenone, crystallises from alcohol in rose-red, rhombic plates, m. p. 235—240°.

*2-Hydroxy-1 : 4-naphthaquinone-4-benzoylcyanomethide*,



prepared from cyanoacetophenone, crystallises from alcohol or acetic acid in long, yellowish-red needles, m. p. 257°.

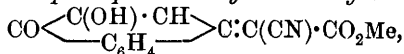
*2-Hydroxy-1 : 4-naphthaquinone-4-(2'-hydroxy-7'-naphthyl)imide*,



obtained from 2 : 7-aminonaphthol, crystallises from alcohol on adding water ; m. p. 290°. On reduction with zinc dust in hot acetic acid containing acetic anhydride and sodium acetate, 1 : 2 : 7'-*triacetoxynaphthylamine*,  $\text{OAc·C}_{10}\text{H}_6\text{·NH·C}_{10}\text{H}_5(\text{OAc})_2$ , is obtained in colourless needles, m. p. 204—205°.

*2-Hydroxy-1 : 4-naphthaquinone-4-(1'-hydroxy-5'-naphthyl)imide*, prepared from 1 : 5-aminonaphthol, crystallises from dilute alcohol.

*2-Hydroxy-1 : 4-naphthaquinone-4-cyanocarboxymethylmethide*,



prepared from methyl cyanoacetate, crystallises from alcohol in silky, yellow needles, m. p. 164°; on methylation with diazomethane the

*methyl ether*,  $\text{CO} \left\langle \begin{array}{c} \text{C(OMe)·CH} \\ \text{—C}_6\text{H}_4\text{—} \end{array} \right\rangle \text{C:C(CN)·CO}_2\text{Me}$ , is obtained, which

forms bright yellow, silky needles, m. p. 155°, and on reduction with zinc and acetic acid gives *methyl 1-hydroxy-2-methoxy-4-naphthylcyanoacetate*,  $\text{OH·C}_{10}\text{H}_5(\text{OMe)·CH(CN)·CO}_2\text{Me}$ , m. p. 128°. The *eurhodole*,

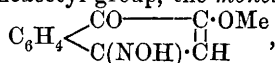
$\text{CO}_2\text{Me·C(CN):C} \left\langle \begin{array}{c} \text{C}_6\text{H}_4\text{·C=N} \\ \text{CH—C·NH} \end{array} \right\rangle \text{C}_6\text{H}_4$ , prepared from the foregoing

methide by the action of *o*-phenylenediamine, crystallises from alcohol in violet-brown, lanceolate needles, m. p. 179°. The *semicarbazone*,

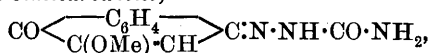
$\text{CO}_2\text{Me·C(CN):C} \left\langle \begin{array}{c} \text{C}_6\text{H}_4\text{·C:N·NH·CO·NH}_2 \\ \text{CH—C·OH} \end{array} \right\rangle$ , separates from alcohol or

acetic acid in yellowish-brown, hexagonal crystals, m. p. 261°.

Attempts to prepare the oxime of methyl 1-hydroxy-2-methoxy-4-naphthylcyanoacetate by the action of hydroxylamine caused the elimination of the cyanoacetyl group, the *monoxime*,

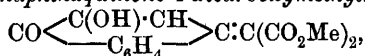


of 2-methoxy-1 : 4-naphthaquinone being obtained ; this substance can also be prepared by the action of hydroxylamine on 2-methoxy-1 : 4-naphthaquinone, and crystallises from alcohol in yellowish-white prisms or needles, m. p. 228° with decomposition. *2-Methoxy-1 : 4-naphthaquinone*, obtained by methylating 2-hydroxy-1 : 4-naphthaquinone, crystallises from alcohol in yellow needles and melts at 146—147° ; the *semicarbazone*,



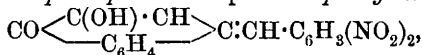
crystallises from acetic acid in golden needles, m. p. 237—238°.

*2-Hydroxy-1:4-naphthaquinone-4-dicarboxymethylmethide,*

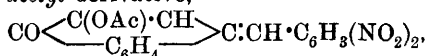


is obtained by condensing 1:2-naphthaquinone-4-sulphonic acid with methyl malonate, and has m. p. 130°; the *oxime* forms yellowish-brown prisms, m. p. 194°, and the semicarbazone, canary-yellow needles, m. p. 199°. The *oxime* of the corresponding diethyl compound,  $\text{CO} \langle \begin{array}{c} \text{C(OH)·CH} \\ \text{C}_6\text{H}_4 \end{array} \rangle \text{C:C(CO}_2\text{Et)}_2$ , forms greenish-yellow crystals, m. p. 171°, and the semicarbazone, bright yellow needles, m. p. 174°.

*2-Hydroxy-1:4-naphthaquinone-4-op-dinitrophenylmethide,*



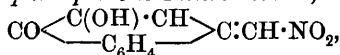
prepared from 2:4-dinitrotoluene, separates from glacial acetic acid in orange-yellow crystals, melts and decomposes at 238—240°, and gives a *phenylhydrazone*,  $\text{N}_2\text{HPh:C} \langle \begin{array}{c} \text{C(OH)·CH} \\ \text{C}_6\text{H}_4 \end{array} \rangle \text{C:CH·C}_6\text{H}_3(\text{NO}_2)_2$ , m. p. 286—288°; the *acetyl* derivative,



forms a yellowish-white, crystalline powder, m. p. 187·5—188°, the *methyl ether*,  $\text{CO} \langle \begin{array}{c} \text{C(OMe)·CH} \\ \text{C}_6\text{H}_4 \end{array} \rangle \text{C:CH·C}_6\text{H}_3(\text{NO}_2)_2$ , crystallises from acetone in lustrous, orange prisms, sinters at 207°, and melts at 216°. The *eurhodole*,  $\text{C}_6\text{H}_4 \langle \begin{array}{c} \text{NH·C—CH} \\ \text{N=C·C}_6\text{H}_4 \end{array} \rangle \text{C:CH·C}_6\text{H}_3(\text{NO}_2)_2$ , separates from acetic acid as a yellowish-brown powder, m. p. 180°.

*2-Hydroxy-1:4-naphthaquinone-4-sym.-trinitrophenylmethide*, prepared from 2:4:6-trinitrotoluene, crystallises from glacial acetic acid in thick, yellow needles, m. p. 260°.

*2-Hydroxy-1:4-naphthaquinone-4-nitromethide,*



prepared from nitromethane, crystallises from acetone on adding light petroleum in small, yellow needles, m. p. 153—156°, and is very sensitive to light; methylation with diazomethane gives not a monomethyl derivative but *2-methoxy-1:4-naphthaquinone-4-methylnitromethide*,  $\text{CO} \langle \begin{array}{c} \text{C(OMe)·CH} \\ \text{C}_6\text{H}_4 \end{array} \rangle \text{C:CMe·NO}_2$ , m. p. 160°.

All the foregoing compounds, containing a hydroxyl group in the ortho-position to the chromophore, are mordant dyes, thus confirming Möhlau and Steinmig's rule (*Zeitsch. Farb.-Ind.*, 3, 35) that a hydroxyl group in this position suffices to produce a mordant dye. The tinctorial properties of the compounds enumerated are described in detail.

W. A. D.

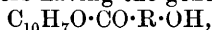
**1:6-Dihydroxyanthraquinone.** OTTO FROBENIUS and EDUARD HEPP (*Ber.*, 1907, 40, 1048—1051).—1:6-Dihydroxyanthraquinones have been described by Farbwerke vorm. Meister, Lucius, and Brüning, and by Wedekind and Co.; the former product is shown to be a pure

substance and the latter to be a mixture containing *isoanthraflavic acid* in quantity.

1:6-Dihydroxyanthraquinone, m. p. 271—272° (not 260° as previously stated), crystallises in orange-yellow needles, and gives a red coloration in concentrated sulphuric acid solution; the *barium* and *calcium* salts are insoluble even in hot water. The *diacetate*, m. p. 205—206°, and *dibenzoate*, m. p. 209—211°, crystallise in citron-yellow needles. Flavopurpurin alone and no hydroxyanthrarufin are produced on oxidation. The compound, erythrohydroxyanthraquinonesulphonic anhydride, obtained by Lifschütz (Abstr., 1884, 1189) from  $\alpha$ -nitroanthraquinonesulphonic acid and potassium nitrite is in reality diazoanthraquinonesulphonic acid. Wedekind and Co.'s product has m. p. 405°; diacetate, m. p. 228°; dibenzoate, m. p. 232—233°.

E. F. A.

**Preparation of the Bornyl Esters of the Aromatic Hydroxycarboxylic Acids.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 175097).—The bornyl esters having the general formula



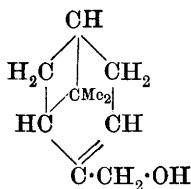
where R is an aromatic group, are of importance in therapeutics and in the preparation of borneol. They may be prepared by warming an aromatic hydroxycarboxylic acid with a terpene such as pinene or camphene or a mixture of these hydrocarbons with or without a condensing agent.

"*Bornyl*" *salicylate*,  $C_{10}H_7O \cdot CO \cdot C_6H_4 \cdot OH$ , b. p. 171—173°/5 mm., which is employed medicinally under the name of "salit," is obtained by heating a mixture of salicylic acid and French oil of turpentine, first at 110° and then gradually to 150°. After removing the unchanged reagents, the ester was obtained as a slightly coloured oil having a faint taste and odour; it is soluble in the ordinary organic media and develops a violet coloration with alcoholic ferric chloride. Its alkali salts are solid, unstable substances readily hydrolysing to yield sodium salicylate and a mixture of borneol and *isoborneol*. The pure bornyl ester is obtained when pure pinene is employed, whilst pure camphene yields the corresponding *isobornyl* ester. G. T. M.

**Myrtenol, a Primary Alcohol,  $C_{10}H_{16}O$ , from the Ethereal Oil of Myrtus Communis.** FRIEDRICH W. SEMMLER and KONRAD BARTELT (Ber., 1907, 40, 1363—1378).—The ethereal oil from *Myrtus communis* contains in the fractions of high-boiling point an alcohol,  $C_{10}H_{16}O$ , which is designated as myrtenol; this is a dicyclic primary alcohol, containing one double linking, and has the pinene structure. A dextrorotatory pinene can be prepared from it. When oxidised by potassium permanganate, myrtenol forms an optically active dibasic pinic acid. When oxidised by chromic acid, it forms the aldehyde,  $C_{10}H_{14}O$ , from which the oxime,  $C_{10}H_{14} \cdot N \cdot OH$ , was obtained; the latter yields the nitrile,  $C_{10}H_{13}N$ , an acid,  $C_{10}H_{14}O_2$ , and a reduced acid,  $C_{10}H_{16}O_2$ . The latter compounds are the first representatives of the dicyclic unsaturated or saturated series of the pinene system.

In addition to myrtenol, the following are present in the ethereal

oil examined: cineol, pinene, dipentene, and camphor. After fractionation, the myrtenol was separated by converting it into *myrtenyl hydrogen phthalate*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{C}_{10}\text{H}_{15}$ , with m. p. 114—115° and  $[\alpha]_D + 21\cdot36'$  in ethyl-alcoholic solution ( $c=50$ ) (temperature not quoted). When an excess of alkali is added, the myrtenol may be distilled off in a current of steam.

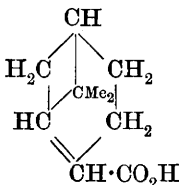


*Myrtenol* has b. p. 102·5°/9 mm., 222—224°/760 mm.,  $D^{20}$  0·9763,  $n_D$  1·49668,  $\alpha_D + 45\cdot45'$  ( $l=1$ ), and is the first example of a primary di-cyclic alcohol.

*Myrtenyl chloride*,  $\text{C}_{10}\text{H}_{15}\text{Cl}$ , obtained by the action of phosphorus pentachloride on myrtenol in light petroleum solution, has b. p. 90°/12 mm.,  $D^{20}$  1·015,  $n_D$  1·49762. When reduced by sodium and ethyl alcohol, it forms a dextrorotatory pinene, with  $\alpha_D + 28^\circ$  ( $l=1$ ), which was identified by conversion into a number of derivatives.

*Myrtenyl ethyl ether*,  $\text{C}_{10}\text{H}_{15}\text{OEt}$ , obtained along with pinene by the reduction of myrtenyl chloride, has b. p. 80—85°/10 mm.,  $D^{20}$  0·899, and  $n_D$  1·4725.

When myrtenol is oxidised in glacial acetic acid solution it is converted into *myrtenal*,  $\text{C}_{10}\text{H}_{14}\text{O}$ , which has b. p. 87—90°/10 mm.,  $D^{20}$  0·9876,  $n_D$  1·50420, and forms an *oxime*,  $\text{C}_{10}\text{H}_{15}\text{ON}$ , which crystallises from ethyl alcohol and has m. p. 71—72°; when boiled with an excess of acetic anhydride, this oxime yields a *nitrile*,  $\text{C}_{10}\text{H}_{13}\text{N}$ , b. p. 100—102°/10 mm.,  $D^{20}$  0·967,  $n_D$  1·49192,  $\alpha_D + 44\cdot30'$  ( $l=1$ ). When this *nitrile* is saponified by alcoholic potassium hydroxide it is converted into *myrtenic acid*,  $\text{C}_{10}\text{H}_{14}\text{O}_2$ , with b. p. 148°/9 mm. and m. p. 54°. Its *methyl ester* has b. p. 99°/9 mm.,  $D^{20}$  1·022, and  $n_D$  1·48616.



*Dihydromyrtenic acid*, obtained by the reduction of myrtenic acid with sodium and amyl alcohol, has b. p. 142—144°/8 mm.,  $D$  1·049, and  $n_D$  1·48519. Towards potassium permanganate it behaves like a saturated acid.

When myrtenol is oxidised by potassium permanganate it is converted into a dextrorotatory *pinic acid*,  $\text{C}_9\text{H}_{14}\text{O}_4$ , b. p. 212—216°/10 mm. Its *dimethyl ester*,  $\text{C}_{11}\text{H}_{18}\text{O}_4$ , has b. p. 121—124°/10 mm.,  $D^{20}$  1·0582,  $n_D$  1·44962, and  $\alpha_D + 13\cdot50'$  ( $l=1$ ). Its *diethyl ester*,  $\text{C}_{13}\text{H}_{22}\text{O}_4$ , has b. p. 142—146°/10 mm.,  $D^{20}$  1·0104,  $n_D$  1·44962, and  $\alpha_D + 8'$  (length of tube and temperature not quoted).

*Myrtenyl formate*,  $\text{C}_{11}\text{H}_{16}\text{O}_2$ , has b. p. 93—97°/10 mm.,  $D^{20}$  1·009, and  $n_D$  1·47936. The *acetate*,  $\text{C}_{12}\text{H}_{18}\text{O}_2$ , has b. p. 105—107°/9 mm.,  $D^{20}$  0·9865, and  $n_D$  1·47838. When this ester is saponified by alcoholic potassium hydroxide the recovered myrtenol has the same rotation as before.

When myrtenol is heated with dilute sulphuric acid, a hydrocarbon,  $\text{C}_{10}\text{H}_{14}$ , is formed, having b. p. 55°/9 mm.,  $D^{20}$  0·858, and  $n_D$  1·49097; it is optically inactive and is probably *p*-cymene. The 4-ring in myrtenol is not so easily broken as that in pinene.

A. McK.



**Santalol.** FRIEDRICH W. SEMMLER and KURT BODE (*Ber.*, 1907, 40, 1124—1145. Compare following abstract; Chapman and Burgess, *Trans.*, 1901, 79, 134; Guerbet, *Abstr.*, 1900, i, 242, 401).—The primary alcoholic nature of santalol has been proved by its oxidation to *santalaldehyde*,  $C_{15}H_{22}O$ , by means of an acetic acid solution of chromic acid. The pure aldehyde, prepared from the semicarbazone by decomposing it slowly with phthalic anhydride, has b. p. 152—155°/10 mm.,  $D^{20}_D$  0.995,  $n_D$  1.51066, and is dextrorotatory. The *semicarbazone*,  $C_{16}H_{25}ON_3$ , after recrystallisation from methyl alcohol, has m. p. 230°. Other products are also formed during the oxidation of santalol, these are laevorotatory, but have not been obtained in a pure state. *d-Santaloloxime*,  $C_{15}H_{23}ON$ , has m. p. 104—105° and b. p. 182—185°/10 mm., and with acetic anhydride yields a *nitrile*,  $C_{15}H_{21}N$ , b. p. 162—166°/9 mm.,  $D^{20}_D$  0.990,  $n_D$  1.5033, and  $\alpha_D + 14^\circ$  (100 mm. tube). On hydrolysis the nitrile yields *santallic acid*,  $C_{15}H_{22}O_2$ , in the form of a viscid oil, b. p. 192—195°/9 mm. Its *copper* and *silver* salts are soluble and its *methyl* ester has b. p. 160—164°/10 mm.,  $D^{20}_D$  1.002, and  $n_D$  1.49097.

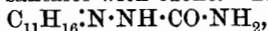
*Santalyl chloride*,  $C_{15}H_{23}Cl$ , obtained by the action of phosphorus pentachloride on a light petroleum solution of santalol, has b. p. 147—155°/10 mm. and  $D^{20}_D$  1.0398; when reduced with sodium and alcohol it yields a sesquiterpene,  $\gamma$ -*santalene*,  $C_{15}H_{24}$ , b. p. 118—120°/9—10 mm.,  $D^{20}_D$  0.9355,  $n_D$  1.5042.

Santalol is not reduced by sodium and alcohol, but with hydriodic acid and phosphorus yields a hydrocarbon,  $C_{15}H_{26}$ , b. p. 125—130°/12 mm.,  $D^{20}_D$  0.8999, and  $n_D$  1.48712.

Oxidation of santanol with permanganate in neutral solution yields a small amount of *dihydroxydihydrosantalol* (*santalolglycerol*),  $C_{15}H_{26}O_3$ , b. p. 215—220°/10 mm., together with *tricycloeksantallic acid*,  $C_{11}H_{16}O_2$  (compare following abstract). The acid is the chief product when 10 equivalents of oxygen are used. It has m.p. 71—72°, b. p. 165—167°/10 mm.,  $D^{20}_D$  1.071. The *copper* and *silver* salts are insoluble, the *amide* melts at 106°, the *methyl* ester has b. p. 125—128°/10 mm.,  $D^{20}_D$  1.0164,  $n_D$  1.47838, and its rotation like that of the acid varies considerably. *tricycloEksantalol*,  $C_{11}H_{18}O$ , obtained by reducing the methyl ester with sodium and absolute alcohol, has b. p. 130—132°/10 mm.,  $D^{20}_D$  0.9859,  $n_D$  1.49478, and the corresponding *tricycloEksantalaldehyde*,  $C_{11}H_{16}O$ , b. p. 125—130°/13 mm.,  $D^{20}_D$  1.012,  $n_D$  1.498.

When oxidised with ozone in benzene solution, santanol yields *tricycloEksantallic acid*, which is quite stable towards permanganate or ozone. The acid is also unaffected when its vapour mixed with carbon dioxide is passed over reduced copper at 500°, or when the acid is fused with potassium hydroxide, but when the calcium salt is distilled a hydrocarbon,  $C_{10}H_{14}$ , resembling cymene is obtained together with an *aldehyde*,  $C_{11}H_{16}O$ , the *semicarbazone* of which has m. p. 189—192°.

A considerable amount of *tricycloEksantalaldehyde* is also formed during the oxidation of santanol with ozone. The *semicarbazone*,



melts at about 156° and may be used for regenerating the pure

aldehyde. The *oxime*,  $C_{11}H_{16} \cdot N \cdot OH$ , has b. p. 140—150°/10 mm.,  $D^{20}_D$  1.03,  $n_D$  1.506, and  $\alpha_D + 1^\circ$ . The *nitrile* of *tricycloeksantalic acid* has b. p. 114—120°/10 mm.,  $D^{20}_D$  1.002,  $n_D$  1.4881,  $\alpha_D + 6^\circ$  (100 mm. tube). The mother substance of the whole series of compounds, namely, *nortricycloeksantalane*,  $C_{10}H_{16}$ , is obtained when the ozonide of santalol is distilled under reduced pressure, b. p. 57—59°/9 mm. or 183.5°/767 mm.,  $D^{20}_D$  0.885,  $n_D$  1.46856,  $\alpha_D - 11^\circ$ . Acids of low boiling point are also formed from the ozonide.

Most of these tricyclo-derivatives can be converted into dicyclic, unsaturated compounds. When a solution of *tricycloeksantalic acid* in methyl alcohol is saturated with hydrogen chloride and kept for some time the *methyl ester* of *hydrochlorodicycloeksantalic acid*,  $C_{12}H_{18}O_2 \cdot HCl$ , is formed, b. p. 154—156°/9—10 mm.,  $D^{20}_D$  1.101,  $n_D$  1.496,  $\alpha_D + 17^\circ$ . When boiled with alcoholic potassium hydroxide the ester yields *dicycloeksantalic acid*,  $C_{11}H_{16}O_2$ , m. p. 64°, b. p. 164—166°/9 mm.,  $[\alpha]_D - 41.81$  in alcoholic solution. The *methyl ester*,  $C_{12}H_{18}O_2$ , has b. p. 125—128°/9 mm.,  $D^{20}_D$  1.0191,  $n_D$  1.48809, and  $\alpha_D - 27^\circ$  (100 mm. tube). The dicyclic unsaturated nature of the acid follows (a) from its behaviour towards permanganate and ozone, both of these reagents readily react with the acid yielding acids of different boiling points, and (b) from its molecular refraction. When the methyl ester is reduced with sodium and alcohol, it yields *dicycloeksantalol*,  $C_{11}H_{18}O$ , b. p. 130—134°/9 mm.,  $D^{20}_D$  0.9791,  $n_D$  1.50051, and  $\alpha_D - 22^\circ$ .

*dicycloEksantalane*,  $C_{10}H_{15}Me$ , is obtained when *tricycloeksantalol* is treated with phosphorus pentachloride in light petroleum solution and the resulting chloride reduced with sodium and alcohol. *Eksantaly chloride* has b. p. 110—114°/10 mm.,  $D^{20}_D$  1.0083, and  $n_D$  1.47348. The hydrocarbon has b. p. 72—74°/10 mm.,  $D^{20}_D$  0.871, and  $n_D$  1.4774. The value of the molecular refraction agrees with that required for a dicyclic system.

*Chlorodihydronordicycloeksantalane*,  $C_{10}H_{17}Cl$ , is formed when *nortricycloeksantalane* is dissolved in methyl alcohol, the solution saturated with hydrogen chloride, and then kept for six hours. It has b. p. 93—96°/8—9 mm. and m. p. 63°. With alcoholic potassium hydroxide it yields *nordicycloeksantalane*, b. p. 62—64°/9 mm. or 186—189°/760 mm.,  $D^{20}_D$  0.8827,  $n_D$  1.4779, and  $\alpha_D - 19^\circ$ . The same hydrocarbon appears to be formed when *tricycloeksantalic acid* is heated with concentrated hydrochloric acid at 180°. *tricycloEksantalic acid*, when treated with 50% sulphuric acid, yields the dicyclic acid together with a *lactone*,  $C_{11}H_{16}O_2$ , b. p. 153—154°/10 mm., and m. p. 102°.

When santalol is heated with alcoholic potassium hydroxide at 160° for two hours the molecule is ruptured at the double bond in the side-chain and the tricyclic system is converted into a dicyclic, the resulting product being *dicycloeksantalol*. When *tricyclosantalol* is treated with a methyl alcoholic solution of hydrogen chloride the product appears to be an *O-methyl ether*, b. p. 145—160°/10 mm.,  $D^{20}_D$  0.958,  $n_D$  1.496, and  $\alpha_D - 30^\circ$ . A *dicyclosantalol* is formed when *tricyclosantalol* is warmed at about 45° with acetic acid and a little concentrated sulphuric acid, it has b. p. 155—175°/10 mm.,  $D^{20}_D$  0.981,  $n_D$  1.5179, and  $\alpha_D - 28^\circ$ .

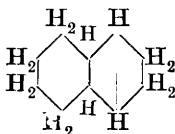
When the methyl ester of *hydrochlorodicycloeksantalic acid* is

reduced with sodium and alcohol, *dihydrodicycloeksantalic acid*,  $C_{11}H_{18}O_2$ , b. p. 166—169°/10 mm. and m. p. 58°, is obtained. The corresponding *methyl ester* has b. p. 127—132°/9 mm.,  $D^{20}_D$  1.009, and  $n_D$  1.48131. *Dihydrodicycloeksantalol*,  $C_{11}H_{20}O$ , obtained by reducing the ester, has b. p. 128—133°/10 mm.,  $D^{20}_D$  0.9724, and  $n_D$  1.492.

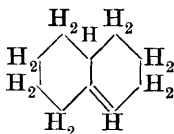
J. J. S.

**Constituents of Essential Oils.** FRIEDRICH W. SEMMLER (*Ber.*, 1907, 40, 1120—1124).—Attention is drawn to the need of exercising great care in applying molecular refraction data to the elucidation of the constitution of natural products. Dicyclic derivatives usually have a higher value than the theoretical. Santalol and its derivatives probably contain a tricyclic system. Santalol itself,  $C_{15}H_{24}O$ , contains a side-chain of 5-carbon atoms, including a double valency and a primary alcoholic group. When oxidised it yields tricyclic eksantalic acid,  $C_{11}H_{16}O_2$ , from which a hydrocarbon,  $C_{10}H_{16}$ , can be obtained by the elimination of carbon dioxide. The molecular increments of these compounds are somewhat less than those required for a dicyclic system with a double valency. When heated with mineral acids they are converted into isomeric compounds the increments of which correspond exactly with those required for a dicyclic system with a double valency. Hence the original compounds presumably contained a tricyclic system.

The formulæ suggested for the two hydrocarbons,  $C_{10}H_{16}$ , are

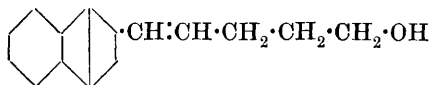
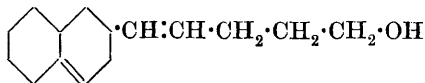


Nortricycloeksantalan.



Nordicycloeksantalan.

and similarly for the santalols,

*tricyclo*Santalol.*dicyclo*Santalol.

as the boiling points and sp. gr. of *nordicycloeksantalan* are identical with those of octahydronaphthalene, although, so far, it has not been possible to obtain naphthalene or any of its derivatives from the hydrocarbon  $C_{10}H_{16}$ .

J. J. S.

**Caoutchouc Nitrosite and its Use for the Analysis of Crude Caoutchoucs and Caoutchouc Products.** PAUL ALEXANDER (*Ber.*, 1907, 40, 1070—1078. Compare *Abstr.*, 1905, i, 223).—The product obtained by the action of nitrous fumes (prepared from starch and nitric acid,  $D$  1.4) on caoutchouc has the composition C 44.92, H 5.37,

N 11.67, independently of the source, agreeing with the formula  $C_9H_{12}O_6N_2$ , and not identical with Harries's nitrosite,  $C_{10}H_{15}O_7N_3$  (Abstr., 1905, i, 223). The same compound was obtained previously by the action of the nitrous decomposition products of lead nitrate (*loc. cit.*). This is the first  $C_9$  derivative of caoutchouc, and, on the basis of Harries's dimethylcyclooctadiene caoutchouc formula, a carbon atom must have been eliminated during the reaction. This was identified as carbon dioxide; probably the methyl groups of caoutchouc are oxidised to carboxyl which is eliminated from that carbon to which both nitro- and carboxyl groups are attached, forming 5 : 6-dinitro-cyclooctene-1-carboxylic acid,  $NO_2 \cdot CH < \begin{matrix} CH_2 \cdot CH_2 \\ CH(NO_2) \cdot CH_2 \cdot CH_2 \end{matrix} \text{---} CH > CH \cdot CO_2H$ . This nitrosate closely resembles Harries's nitrosite (*loc. cit.*), but decomposes at 90—110°.

One gram of caoutchouc, purified by exhaustive extraction with acetone, yields about 2.1 grams of nitrosate, whereas 1 gram of vulcanised caoutchouc gives rise to 2.4 grams of sulphur free nitrosate.

The observations made with caoutchoucs of different origin show them all to contain a hydrocarbon,  $C_{10}H_{16}$ , but that the extent to which this is polymerised probably varies with different natural products.

An additive product of caoutchouc with picric acid could not be prepared. E. F. A.

**Albans from Ficus Vogelii.** DAVID SPENCE (*Ber.*, 1907, 40, 999—1000).—The genetic relationship of the sugar-like substances to caoutchouc and the gums having been suggested by Tschirch, it seemed probable that intermediate substances might be found in the resins. From this point of view the author has investigated the resin obtained by extraction of the caoutchouc of *Ficus Vogelii* with boiling acetone. On repeated recrystallisation of the resin from absolute alcohol, two isomeric substances,  $C_{16}H_{26}O$ , m. p. 201—205° and 154°, are obtained. These are neutral to acids or alkalis and are not attacked by alcoholic potassium hydroxide. In agreement with Tschirch's nomenclature (Abstr., 1905, i, 452), the names  $\alpha$ - and  $\beta$ -alban are suggested. G. Y.

**Linamarin, the Cyanogenetic Glucoside of Flax.** ARMAND JORISSEN (*Bull. Acad. roy. Belg.*, 1907, 12—17. Compare Jorissen, Abstr., 1885, 181, with Hairs, Abstr., 1892, 502; Dunstan and Henry, Abstr., 1904, ii, 71, and with Auld, Abstr., 1906, ii, 794).—Dunstan, Henry, and Auld (*loc. cit.*) have shown that the cyanogenetic glucoside (phaseolunatin) contained in the beans of *Phaseolus lunatus* is identical with the linamarin which Jorissen and Hairs isolated from the embryo flax plants, and have suggested that the name linamarin should be superseded by phaseolunatin. The author claims that as the flax glucoside was isolated and described by him sixteen years ago the name linamarin should be adhered to. Attention is also directed to Kohn-Abrest's statement (Abstr., 1906, ii, 625) that the beans of *Phaseolus lunatus* contain more than one cyanogenetic glucoside (see, however, Dunstan and Henry, *Ann. Chim. Phys.*, 1907, [viii], 10, 118). T. A. H.

**Natural Colouring Matters.** LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1907, 3, 287—306).—1. *Bixin* [with LADISLAUS MATEJKO] (compare Abstr., 1906, i, 760). 2. *Constituents of the Root of Datisca Cannabina* [with A. KORCZYŃSKI] (compare Schunck and Marchlewski, Abstr., 1904, i, 142, 340).—Datiscetin has the composition  $C_{15}H_{10}O_6$ , and after repeated crystallisation from glacial acetic acid has m. p. 268—269°. It contains no methoxy-groups, does not reduce Fehling's solution, but readily reduces an ammoniacal solution of silver nitrate. A *tetra-acetyl* derivative,  $C_{15}H_6O_6Ac_4$ , is readily obtained by Liebermann's method. It crystallises from ether in colourless needles, m. p. 138°. The *tetrabenzoyl* derivative, obtained by the action of benzoyl chloride in the presence of pyridine, crystallises from dilute acetone in colourless needles, m. p. 190—191°. The *tetrabenzenesulphonyl* derivative,  $C_{15}H_6O_6(SO_2Ph)_4$ , crystallises from glacial acetic acid in needles, m. p. 188°. When the glucoside datiscin is hydrolysed with dilute sulphuric acid, datiscetin and dextrose (not rhamnose) are formed. The formula  $C_{21}H_{20}O_{11}, H_2O$  is suggested for the glucoside.

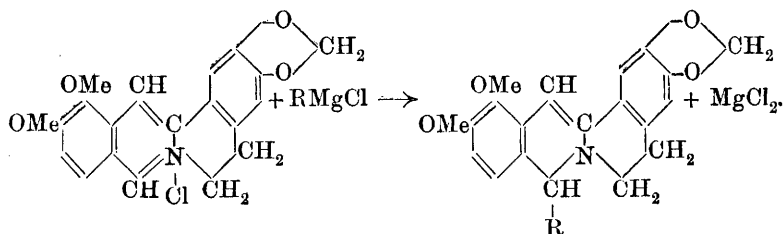
3. *Chlorophyll* [with P. KOZŃIEWSKI] (compare Willstätter, this vol., i, 69, 71).—Chlorophyll which has been completely freed from *allochlorophyll* and *lipochrome* yields *phyllocyanin* and *phylloxanthin* when its ethereal solution is shaken with concentrated hydrochloric acid, and hence both compounds are probably derived from the same substance. *Phylloxanthin* is not transformed into *phyllocyanin* when kept in contact with hydrochloric acid at the ordinary temperature.

J. J. S.

**Kamala and Rottlerin.** HANS TELLE (*Arch. Pharm.*, 1907, 245, 69—70).—A claim of priority against Thoms (*ibid.*, 244, 644) (compare Abstr., 1906, i, 973).

C. F. B.

**Preparation of Berberine Derivatives.** EMANUEL MERCK (D.R.-P. 179212).—The salts of berberine, when treated with the Grignard reagent, interact to form alkylidihydroberberines in accordance with the following diagram :



*Benzylidihydroberberine*, m. p. 161—162°, obtained from berberine chloride or cyanide by the action of magnesium benzyl chloride, crystallises in small, rhombic plates; *hydrochloride*, m. p. 165—166°. *Phenylidihydroberberine*, m. p. 194—195°, forms brownish-yellow plates with pointed ends. *Methylidihydroberberine*, yellow crystals, m. p. 134°, was prepared from berberine chloride and magnesium methiodide; *hydriodide*, pale yellow leaflets, m. p. 249°. The following bases were

similarly obtained: *ethyl dihydroberberine*, leaflets, m. p. 164—165°; *hydriodide* decomposes at 223°; *propyldihydroberberine*, leaflets, m. p. 132°, hydriodide decomposing at 207°. G. T. M.

**Carnosine and Ignotine.** WLADIMIR VON GULEWITSCH (*Zeit.-sch. physiol. Chem.*, 1907, 51, 258—260. Compare Abstr., 1900, i, 516; this vol., i, 264)—Polemical, a reply to Kutscher (this vol. i, 337).

W. D. H.

**Solubility and Melting Point of Morphine.** EDWARD J. GUILD (*Pharm. J.*, 1907, [iv], 24, 357).—Many of the values recorded for the solubility of morphine are much too high, probably on account of the presence of traces of codeine in the samples tested. Determinations of the solubility of a specimen of morphine, which had been crystallised from alcohol and subsequently washed with alcohol and ether, showed that the hydrated alkaloid,  $C_{17}H_{19}O_3N \cdot H_2O$ , is soluble in water to the extent of about 1 in 5200. The electrical conductivity of the solution is considerably greater than that of pure water. The m. p. of morphine is of no value as a test of purity. The anhydrous alkaloid gradually darkens above 225° and melts to a dark brown tar at 245—250°; this decomposition is not attended by any loss in weight. E. G.

**Brucine Oxide.** AMÉ PICTET and G. JENNY (*Ber.*, 1907, 40, 1172—1175).—*Brucine oxide*,  $C_{23}H_{26}O_5N_2 \cdot 4\frac{1}{2}H_2O$ , m. p. 124—125° (anhydrous, 199° decomp.), obtained in a similar manner to strychnine oxide (Abstr., 1905, i, 816), forms large, colourless, rhombic prisms [ $a : b : c = 0.54673 : 1 : 0.44734$ ]. The aqueous solution has a neutral reaction, an intensely bitter taste, and  $[\alpha]_D^{25} - 1.63^\circ$ . The colour reactions of the oxide are like those of brucine itself. In the crude state the oxide develops a blue coloration in starch potassium iodide solution, but loses this property after repeated crystallisation from water; the same is true of strychnine oxide. The physiological action of brucine oxide is less pronounced than that of the alkaloid.

The oxide, which is reconverted into brucine by sulphurous acid, behaves as a monoacid base; the salts are lævorotatory in aqueous solution and are changed by sulphurous acid into the salts of brucine. The *hydrochloride*,  $C_{23}H_{26}O_5N_2 \cdot HCl \cdot H_2O$ , m. p.  $> 300^\circ$ ,  $[\alpha]_D^{25} - 13.95^\circ$ ; *platinichloride*,  $(C_{23}H_{26}O_5N_2)_2 \cdot H_2PtCl_6$ ; *nitrate*,  $C_{23}H_{26}O_5N_2 \cdot HNO_3 \cdot H_2O$ ,  $[\alpha]_D^{30} - 11.36^\circ$ ; *hydrogen sulphate*, and the *picrate* are mentioned.

C. S.

**Researches on the Hydroxypyrroles.** ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 271—275. Compare Abstr., 1904, i, 526; this vol., i, 153).—In continuation of the study of the action of nitrous acid on indoles and pyrroles (*loc. cit.*), the authors are investigating the behaviour towards this acid of derivatives in which the iminic hydrogen is replaced by hydroxyl. The present paper contains an account of the results obtained with 1-hydroxy-2:5-dimethylpyrrole.

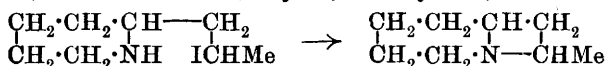
3-Nitroso-1-hydroxy-2:5-dimethylpyrrole, obtained by the action of sodium ethoxide and amyl nitrite on 1-hydroxy-2:5-dimethylpyrrole, exhibits behaviour best explained by the tautomeric structure

$\text{NO} \leq \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CMe} \cdot \text{C} \cdot \text{NOH} \end{smallmatrix}$ ; it crystallises from ether in long, orange-coloured needles which begin to decompose without melting at about  $80^\circ$  and dissolves readily in alcohol or water and sparingly in benzene. This compound is characterised by the ease with which it undergoes hydrolysis accompanied by opening of the ring; different hydrolytic reagents yield various products, which are, however, all simply related to the original substance. In every case the final product of hydrolysis is the dioxime of a trione,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CMe}(\text{N} \cdot \text{OH})$ , which could not be isolated.

In presence of hydroxylamine, however, the corresponding trioxime,  $\text{OH} \cdot \text{N} : \text{CMe} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH}_2 \cdot \text{CMe} : \text{N} \cdot \text{OH}$  (compare Angeli, Angelico, and Calvello, Abstr., 1904, i, 188, 447), is obtained. This trioxime readily loses water, yielding the *anhydride*,  $\text{OH} \cdot \text{N} : \text{CMe} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{N} \\ \text{N} - \text{O} \end{smallmatrix}$ , which crystallises from water in colourless needles, m. p.  $83^\circ$ , and gives a *benzoyl* derivative,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_3\text{Bz}$ , crystallising from a mixture of benzene and light petroleum in needles, m. p.  $106^\circ$ .

3-Nitroso-1-hydroxy-2:5-dimethylpyrrole yields a *benzoyl* derivative,  $\text{C}_{20}\text{H}_{18}\text{O}_5\text{N}_2$ , which crystallises from alcohol in shining, colourless plates, m. p.  $169^\circ$ . When boiled with 25% sulphuric acid, the sodium derivative of the nitrous compound is converted into the compound  $\text{C}_6\text{H}_8\text{O}_2\text{N}_2$ , m. p.  $117^\circ$  (compare Angelico and Calvello, Abstr., 1904, i, 447).  
T. H. P.

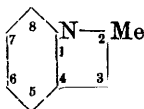
**2-Ethylconidine and some Piperidine Bases.** KARL LÖFFLER and PHILLIP PLÖCKER (*Ber.*, 1907, 40, 1310—1324).—It has previously been shown that 2- $\beta$ -iodopropylpiperidine, when warmed with sodium hydroxide, forms a saturated, dicyclic, tertiary base, thus:



The latter base resembles Hofmann's " $\epsilon$ -coniceine," prepared from the iodoconine, obtained by heating conhydrine with fuming hydriodic acid, Hofmann's base being, however, optically active. It is accordingly suggested that conhydrine and 2- $\beta$ -iodopropylpiperidine are identical in structure.

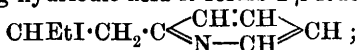
It is shown that dicyclic compounds, containing both a 4- and a 6-ring, may also be obtained from 2- $\beta$ -hydroxybutylpiperidine and 2- $\omega$ -hydroxyisopropylpiperidine respectively.

With regard to the nomenclature of this new type of compound, the base, obtained from 2- $\beta$ -hydroxypropylpyridine, is termed 2-methylconidine (see annexed scheme).

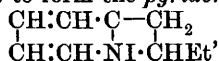


2- $\beta$ -Hydroxybutylpyridine, obtained by heating  $\alpha$ -picoline, water, and propaldehyde for eighteen to twenty hours at  $160$ — $170^\circ$ , has b. p.  $124$ — $126^\circ/14$  mm. (Matzdorff gives b. p.  $125$ — $127^\circ/18$  mm.). When

heated with fuming hydriodic acid it forms 2- $\beta$ -iodobutylpyridine,



it forms a yellow oil which in alcoholic solution undergoes intramolecular rearrangement to form the *pyridonium iodide*,



m. p. 153—154°.

2-*β*-Hydroxybutylpyridine,  $\text{OH}\cdot\text{CHET}\cdot\text{CH}_2\cdot\text{CH}\langle\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{NH}-\text{CH}_2 \end{array}\rangle\text{CH}_2$ , obtained by the reduction of 2-*β*-hydroxybutylpyridine by sodium and ethyl alcohol, boils at 125—130°/15 mm., and has m. p. 46—55°. Since two racemic forms are possible, owing to the reduction, the product probably contains a little of the stereoisomeride. It was converted into its iodide by heating with fuming hydriodic acid and red phosphorus for eight hours at 140°; the crude iodide, obtained as an oil, was then heated with concentrated aqueous potassium hydroxide (1:1), when 2-ethylconidine,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{N}-\text{CHET} \end{array}$ , was obtained; the latter was purified by crystallisation of its picrate (m. p. 198°); it has b. p. 176—183° and  $D_4^{15}$  0.8991; it is possibly mixed with a diastereoisomeride. The *aurichloride* has m. p. 132—135°; the *platinichloride* has m. p. 205—210 (decomp.); the *mercurichloride* separates in prisms, m. p. 220—221°; the *ethiodide* has m. p. 222° (decomp.).

2-*β*-Hydroxybutylpyridine, obtained by the condensation of *n*-propaldehyde with  $\alpha$ -picoline, was heated with concentrated sulphuric acid and glacial acetic acid for six hours at 160—165°; a product was obtained, b. p. 190—210°, containing butenylpyridine, which was identified by means of its platinichloride, m. p. 140—150° (decomp.) (Matzdorff gives 140°); the *aurichloride* has m. p. 154—156° (decomp.); the *picrate* has m. p. 154°, and the *mercurichloride*, m. p. 93—94°. The yield of butenylpyridine was small.

2-*β*-Hydroxybutylpyridine was converted into 2-butylpyridine, according to Willstätter's method, the hydroxy-group being first replaced by iodine and the resulting iodide then reduced by zinc dust in acid solution. *α*-Butylpyridine picrate has m. p. 94° and serves for the purification of the free base,  $\text{C}_9\text{H}_{13}\text{N}$ , which is a transparent oil with b. p. 189—192° and  $D_4^{15}$  0.9135; the *aurichloride* has m. p. 85°; the *platinichloride*, m. p. 144—145°, and the *mercurichloride*, m. p. 102°.

When 2-*β*-hydroxybutylpyridine was heated in a bomb-tube with fuming hydrobromic acid and red phosphorus for eight hours at 130—140°, 2-*β*-bromobutylpyridine was obtained; it undergoes molecular rearrangement into the pyridonium bromide, m. p. 135—140°, a syrup, which was identified by its conversion into the pyridonium chloride (*supra*) by agitating it with freshly-precipitated silver chloride.

When the product of the bromination of 2-*β*-hydroxybutylpyridine was reduced by zinc dust and hydrochloric acid, 2-butylpyridine was not obtained, but a base with b. p. 197°, and unsaturated, since it reduces permanganate; it forms a *platinichloride*,  $(\text{C}_9\text{H}_{11}\text{N}, \text{HCl})_2\text{PtCl}_4$ , with m. p. 162—163° (decomp.); a *picrate* with m. p. 153°; an *aurichloride* with m. p. 130°, and a *mercurichloride* with m. p. 120—130°. The substance is not identical with butenylpyridine.

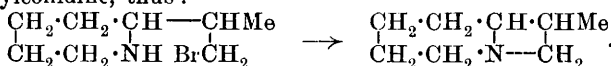


*2-Butylpiperidine*,  $C_{19}H_{19}N$ , obtained by the reduction of 2-butylpyridine with sodium and ethyl alcohol, is a transparent, mobile liquid with b. p.  $186-189^\circ$  and  $D^{15}_4$  0.8529. It has an odour resembling that of couine. Its *hydrochloride* has m. p.  $181-182^\circ$  and its *platinichloride*, m. p.  $137-140^\circ$ .

Attempts were made to resolve 2-butylpiperidine into its optically active components. When the *dl*-base was neutralised by *d*-tartaric acid, the crop obtained yielded a base with  $\alpha_D + 6.537^\circ$  ( $l=1$ ) and  $D$  0.8512. On further treatment of this product, a base having  $\alpha_D + 13.41^\circ$  ( $l=1$ ) was obtained, but the purification of the *d*-base was not further effected. A *platinichloride* was obtained, having m. p.  $131-132^\circ$ . A *laevorotatory* base, having  $\alpha_D - 15.96^\circ$  ( $l=1$ ) and  $D$  0.8533, was obtained by decomposing the mother liquor from the previous crystallisation of the *d*-base *d*-tartrate and neutralising the *laevorotatory* product with *l*-tartaric acid.

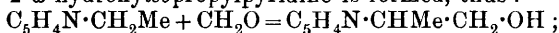
A. McK.

**3-Methylconidine and some Pyridine Bases.** KARL LÖFFLER and ALFRED GROSSE (*Ber.*, 1907, 40, 1325—1336. Compare preceding abstract).—2-*ω*-Hydroxyisopropylpiperidine may be converted into 3-methylconidine, thus:

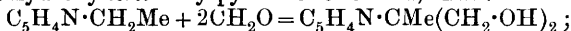


Attempts to obtain 2-ethylpyridine by heating 2- $\beta$ -hydroxyethylpyridine with concentrated hydrochloric acid and glacial acetic acid in order to form  $\alpha$ -vinylpyridine, which could then be reduced, were unsuccessful. 2-Ethylpyridine was obtained by heating 2- $\beta$ -hydroxyethylpyridine with fuming hydrobromic acid and phosphorus in a bomb-tube at  $135^\circ$  for ten to twelve hours and then reducing by zinc dust and acid, according to Willstätter's method.

When formaldehyde acts on 2-ethylpyridine, three reactions take place: (1) 2- $\omega$ -hydroxyisopropylpyridine is formed, thus:



(2) 2-di- $\omega$ -hydroxy-*tert.*-butylpyridine is formed, thus:



(3) 2- $\alpha$ -methylvinylpyridine is formed by the elimination of water from 2- $\omega$ -hydroxyisopropylpyridine, thus:  $C_5H_4N \cdot CHMe \cdot CH_2 \cdot OH = H_2O + C_5H_4N \cdot CMe \cdot CH_2$ .

2-Di- $\omega$ -hydroxy-*tert.*-butylpyridine has b. p.  $168-171^\circ/13$  mm.; its *picrate* has m. p.  $116-117^\circ$ ; its *aurichloride*, m. p.  $125-126^\circ$ , and its *platinichloride*, m. p.  $153-155^\circ$ .

2- $\alpha$ -Methylvinylpyridine has b. p.  $170-173^\circ$ , has an odour reminiscent of 2-vinylpyridine, is unsaturated, has  $D^{15}_4$  0.9706; its *aurichloride* has m. p.  $135^\circ$ ; its *platinichloride*, m. p.  $163-164^\circ$ , and its *picrate*, m. p.  $148-149^\circ$ . When reduced by alcohol and sodium, it is converted into Ladenburg's isopropylpiperidine.

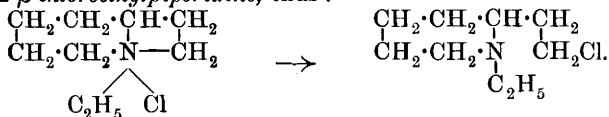
2-*ω*-Iodoisopropylpyridine,  $CH_2I \cdot CHMe \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{N} - \text{CH} \end{smallmatrix} \text{CH}$ , obtained by heating 2- $\omega$ -hydroxyisopropylpyridine in a bomb-tube for ten hours at  $130-135^\circ$  with fuming hydriodic acid and red phosphorus, is an oil which was characterised by its *platinichloride*, m. p.  $142-145^\circ$  (decomp.),

h h 2



white powder by the action of alkali on the preceding compound, but owing to its hygroscopic nature was not analysed. When agitated with freshly-precipitated silver chloride, it was converted into conidine ethochloride, from which the *platinichloride*,  $(C_9H_{13}NCl)_2PtCl_4$ , was obtained, m. p.  $178^\circ$  (decomp.).

When the ethochloride is heated at  $170^\circ$ , ethyl chloride is not eliminated, but the four-membered ring is broken with the formation of 1-ethyl-2- $\beta$ -chloroethylpiperidine, thus :



The latter compound has  $D^{15}_D$  0.9964, forms a *platinichloride* with m. p.  $168-170^\circ$ , and an *aurichloride* with m. p.  $109-110^\circ$ .

When 1-ethyl-2- $\beta$ -chloroethylpiperidine is allowed to remain at the ordinary temperature for a long time, an oil separates, the four-membered ring is again closed, the chlorine atom attaching itself to nitrogen; the *platinichloride*,  $(C_9H_{13}NCl)_2PtCl_4$ , obtained from this product has, however, the m. p.  $192-193^\circ$  and not  $178^\circ$  as might have been expected. The latter curious observation may be due to dimorphism or may be interpreted in the light of Ladenburg's theory of tervalent asymmetric nitrogen.

A. McK.

**Resolution of Phenyl- $\alpha$ -picolylalkine [2- $\beta$ -Hydroxy- $\beta$ -phenylethylpyridine] into its Optically-active Components.** KARL LÖFFLER and HERBERT GRUNERT (*Ber.*, 1907, 40, 1342—1347).—2- $\beta$ -Hydroxy- $\beta$ -phenylethylpyridine was first obtained by Roth (*Abstr.*, 1907, i, 165) by heating benzaldehyde,  $\alpha$ -picoline, and water in a sealed tube at  $135^\circ$ . The modification of this method, as described by Bach (*ibid.*, 610), who conducted the heating at  $160^\circ$ , was found unsuitable by the authors, who obtained stilbazole as the main product at this temperature. Several of the data given by Roth and Bach are inaccurate.

2- $\beta$ -Hydroxy- $\beta$ -phenylethylpyridine, obtained by Roth's method, separates from water in glistening leaflets, m. p.  $107-108^\circ$  (Roth gives  $96-97^\circ$ ). The *platinichloride* has m. p.  $174-175^\circ$  (Roth gives  $170-172^\circ$ ); the *aurichloride* has m. p.  $141-142^\circ$  (Roth gives  $131-132^\circ$ ); the *hydrobromide* separates from water in silky needles, m. p.  $80-81^\circ$ ; the *picrate* has m. p.  $123-124^\circ$ .

An attempt to resolve 2  $\beta$ -hydroxy- $\beta$ -phenylethylpyridine into its optically active components by means of *d*-tartaric acid failed, the hydrogen *d*-tartrate obtained apparently being partially racemic. The base was resolved by means of Reyehler's *d*-camphorsulphonic acid. 1-2- $\beta$ -Hydroxy- $\beta$ -phenylethylpyridine, obtained from the more sparingly soluble camphorsulphonate, has  $[\alpha]_D^{25} -36.44^\circ$  in chloroform solution and m. p.  $128-129^\circ$ . Its *platinichloride* has m. p.  $163^\circ$  and its *aurichloride*, m. p.  $138^\circ$ .

The preparation of the pure *d*-base was not successful.

This is the first case of the resolution of an alkine into its optical antipodes.

A. McK.

**Colour Phenomena in Alkaline Isatin Solutions.** GUSTAV HELLER [and, in part, OTTO NÖTZEL] (*Ber.*, 1907, 40, 1291—1300. Compare Heller and Mayer, *Abstr.*, 1906, i, 585; Peters, this vol., i, 239, and following abstract).—The constitutions of the metallic derivatives of isatin and the causes underlying the changes of colour observed in alkaline solutions of isatin are discussed. Sodioisatin, formed by the action of sodium ethoxide on isatin, is considered to be an *N*-derivative,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO}^- \\ \text{N} \end{smallmatrix}\text{Na}\rangle\text{CO}$ , as it yields *N*-benzoylisatin with benzoyl chloride at the laboratory temperature, and *N*-methyl- and *N*-ethyl-isatins with methyl and ethyl iodides respectively at 100°. When dissolved in water, this sodium derivative undergoes the same changes of colour as are observed on dissolving isatin in an aqueous alkali, the solution which is at first violet-red gradually becoming yellow. This change, which is accelerated by heat and by addition of an excess of the alkali, results in the formation of sodium isatoate; it is probable that the *O*-sodium derivative,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{N} \end{smallmatrix}\rangle\text{C}\cdot\text{ONa}$ , is formed as an intermediate product of the change. Conversely, sodium isatoate is converted into isatin by the action of hydrochloric acid.

When treated with aqueous silver nitrate, *N*-sodium isatin yields the *O*-silver derivative, which with methyl iodide forms *O*-methylisatin (von Baeyer and Oeconomides, *Abstr.*, 1883, 201). This reacts readily at the ordinary temperature with aniline, forming  $\alpha$ -isatinanilide (Sandmeyer, *Abstr.*, 1903, i, 486), which with an excess of aniline forms the dianil readily at the moment of its formation, but after isolation only when heated with aniline. With phenylhydrazine, *O*-methylisatin forms isatinphenylhydrazone,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix}\rangle\text{C:N}\cdot\text{NHPh}$ , which is formed also by the action of the hydrazine on  $\alpha$ -isatinanilide and is identical with benzeneazoindoxyl (von Baeyer, *Abstr.*, 1884, 74).

When heated with iodine and ether at 100°, *N*-sodium isatin yields an unstable, blue compound, which is decomposed by hot water, forming isatin and iodine.

Isatindianil,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C(NPh)} \\ \text{NH} \end{smallmatrix}\rangle\text{C:NPh}$ , crystallises from benzene in dark red prisms, m. p. 210°, is stable towards alkalis, but is hydrolysed by hydrochloric acid, forming isatin, and is decolorised by reducing agents, becoming again red on exposure to air.

The action of methyl iodide on silver isatoate leads to the formation of isatin and *N*-methylisatin. G. Y.

**Conductivity of *N*-Sodioisatin and Sodium Isatoate in Aqueous Solution.** ERNST DEUSSEN, GUSTAV HELLER, and OTTO NÖTZEL (*Ber.*, 1907, 40, 1300—1303. Compare preceding abstract).—The change of *N*-sodioisatin in aqueous solution into sodium isatoate, and the conversion of sodium isatoate into isatin and sodium chloride by the action of hydrochloric acid are accompanied by corresponding changes in the conductivities of the solutions. The conductivity measurements were carried out at 25°.

Three minutes after formation, a 0.5% solution of *N*-sodium isatin

has the specific conductivity  $\chi.10^2 = 0.244$ , and after 230 minutes,  $\chi.10^2 = 0.209$ ; this final specific conductivity is identical with that of a solution of sodium isatoate of corresponding strength. The curve representing the change does not permit of any conclusion as to the intermediate formation of *O*-sodium isatin. Sodium isatoate has the molecular conductivity  $\mu = 64.1, 68.4, 71.1$ , and  $77.5$ , with  $v = 10, 20, 40$ , and  $80$  respectively. These values are compared with those obtained for sodium *o*-aminobenzoate:  $\mu = 66.5, 68.0$ , and  $71.4$ , with  $v = 32, 64$ , and  $128$  respectively.

On addition of 5 c.c. *N*/10 hydrochloric acid to a solution of 0.0935 gram of sodium isatoate in 20 c.c. of water, the yellow solution gradually becomes red and after some time isatin commences to separate. After two minutes the solution has the conductivity  $\chi.10^2 = 0.630$ , and, after twenty-eight and a quarter hours,  $\chi.10^2 = 0.287$ . From this the specific conductivity of isatoic acid is calculated as  $\chi.10^2 = 0.41$  with  $v = 50$ , and its degree of dissociation as  $\alpha = \mu_v/\mu_\infty = 0.54$ .

G. Y.

**Preparation and Properties of 3-Methylcinchonic and 2-Hydroxy-3-methylcinchonic Acids.** G. ORNSTEIN (*Ber.*, 1907, 40, 1088—1095).—As both of these acids contain a methyl group and a benzene nucleus contiguous to the carboxyl group, it was expected that they would conform to V. Meyer's esterification rule, and the author's experiments confirm this.

3-Methylcinchonic acid was obtained by heating isatin, propaldoxime, and potassium hydroxide for twelve to sixteen hours on the water-bath (von Miller, *Abstr.*, 1890, i, 325). Its *hydrochloride* crystallises in needles, m. p.  $240-241^\circ$ ; the *picrate* in yellow needles, m. p.  $222-223^\circ$ ; the *platinichloride* is a yellow powder, and the *sodium* and *silver* salts are white powders. On heating the silver salt it decomposes, giving 3-methylquinoline (*Abstr.*, 1885, 1079). The esters are obtained by heating the silver salt and alkyl iodide in a sealed tube at  $100-150^\circ$  for five hours. The *ethyl* ester does not crystallise; its *picrate*, m. p.  $175-176^\circ$ , and its *platinichloride* m. p.  $224-225^\circ$ ; the *methyl* ester is a white powder which does not react with ammonia. The *chloride*,  $C_{11}H_8ONCl$ , prepared by heating the acid with thionyl chloride in a closed tube at  $100^\circ$  for five hours, crystallises in white needles, and the *amide*,  $C_{11}H_{10}ON_2$ , obtained from its benzene solution and ammonia, forms white needles, m. p.  $228-229^\circ$ , stable towards 15% potassium hydroxide, but hydrolysed by nitrous acid. The *anilide*,  $C_{17}H_{14}ON_2$ , forms white flakes, m. p.  $238-239^\circ$ .

2-Hydroxy-3-methylcinchonic acid (Meyer, *Abstr.*, 1906, i, 108) was obtained by fusing methylcinchonic acid and potassium hydroxide; the *sodium* and *silver* salts are white. 2-*Chloro-3-methylcinchonic chloride*,  $C_6H_4 \begin{smallmatrix} C(COCl):CMe \\ \parallel \\ N=CCl \end{smallmatrix}$ , m. p.  $52^\circ$ , crystallises in yellow, prismatic needles and yields 2-*chloro-3-methylcinchonic acid*,  $C_{11}H_8O_2NCl$ , when heated with water. It forms small, white needles, m. p.  $191-192^\circ$ . When heated in a sealed tube at  $120^\circ$  with water, chlorine is removed and 2-hydroxy-3-methylcinchonic acid is regenerated. 2-*Chloro-3-methylcinchonamide*,  $C_{11}H_9ON_2Cl$ , crystallises in

white needles, m. p. 270—271°; the *anilide*,  $C_{17}H_{18}ON_2Cl$ , forms white flakes, m. p. 267—268°. *Methyl 2-chloro-3-methylcinchonate*,  $C_{12}H_{10}O_2NCl$ ,

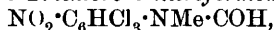
prepared from the chloride, crystallises in white needles, m. p. 78—79°. *Methyl 2-methoxy-3-methylcinchonate*,  $C_{13}H_{18}O_3N$ , obtained by heating the chloride in a sealed tube at 100° for two hours, forms white needles, m. p. 184—185°. All experiments to hydrolyse these esters, or to prepare the free acid, were without result. Heating the 2-methoxy-ester at 180° with water resulted in replacement of the methoxyl group by hydroxyl, and the amide and anilide of 2-hydroxy-3-methylcinchonic acid could also be obtained by heating the corresponding derivatives of chloromethylcinchonic acid with water at 180°; the *amide*,  $C_{11}H_{10}O_2N_2$ , m. p. 353—354°; the *anilide*,  $C_{17}H_{14}O_2N_2$ , has m. p. 314—315°. *2-Anilino-3-methylcinchonic anilide*,  $C_{23}H_{19}ON_3$ , prepared by heating the chloride and aniline at 200°, forms white crystals, m. p. 322—323°.

3-Methylcarbostyryl,  $C_{10}H_9ON$ , obtained by heating silver hydroxy-methylcinchonate in a current of carbon dioxide, crystallises from acetone in glistening needles, m. p. 234—235°, and 2-chloro-3-methylquinoline,  $C_{10}H_8NCl$ , obtained by heating the carbostyryl with phosphorus pentachloride at 130—140°, forms crystals, m. p. 89—90°.

W. R.

**Preparation of Chlorinated Amidines.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 178299).—2:4:5-*Trichloro-6-nitroacetanilide*, m. p. 194°, obtained by nitrating 2:4:5-trichloroacetanilide, m. p. 186—187°, when reduced with iron and dilute acetic acid in the presence of toluene, yields *acetyl-2:4:5-trichloro-o-phenylenediamine*, m. p. 200°, and the more soluble 2:4:5-trichlorophenylethylenylamidine, m. p. 285°. The product consists entirely of the latter substance when the mixture is heated either alone at 200—290° or with glacial acetic acid at 100°.

2:4:5-*Trichloro-6-nitroformanilide*, m. p. 164°, obtained from 2:4:5-trichloroformanilide, m. p. 172—173°, yields 2:4:5-trichlorophenylmethenylamidine, m. p. 303—304°, and *formyl-2:4:5-trichloro-o-phenylenediamine*, m. p. 306°; the latter base, on melting, changes into the former. 2:4:5-*Trichloro-6-nitroformomethylanilide*,



m. p. 124—125°, yields on reduction 2:4:5-trichlorophenylmethylmethenylamidine, m. p. 159—160°, and *formyl-2:4:5-trichloromethyl-o-phenylenediamine* having the same melting point. 2:4:5-*Trichloro-6-nitroacetoethylanilide*, m. p. 87—89°, furnishes on reduction a mixture of diamine and amidine, which on heating with glacial acetic acid gives the *acetate*, m. p. 98—99°, of the amidine, and this substance on heating at 100° yields the free 2:4:5-trichlorophenylethylenylamidine, m. p. 116—117°.

*Tetrachloro-o-nitroacetanilide* gives an *acetyl-o-diamine*, m. p. 223—224°, and *tetrachlorophenylethylenylamidine*, m. p. 300°.

*Tetrachloro-o-nitroacetoethylanilide* furnishes an *acetyl-o-diamine*, m. p. 203—204°, and *tetrachlorophenylethylenylamidine*, m. p. 149°.

*Tetrachlorobenzylenylamidine*, m. p. 176—177°, and *acetyltetra-*

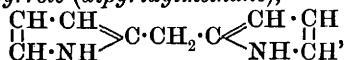
*chlorobenzyl-o-phenylenediamine*, m. p. 135—137°, are similarly produced from tetrachloro-*o*-nitroacetobenzylanilide.

*Benzoyl-2:4:5-trichloro-o-nitroaniline* on reduction gives *benzoyl-2:4:5-trichloro-o-phenylenediamine*, m. p. 205—207°, and this on distillation under reduced pressure furnishes *2:4:5-trichlorobenzyl-benzenylamidine*, m. p. 268—269°. G. T. M.

**Action of Formaldehyde and of Methylene Chloride on Pyrrole.** AMÉ PICTET and AUGUSTE RILLIET (*Ber.*, 1907, 40, 1166—1172).—When pyrrole is shaken with a cold 40% formaldehyde solution a vigorous reaction ensues and a hard, insoluble, dark red compound is formed. When a few drops of sulphuric acid are added to a mixture of pyrrole and 4% formaldehyde solution, a condensation product, *formaldehyde-pyrrole*,  $C_{11}H_{12}ON_2$ , is formed, which is insoluble in all the ordinary solvents. It has no definite melting point, changes in colour to red on exposure to the air, and turns black when heated with concentrated hydrochloric acid. When subjected to destructive distillation, it yields as chief product 2-methylpyrrole, and thus the condensation appears to be of the same type as that observed by Dennstedt and Zimmermann (*Abstr.*, 1886, 1043) in the case of paraldehyde and pyrrole. When the condensation product is distilled with zinc dust the chief product is  $\alpha$ -picoline.

When potassium pyrrole and methylene chloride are heated for two hours at 120—130° (compare Ciamician and Dennstedt, *Abstr.*, 1881, 826), a mixture of two condensation products is obtained which may be separated by means of their different solubilities in alcohol. 1:1-*Methylenedipyrrole*,  $CH_2(C_4NH_4)_2$ , crystallises from alcohol in colourless needles, m. p. 112°, is insoluble in cold water, acids, or alkalis, and does not yield a potassium derivative.

2:2-*Methylenedipyrrole* (*dipyridylmethane*),

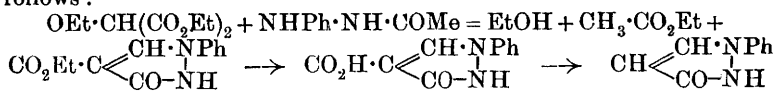


is readily soluble in alcohol, but crystallises from light petroleum in colourless plates or broad needles, m. p. 66°. It reacts vigorously with potassium, yielding a colourless solid, insoluble in ether. The 1:1-derivative is converted into the isomeric 2:2-derivative when heated for four hours at 300°.

Both compounds have been distilled through hot tubes in the hope of obtaining 2-pyridyl-3-pyrrole, and thus arriving at a second synthesis of nicotine, but without success, pyridine itself being the only product of a pyridine-like nature which was isolated. J. J. S.

**Preparation of 1-Phenyl-3-pyrazolone.** AUGUST MICHAELIS and E. REMY (*Ber.*, 1907, 40, 1020—1021).—The condensation of ethyl ethoxymethylenemalonate with acetylphenylhydrazine may be effected by means of phosphorus trichloride or oxychloride. By saponification of the product, 1-phenyl-3-pyrazolonecarboxylic acid, m. p. 216°, is obtained, which, when distilled, loses carbon dioxide with

the formation of the 3-pyrazolone. The action is represented as follows:



1-Phenyl-3-pyrazolone,  $\text{C}_9\text{H}_8\text{ON}_2$ , separates from alcohol in glistening leaflets, m. p. 155—156°, and is soluble in alkalis. A. McK.

**Phosphorus Tribromide as a Reducing Agent (Conversion of Pyrazolones into Pyrazoles).** RICHARD STOERMER and O. MARTINSEN (*Annalen*, 1907, 352, 322—343. Compare Stoermer, Abstr., 1904, i, 181).—It was shown (*loc. cit.*) that when heated with phosphorus tribromide in a sealed tube at high temperatures a number of substances containing the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$  or  $\cdot\text{NH}\cdot\text{CO}\cdot$  are converted into the corresponding compounds containing the groups  $\cdot\text{CH}:\text{CH}\cdot$  and  $\cdot\text{N}:\text{CH}\cdot$  respectively. The work has been extended to establish the general nature of this reaction in the pyrazolone series. The results show that phosphorus tribromide is at least as good a reducing agent for such substances as phosphorus pentasulphide, and that cleaner products are obtained than when the latter is employed. The mechanism of the reduction of the pyrazolones cannot be that suggested previously in the case of the lactones, since no similar intramolecular transposition of alkyl groups takes place, but alkyl groups attached to the carbon atom in the  $\alpha$ -position to the carbonyl are removed along with the oxygen. At low temperatures, bromopyrazoles are formed (compare Michaelis and Behn, Abstr., 1900, i, 693); as these are reduced to pyrazoles when heated with phosphorus tribromide in a sealed tube at higher temperatures they probably form intermediate products in the direct reduction of the pyrazolones. It is found that increased yields are obtained if yellow or red phosphorus is added to the tribromide.

The bispyrazolones are reduced to bispyrazoles if position 4 is occupied by oxygen, but fission of the molecule takes place with bis-4-alkylpyrazolones as also in the case of 4-benzylidenepyrazolones.

The 3-pyrazolones are reduced less easily than the pyrazolones, whilst with 1:5-diphenyl-3-pyrazolone the reaction leads to the formation of the bromopyrazole only.

Contrary to Stoermer's previous statement (*loc. cit.*), it is found now that the action of phosphorus tribromide on 1-phenyl-3:4:4-trimethylpyrazolone leads to the formation of 1-phenyl-3:4-dimethylpyrazole, b. p. 285—285.5° (275—278°: Steck, *Diss.*, Jena, 1896); the picrate, m. p. 122.5°; the platinichloride, m. p. 180—181° (decomp.); the methiodide, m. p. 162°, and the aurichloride, m. p. 166—167° were prepared.

1-Phenyl-3-methyl-4-ethylpyrazole, b. p. 294.5—295.5°, is obtained from the corresponding pyrazolone in a 55% yield; the picrate, yellow crystals, m. p. 129.5—130°; the platinichloride, small, yellowish-red crystals, m. p. 169°; the aurichloride, yellow needles, m. p. 141—142°.

1:4-Diphenyl-3-methylpyrazole, m. p. 41.5—42.5°, b. p. 220—224°/19 mm., is obtained from the 5-pyrazolone in a 45% yield.

1-Phenylpyrazole is formed in a 54% yield by the action of phos-



phorus tribromide and yellow phosphorus on 1-phenylpyrazolone at 215—225°.

The product, obtained on heating 1-phenyl-5-methyl-3-pyrazolone with phosphorus tribromide with or without the addition of red or yellow phosphorus, contains bromine which can be removed completely only on treatment with tin and hydrochloric acid. 1-Phenyl-5-methylpyrazole, obtained in this manner, b. p. 263.5°/762 mm. (corr.) (compare Claisen and Roosen, Abstr., 1894, i, 345; Bülow and Schlesinger, Abstr., 1900, i, 58; 1901, i, 98) and on oxidation, yields 1-phenylpyrazole-5-carboxylic acid. The platinichloride, m. p. 198—199°; the picrate, m. p. 97—98°, is formed together with a small amount of a substance, m. p. 192—193°; the aurichloride separates from alcoholic-hydrochloric acid in small crystals, m. p. 124—125°; the methiodide, m. p. 256—257° (287°: Bülow and Schlesinger, *loc. cit.*); the ethiodide, m. p. 208°. Claisen and Schlesinger's 1-phenyl-5-methylpyrazole was a mixture of this base with a small amount of 1-phenyl-3-methylpyrazole.

4 : 4'-Bis-1-phenyl-3-methylpyrazole,  $C_{20}H_{16}N_4$ , formed from 4 : 4'-bis-1-phenyl-3-methyl-5-pyrazolone, crystallises in white needles, m. p. 150°; the picrate forms scarlet needles, m. p. 159—160°; the platinichloride, small needles, decomposing when heated; the aurichloride, long needles, m. p. 207—208°. The methiodide,  $C_{21}H_{21}N_4I$ , crystallises in colourless leaflets, m. p. 236—237°; the dimethiodide,  $C_{22}H_{24}N_4I_2$ , forms small crystals, m. p. 182—183°, losing 1 mol. of methyl iodide, becomes brown on exposure to air, resolidifies when heated above its melting point, and then melts again at above 220° (decomp.).

4 : 4-Bis-1 : 3-diphenylpyrazole,  $C_{30}H_{22}N_4$ , m. p. 231.5—232°, formed from the bispyrazolone in an almost theoretical yield, closely resembles Claisen and Roosen's 3 : 3'-bis-1 : 5-diphenylpyrazole (*loc. cit.*)

When heated with phosphorus tribromide and red phosphorus, 4 : 4'-bis-1-phenyl-3 : 4-dimethylpyrazolone and 4 : 4'-bis-1-phenyl-3-methyl-4-ethylpyrazolone yield 1-phenyl-3 : 4-dimethylpyrazole and 1-phenyl-3-methyl-4-ethylpyrazole respectively.

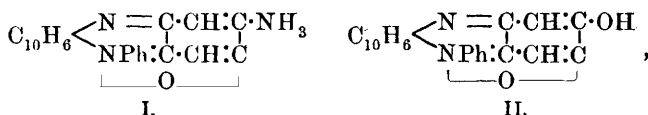
The action of phosphorus tribromide and red phosphorus on 1 : 1'-diphenyl-4 : 4'-benzylidene-3 : 3'-dimethyldipyrazolone leads to the formation of 1-phenyl-3-methylpyrazole and 1-phenyl-4-benzyl-3-methylpyrazole,  $C_{17}H_{16}N_2$ , which forms stout crystals, m. p. 62—63°, b. p. 260—270°, is readily soluble in organic solvents or concentrated acids, and gives the pyrazoline reaction. G. Y.

**Preparation of 5 : 5-Dialkylbarbituric Acids.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 178934).—It is now found that dialkylbarbituric acids may be obtained by condensing dialkylmalonic esters and carbamide with disodium cyanamide. Ethyl diethylmalonate, carbamide, and disodium cyanamide intimately mixed and heated for three hours at 105—110° readily furnish 5 : 5-diethylbarbituric acid.

G. T. M.

**Action of Hydroxylamine on isoRosindone.** FRIEDRICH KEHRMANN and HERMANN PRAGER (*Ber.*, 1907, 40, 1234—1237. Compare Kehrman and Gottrau, Abstr., 1905, i, 670; Fischer and Hepp, Abstr., 1900, i, 460; 1903, i, 654).—Contrary to the view of Fischer and Arntz (this vol., i, 94), the aminoisorosindone formed by the

action of hydroxylamine on *isorosindone* must have the constitution (I), as the corresponding hydroxy*isorosindone* is identical with the product (II),



obtained by condensation of 4:5-dihydroxy-*o*-benzoquinone with phenylnaphthylenediamine. This observation is in opposition to Fischer and Arntz's statement that the action of alkyl iodides and potassium hydroxide on their hydroxy*isorosindone* leads to the formation of ethers of naphthasafranols.

2-Amino-5-hydroxy-*p*-benzoquinone,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{O}_2 \cdot \text{NH}_2$ , prepared by heating aminohydroxybenzoquinoneimide with sodium hydroxide, is obtained as a brown, crystalline powder, decomposing at about  $260^\circ$ ; it forms a brown solution in concentrated sulphuric acid, becoming rose-coloured on dilution, and is converted into dihydroxybenzoquinone when heated with sulphuric acid. It yields crystalline condensation products with alkylated *o*-diamines and *o*-aminophenols.

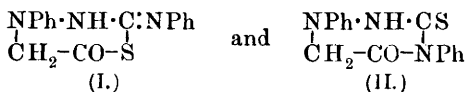
G. Y.

**Preparation of a Hydriodide of 4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone.** GIULIO NARDELLI and VINCENZO PAOLINI (D.R.-P. 180120) — 4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone hydriodide,  $\text{C}_{13}\text{H}_{17}\text{ON}_3\text{HI}$ , m. p.  $205^\circ$ , is produced by adding fuming hydriodic acid (sp. gr. 1.7) to a saturated aqueous solution of the pyrazolone derivative and evaporating the solution to dryness. The crystalline residue is very soluble in cold water, but dissolves only sparingly in hot alcohol, and is quite insoluble in ether, benzene, or ethyl acetate.

Owing to its great solubility in water, this salt is particularly useful in intravenous injections when, besides being a carrier of iodine, it also has antipyretic, antineuralgic, and antirheumatic properties.

G. T. M.

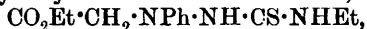
**Inner Anhydrides of Thiosemicarbazide Acetic Acids.** MAX BUSCH and EDUARD MEUSSDÖRFFER (*Ber.*, 1907, 40, 1021—1026). — *as*-Ethyl phenylhydrazinoacetate,  $\text{NH}_2 \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , combines with phenylthiocarbimide to form ethyl diphenylthiosemicarbazinoacetate, which, when saponified, yields, in addition to the corresponding acid, an anhydride for which the two formulæ



were suggested (Busch, Schneider, and Walter, *Abstr.*, 1904, i, 97), formula I having been preferred.

The behaviour of ethyl phenylthiosemicarbazinoacetate,  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$ ,

and of ethyl phenylethylthiosemicarbazinoacetate,



has now been studied. Each of these esters, when carefully saponified by alcoholic potassium hydroxide, yields, in addition to the corresponding acid, an inner anhydride. Each of these cyclic anhydrides exhibits a much greater stability towards alkali than does the diphenyl-compound referred to; they can be dissolved in cold alkalis and are not decomposed until they are warmed. The formation of disulphides

shows that the compounds in question possess the properties of mercaptans. They accordingly react in the tautomeric form of formula II, namely, as of the annexed type.

*Ethyl phenylthiosemicarbazinoacetate*,  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_3\text{S}$ , obtained from potassium thiocyanate and ethyl phenylhydrazinoacetate hydrochloride, forms white crystals, m. p. 115—116°.

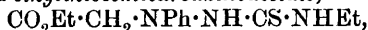
*Ketophenyltetrahydro-1:2:4-triazinethiol*, obtained by saponifying the preceding ester and then acidifying the resulting potassium salt, separates from dilute alcohol in yellow leaflets, m. p. 172—173°. When its solution in alkali is acidified with acid, the original compound is precipitated. Its *methyl ether*, obtained by the action of

methyl iodide on the potassium salt, separates from alcohol in glistening needles, m. p. 196—197° (decomp.).

When oxidised by ferric chloride, ketophenyltetrahydro-1:2:4-triazinethiol forms the *disulphide*,  $(\text{C}_9\text{H}_8\text{ON}_3)_2\text{S}_2$ , which separates from ethyl acetate in glistening, yellow needles, m. p. 159°.

*Phenylthiosemicarbazinoacetic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , obtained by gently warming the ester with dilute sodium hydroxide, separates from water in colourless crystals, m. p. 186° (decomp.).

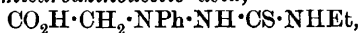
*Ethyl 1-phenyl-4-ethylthiosemicarbazinoacetate*,



obtained from ethyl thiocarbimide and *s*-ethyl phenylhydrazinoacetate, separates from a mixture of ether and light petroleum in transparent, monoclinic prisms, m. p. 84°. When saponified, it forms 1-phenyl-

4-ethyl-5-ketotetrahydro-1:2:4-triazinethiol, which separates from a mixture of benzene and light petroleum in needles, m. p. 145°. It is a weak acid, which separates unchanged when its sodium salt in aqueous solution is acidified. Its *disulphide*,  $(\text{C}_{11}\text{H}_{12}\text{ON}_3)_2\text{S}_2$ , separates from alcohol in orange-red needles, m. p. 123°.

*Phenylethylthiosemicarbazinoacetic acid*,



forms colourless crystals, m. p. 155°.

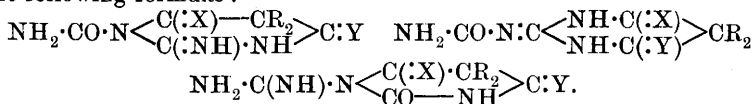
A. McK.

**Ammonium Salt of 5-Hydroxy-1:2:3-triazole-1-acetamide (1:2:3-Triazole-5-one-1-acetamide).** THEODOR CURTIUS and ERNST WELDE (*Ber.*, 1907, 40, 1197—1200. Compare *Abstr.*, 1906, i, 404, 940; this vol., i, 95).—The authors are unable to state at present whether the violet compound obtained by the action of sodium nitrite

and acetic acid on ammonium 5-hydroxy-1:2:3-triazole-1-acetamide is a nitroso- or an isonitroso-compound similar to Dimroth and Taub's ammonium 4-isonitroso-1-phenyl-5-triazolone (*Ber.*, 1906, **39**, 1387); they regard it provisionally as ammonium 4-nitroso-5-hydroxy-1:2:3-triazole-1-acetamide,  $\text{N}=\text{N}=\text{N} \begin{matrix} \text{C}(\text{NO})\text{:C}(\text{ONH}_4) \end{matrix} \text{N} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 138° (decomp.), not 120° (compare Abstr., 1906, i, 404). It forms anisotropic, violet-yellow, dichroic plates, does not give Liebermann's reaction, and by treatment with bromine water yields a colourless dibromocompound which does not contain the NO or NH<sub>4</sub> groups and requires investigation. C. S.

**Preparation of Pyrimidine Derivatives.** EMANUEL MERCK (D.R.-P. 180119).—It has now been found that guanylcarbamide condenses readily with dialkylmalononitriles, dialkylmalonyl chlorides, or ethyl cyanodialkylacetates, this reaction taking place either with or without the addition of alkalis.

Guanylcarbamide hydrochloride and ethyl cyanodiethylacetate, when condensed in alcoholic sodium ethoxide, yield a product which decomposes above 300° and dissolves in acids or alkalis, although very sparingly soluble in water, ether, or alcohol. On acid hydrolysis, it furnishes a good yield of diethylbarbituric acid. Guanylcarbamide hydrochloride and diethylmalononitrile yield a similar condensation product, which decomposes at 230—232° and gives diethylbarbituric acid on hydrolysis. With free guanylcarbamide and diethylmalonyl chloride a pyrimidine derivative is obtained, which decomposes above 350° and is hydrolysed by mineral acids. These condensation products are not homogeneous substances, but contain mixtures of compounds having the following formulæ:



These possibilities arise from the tautomeric nature of guanylcarbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$  and  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \cdot \text{C}(\text{NH}_2)_2$ .

All the condensation products obtained, however, by the foregoing condensation with this base readily yield 5:5-dialkylbarbituric acids.

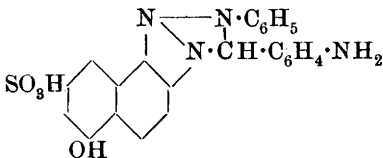
G. T. M.

**1-Amino-1:3:4-triazole-2:5-dicarboxylic Acid.** THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, **40**, 1194—1197. Compare this vol., i, 359).—The potassium salt of a dibasic acid isomeric with bisdiazooacetic acid, obtained by Hantzsch and Silberrad (*Abstr.*, 1900, i, 261) by the prolonged action of concentrated potassium hydroxide on ethyl diazoacetate, is the normal salt of 1-amino-1:3:4-triazole-2:5-dicarboxylic acid. The free acid,  $\text{NH}_2 \cdot \text{N} \begin{matrix} \text{C}(\text{CO}_2\text{H})\text{:N} \\ \text{C}(\text{CO}_2\text{H})\text{:N} \end{matrix} \cdot \text{H}_2\text{O}$ , m. p. 77° (decomp.), is obtained by the action of a large excess (30 mol.) of 30% sulphuric acid at 0°. It crystallises in colourless, glistening needles and decomposes with

extraordinary ease; by treatment with hydrochloric or sulphuric acid, warm water, or alcohol it loses carbon dioxide, and at its melting point decomposes into water, carbon dioxide, and 1-amino-1:3:4-triazole. By the action of potassium hydroxide on an aqueous solution of the acid the normal potassium salt is regenerated. C. S.

**Preparation of Aminoaryl Derivatives of 5-Hydroxy-1:2-Naphthatriazine-7-sulphonic Acid.** LEOPOLD CASSELLA & CO. (D.R.-P. 180031).—6-Amino- $\alpha$ -naphthol-3-sulphonic acid gives rise to a series of hydroxynaphthatriazines containing amino-groups attached to the aromatic nuclei in the triazine ring. On account of this constitution, these complex triazines couple with diazo-compounds in alkaline solutions to furnish azo-derivatives which are diazotisable.

The triazine is produced by coupling diazobenzene chloride with 6-amino- $\alpha$ -naphthol-3-sulphonic acid in acid solution and then condensing the intermediate azo-compound with *m*-aminobenzaldehyde. The free triazine-sulphonic acid is sparingly soluble in water, but its sodium salt dissolves readily in this medium.



The patent describes the preparation of other complex triazines of the foregoing type containing one or more amino-groups attached to the benzene nuclei. G. T. M.

**Notes on Bülow's Papers: "So-called Dihydropyrazines"** and "Decomposition Products of Acylhydrazones of Esters of 1:3-Ketocarboxylic Acids." THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, 40, 1470—1477. Compare Abstr., 1906, i, 939; this vol., i, 21, 262, 359; also Bülow, Abstr., 1906, i, 905; this vol., i, 99).—Dihydropyrazine is probably 1-amino-1:3:4-triazole, but conclusive evidence for this view has not been brought forward; Pinner (Abstr., 1898, i, 94), Stollé (*J. pr. Chem.*, 1906, [ii], 73, 277), and Busche (Abstr., 1901, i, 488, 616) have shown that compounds previously supposed to contain a six-membered ring can be more conveniently represented as amino-derivatives of a five-membered ring system.

It is pointed out that the genetic relationship between 1-aminotriazole and the so-called dihydropyrazinedicarboxylic acid does not prove the constitution of the latter compound, since the six-membered ring system of bisdiazooacetic acid at its melting point or even at 100° can be converted into 1-aminotriazole. It is, however, highly probable that the so-called dihydropyrazinedicarboxylic acid is 1-aminotriazole-dicarboxylic acid, as it yields 1-aminotriazole at the ordinary temperature.

Several of the compounds prepared by Bülow have been previously described and investigated by Wolff (Abstr., 1904, i, 722). J. J. S.

**Hydrolysis of 1:2:4:5-Tetrazine-3:6-dicarboxylic Acid.** THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, 40, 1176—1193).—The hydrolysis of tetrazinedicarboxylic acid by

water is a much more complicated process than that of its amide (compare Abstr., 1906, i, 939). According to Hantzsch and Lehmann (Abstr., 1901, i, 132), the hydrolysis of the acid (which they call bisazoxyacetic acid) yields hydraziacetic acid:  $C_4H_4O_6N_4 + H_2O = C_2H_4O_2N_2 + N_2 + 2CO_2 + H_2O$ ; in the presence of acid, the hydraziacetic acid decomposes into hydrazine and oxalic acid.

The authors question this interpretation of the hydrolysis. In the first place the salts of hydraziacetic acid are hydrolysed readily, yielding hydrazine and glyoxylic acid (Curtius and Jay, Abstr., 1894, i, 324). Also only one-third of the nitrogen in tetrazinedicarboxylic acid is liberated in the elementary state during hydrolysis, together with traces of carbon dioxide. They find that Hantzsch and Lehmann's hydraziacetic acid is the *hydrogen hydrazine* salt of the oxalyldiazonate of glyoxylic acid,  $CO_2H \cdot CH \cdot N \cdot NH \cdot CO \cdot CO_2H \cdot N_2H_4$ , m. p.  $243^\circ$  (decomp.). The substance is obtained in better yield by rapidly boiling tetrazinedicarboxylic acid with water, and is synthesised by treating a warm aqueous solution of hydrazino-oxalic acid with the calculated quantity of a 3% solution of glyoxylic acid and, after cooling, with hydrazine hydrate. The methyl ester,  $C_5H_6O_5N_2$ , obtained from the silver salt, has m. p.  $117^\circ$  (Hantzsch and Lehmann,  $102^\circ$ ), and is not converted by mercuric oxide into ethyl diazoacetate.

*Benzylidenehydrazino-oxalic acid*,  $CHPh \cdot N \cdot NH \cdot CO \cdot CO_2H$ , m. p.  $179-180^\circ$ , obtained by decomposing tetrazinedicarboxylic acid with water at  $30^\circ$  and adding benzaldehyde, forms long, white needles, and is decomposed by dilute hydrochloric acid, yielding benzaldehyde, hydrazine, and oxalic acid.

*Hydrazino-oxalic acid hydrochloride*,  $CO_2H \cdot CO \cdot NH \cdot NH_2 \cdot HCl$ , prepared by triturating the preceding compound with concentrated hydrochloric acid, forms a white, crystalline mass, sinters at  $121^\circ$ , and has m. p.  $128-129^\circ$  (decomp.). Its aqueous solution and benzaldehyde form the benzylidene compound, whilst from the solution in boiling water separate colourless crystals of *hydrazino-oxalic acid*,  $NH_2 \cdot NH \cdot CO \cdot CO_2H$ , m. p.  $>300^\circ$ , the *silver* salt of which,  $C_2H_3O_3N_2Ag$ , is stable to light.

The hydrolysis of tetrazine itself by water is not a simple process. The anticipated products would be one molecule each of formaldehyde, formic acid, hydrazine, and nitrogen, with the intermediate production of formaldehydeformylhydrazone; the products actually obtained do not include formaldehyde, and contain more hydrazine and less nitrogen than the above-mentioned quantities. The investigation of the reaction is still in progress.

The authors cannot confirm Hantzsch and Lehmann's statement (*loc. cit.*) that their so-called hydraziacetic acid results by the reduction of bisdiazooacetic acid or of tetrazinedicarboxylic acid by sodium amalgam at  $0^\circ$ .

When bisdiazooacetic acid is crystallised from water, yellow crystals of the hydrated acid, m. p.  $149-155^\circ$ , are deposited; from the filtrate, after long keeping, slender, yellow needles are obtained consisting of *hydrogen hydrazine bisdiazooacetate*, m. p.  $188-189^\circ$  (decomp.); the same salt is formed from bisdiazooacetic acid by prolonged boiling with water or by treatment with the requisite quantity of hydrazine. The

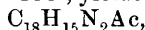
substance yields tetrazinedicarboxylic acid with nitrous acid, benzylideneazine with benzaldehyde, and bisdiazooacetic acid when its alkaline solution is acidified.

Hantzsch and Silberrad seem to have mistaken this salt for anhydrous bisdiazooacetic acid (Abstr., 1900, i, 261). The latter is obtained by treating the hydrated acid with absolute alcohol, filtering, and evaporating the filtrate in a vacuum over sulphuric acid; it forms strongly polarising, yellow, prismatic crystals, and has the same melting point as the hydrated acid. Both acids are converted into 1-amino-1:3:4-triazole at 100°, whereas the hydrogen hydrazine salt is stable at this temperature.

C. S.

**Action of [Potassium Ferrocyanide on Diazo-salts.** A. EHRENPREIS (*Bull. Acad. Sci., Cracow*, 1906, 265—270).—Griess (this Journ., 1876, i, 932) found that diazobenzene chloride is decomposed by potassium ferrocyanide in aqueous solution with formation of nitrogen, azobenzene, and a red oil. The author has studied this reaction and extended it to other diazonium salts.

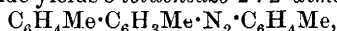
Reduction of the red oil from diazobenzene chloride, with zinc dust and a small amount of ammonia in alcoholic solution, leads to the formation of *triphenylhydrazine*,  $\text{NPh}_2 \cdot \text{N} \cdot \text{HPh}$ , which separates in hard, glistening crystals, m. p. 136—138°, yields an *acetyl* derivative,



needles, m. p. 152.5°, and, when treated with stannous chloride in concentrated hydrochloric acid, undergoes the semidine transformation, forming *aminotriphenylamine*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NPh}_2$ , m. p. 136°. This gives reactions for a primary base and is readily acetylated. When oxidised with mercuric oxide in benzene solution, triphenylhydrazine forms a red oil, b. p. 270°, which is identical probably with the product of the action of potassium ferrocyanide on diazobenzene chloride; it may have the constitution  $\text{C}_6\text{H}_4 \begin{smallmatrix} \swarrow \text{NPh} \\ \searrow \text{NPh} \end{smallmatrix}$ .

Contrary to the statement of Bandrowski and Prokopeczko (Abstr., 1904, i, 635), the derivatives of benzenehydrazodiphenyl, m. p. 217° and 178°, are isomeric mono- and not di-acetyl compounds.

When treated with potassium ferrocyanide in aqueous solution, *o*-diazotoluene chloride yields *o*-tolueneazo-2:2'-dimethyldiphenyl,



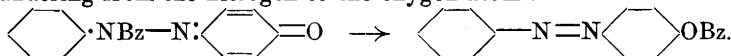
red crystals, m. p. 104°, and a red oil. Under the same conditions, *p*-diazotoluene chloride yields *p*-tolueneazo-4:4'-dimethyldiphenyl, m. p. 118°, and a red oil. The product, obtained on reduction of this, is very readily oxidised.

The action of potassium ferrocyanide on *m*-diazotoluene chloride leads to the formation of a brown, viscid oil, which can be distilled, and forms a *hydrochloride*,  $\text{C}_{15}\text{H}_{15}\text{NCl}$ , crystallising in silver-white plates.

G. Y.

**Quinonoid Compounds. XII. Transformation of Benzoquinonephenylhydrazones into Oxyazo-compounds.** RICHARD WILLSTÄTTER and HANS VERAGUTH (*Ber.*, 1907, 40, 1432—1437).—When a cold dry ethereal solution of benzoquinonebenzoylphenyl-

hydrazone is shaken with powdered potassium hydroxide for twenty-four hours, it is converted into benzoxyazobenzene, the acyl group wandering from the nitrogen to the oxygen atom :



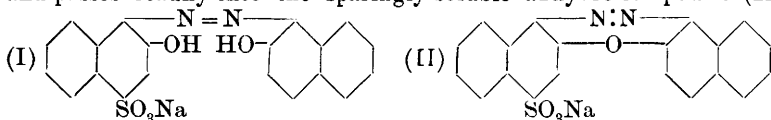
This is a perfectly general transformation and is shown by benzoquinonephenylcarbethoxyhydrazone,  $\text{O}:\text{C}_6\text{H}_4:\text{N}\cdot\text{NPh}\cdot\text{CO}_2\text{Et}$ , and benzoquinoneacetylphenylhydrazone, the change in these cases taking place best in the boiling ethereal solution.

These results are in opposition to the views of Farmer and Hantzsch (Abstr., 1900, i, 122), as there is no reason to suppose free oxyazobenzene as unstable when the *N*-acyl quinonoid derivative is the less stable isomeride. McPherson's conclusions (Abstr., 1900, i, 123) as to the constitution of oxyazobenzene, based on the hydrolysis of benzoquinonephenylhydrazones, are also invalidated in the light of these results.

*Benzoquinonephenylcarbethoxyhydrazone*, prepared by the condensation of ethyl formate phenylhydrazide (m. p. 24–25°) and benzoquinone, crystallises in yellow prisms, m. p. 96–97°.

W. R.

**Preparation of 2'-Hydroxynaphthalene-1-azo- $\beta$ -naphthol-4'-sulphonic Acid.** ANILINFARBEN- & EXTRACT-FABRIKEN VORMALS J. R. GEIGY (D.R.-P.177925).—2'-Hydroxynaphthalene-1-azo- $\beta$ -naphthol-4'-sulphonic acid, prepared by combining 1-diazo- $\beta$ -naphthol-4-sulphonic acid with alkaline- $\beta$ -naphthol, separates in the form of its *disodium* salt which is not suitable for dyeing purposes. The *monosodium* salt (I), obtained by cautiously neutralising the disodium salt with a mineral acid or by acidifying its solution with acetic acid, is unstable and passes readily into the sparingly soluble anhydro-compound (II)



which separates in copper-coloured crystals.

It is now found that the free sulphonic acid can be precipitated in the form of a hydrogen chloride additive compound by adding excess of hydrochloric acid to the aqueous solution of the monosodium salt. On gently heating, this additive product loses hydrogen chloride and furnishes the free sulphonic acid, a greenish-black powder with a bronze reflex which is soluble even in cold water. Its aqueous solution is stable at 100°, but the addition of sodium chloride or sulphate at 60–70° determines the formation of the sparingly soluble sodium salt of the anhydro-compound.

G. T. M.

**Water in Proteins.** FRANCIS G. BENEDICT and CHARLOTTE R. MANNING (*Amer. J. Physiol.*, 1907, 18, 213–221).—The hygroscopic nature of proteins renders the usual process of drying by heating in an air-bath at 110° useless in exact work. This error may be as high as 1%. The removal of final traces of moisture can



be effected by subsequent desiccation in a high vacuum for two weeks. The experiments recorded were made with gelatin, collagen, elastin, edestin, legumin, and conglutin. In many cases after desiccation at room temperature in a high vacuum until constant weight was reached (about two weeks), a subsequent stay in an air-bath at 100° for a few hours caused them to take up water again in small amount. This is again removable by a high vacuum for two weeks. No oxidation or volatilisation could be detected when the heating lasted for five hours.

W. D. H.

**Hydrolysis of Phaseolin.** THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, 18, 295—308).—Phaseolin, formerly called legumin, is a globulin, and forms nearly all the protein substance of the white kidney bean. The following substances were obtained on hydrolysis; the figures are percentages calculated on a water-free and ash-free basis: glycine, 0.55; alanine, 1.8; valine, 1.04; leucine, 9.65; proline, 2.77; phenylalanine, 3.25; aspartic acid, 5.24; glutamic acid, 14.54; serine, 0.38; tyrosine, 2.18; arginine, 4.89; histidine, 1.97; lysine, 3.92; ammonia, 2.06: total 54.27. Oxyproline and tryptophan were present, but not estimated. The figures coincide very well with those published by Abderhalden and Babkin on the legumin of the white bean.

W. D. H.

**Reduction of Derivatives of the Colouring Matter of Blood by Means of Zinc and Hydrochloric Acid.** J. MERUNOWICZ and JEAN ZALESKI (*Bull. Acad. Sci., Cracow*, 1906, 729—733).—Hoppe-Seyler (*Abstr.*, 1889, 787) and Nencki and Sieber (*Abstr.*, 1888, 971) showed that on reduction in acid solution, hæmatoporphyrin yields a yellow solution which gives reactions for urobilin, but differs from this in undergoing change to reddish- or violet-brown on exposure to air. The authors have observed that this change of colour takes place most easily when hæmato- or meso-porphyrin is reduced by means of zinc dust; the reduced solution is colourless and optically inactive; the change of colour through yellow to reddish-brown takes place equally in acid or alkaline solution. As the absorption spectrum of the yellow solution exhibits urobilin bands, whilst the reddish-brown solution shows in addition bands of the spectrum of acid, or alkaline, porphyrin, the authors separated the porphyrin formed in this manner by oxidation of the leuco-compound, and find it to be identical with the hæmato- or meso-porphyrin reduced. Hæmin undergoes similar changes when reduced with zinc dust in alcoholic-acetic acid solution, yielding on exposure to air solutions giving the spectra of urobilin and hæmatoporphyrin, whilst if the hæmin is reduced in acetic and hydriodic acids meso-porphyrin is formed by the oxidation. With iodine or bromine, the colourless solution of the leuco-compound yields mixtures of amorphous substances which are soluble in alcohol, but insoluble in water.

From the amount of oxygen absorbed by reduced meso-porphyrin it is concluded that the leuco-compound contains 4 atoms of hydrogen more or 2 atoms of oxygen less than the dye.

G. Y.

**Reaction Velocity Between Opsonin and Red Blood Corpuscles.** J. O. WAKELIN BARRATT (*Zeitsch. physikal. Chem.*, 1907, 58, 467—474).—The velocity with which red blood corpuscles combine with opsonin (compare *Proc. Roy. Soc.*, 1907, B, 79) has been determined, and, although the reaction is heterogeneous, it appears to be bimolecular. The various possibilities, for example, the colloidal or crystalloid nature of the active constituent of the corpuscles, the colloid or crystalloid nature of opsonin, the reaction depending on diffusion, adsorption, or chemical action, are discussed. J. J. S.

**Catalytic Decomposition of Hydrogen Peroxide by the Catalase of the Blood.** C. A. LOVATT EVANS (*Biochem. J.*, 1907, 2, 133—155).—For each concentration of enzyme there is an optimum concentration of hydrogen peroxide. The optima do not vary directly as the enzyme concentrations, but more nearly as their square roots. The numerous departures from the rule, however, necessitate the introduction of more complicated hypotheses. W. D. H.

**An Enzyme in Cortinellus Edodes which Splits Nucleic Acid.** T. KIKKŌJI (*Zeitsch. physiol. Chem.*, 1907, 51, 201—206).—Nuclease has already been described as occurring in yeast and other fungi; the enzyme now described in a Japanese fungus is probably the same ferment. It splits nucleic acid with the formation of purine bases and phosphoric acid; it is destroyed by heat; it acts best in a neutral or faintly acid medium; it is inhibited by 0.5% acetic acid and by 0.5% sodium carbonate. In neutral solution it is salted out by ammonium sulphate. W. D. H.

**Action of Light on Invertin in the Absence and Presence of Cane Sugar and other Substances.** A. JODLBAUER (*Biochem. Zeitsch.*, 1907, 3, 488—502).—The presence of sucrose inhibits the destructive influence of light on invertin. Solutions of sodium chloride, sodium sulphate, carbamide, and glycerol, equimolecular with a 20% sucrose solution, produce no such effect. Glycine also has no action, but mannitol has a slight inhibiting effect. Dextrose, lævulose, *d*-mannose, *d*-galactose, lactose, and maltose act similarly to sucrose; starch and dextrin have no effect. All the substances mentioned however, increase the resistance of the enzyme towards destruction by heat. W. D. H.

**Influence of Oxygen on the Destruction of Ferments (Invertin) by Heat.** A. JODLBAUER (*Biochem. Zeitsch.*, 1907, 3, 483—487).—The effect of various parts of the spectrum on invertin rendered necessary the investigations of the question stated in the title. The destruction was found to be equal whether oxygen or hydrogen was present. The destruction by the visible rays of the spectrum occurs only in the presence of oxygen. Photolability and thermolability are thus different phenomena. W. D. H.

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## Organic Chemistry.

**Equilibrium of Methane.** M. MAYER and V. ALTMAYER (*Ber.*, 1907, 40, 2134—2144).—The reaction  $C + 2H_2 \rightleftharpoons CH_4$  in the presence of nickel or cobalt has been studied from both sides of the equation at temperatures between 470° and 620°. The authors develop the equation  $CT' = -18507 + 5.9934T' \log T' + 0.002936T'^2 + RT' \log p/p_1^2$ , where  $p$  and  $p_1$  represent the partial pressure of methane and of hydrogen at the temperature  $T'$ . The average value of the constant  $C$  is 21.6 with nickel as catalyst and 21.1 with cobalt in those experiments in which the initial gas is methane;  $C = 20.8$  with each catalyst when the initial gas is hydrogen.

Putting  $C = 21.1$  in the equation, the authors calculate that under one atmosphere the % of  $CH_4$  at 250° is 98.79, and at 850°, 1.59. Hence doubts are expressed as to Bone and Jerdan having really effected the synthesis of methane at 1200° (*Trans.*, 1897, 71, 41), the suggestion made being that the carbon employed contained impurities which yielded methane.

C. S.

**Catalytic Reactions at High Temperatures and Pressures.**

**XIII. Catalytic Isomerisation of Butylene.** WLADIMIR IPATIEFF and W. SZYROWECKY (*Ber.*, 1907, 40, 1827—1830. Compare *Abstr.*, 1903, i, 593, 594; this vol., i, 6).—Whilst the decomposition of *isobutyl* alcohol in contact with alumina leads to the formation of *isobutylene* only, which is formed also by the decomposition of trimethylcarbinol, a mixture of the three butylenes is obtained when *isobutyl* alcohol is passed through a copper tube containing zinc chloride. This does not result from isomerisation of *isobutylene* first formed, since it was found that the butylenes do not undergo isomerisation when passed over zinc chloride at various temperatures. It is now found that *sec.*-butyl alcohol when passed through a copper tube containing alumina at 450° yields  $\beta$ -butylene and only traces of *isobutylene*, but if passed over zinc chloride at the same temperature forms  $\beta$ -butylene together with considerable quantities of *isobutylene*, methyl ethyl ketone, and a liquid, unsaturated hydrocarbon, which is probably the product of the decomposition of an ether formed in the first stage of the reaction (compare *Abstr.*, 1904, ii, 645). It is considered that under the influence of the strong dehydrating action of the zinc chloride a portion of the *sec.*-butyl alcohol loses water in such manner as to form the *cyclo*-propane derivative,  $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > CHMe$ , which undergoes isomerisation into *isobutylene*.

*sec.*-Butyl alcohol, free from *tert.*-butyl alcohol, is prepared by the action of hydrogen on methyl ethyl ketone in presence of nickel oxide. Contrary to Scheschukoff's statement (*Abstr.*, 1886, 680), *sec.*-butyl iodide dissolves in hot water, being hydrolysed to *sec.*-butyl alcohol.

G. Y.

**Physical Properties of Liquid and Solid Acetylene.**

DOUGLAS MCINTOSH (*J. Physical Chem.*, 1907, 11, 306—317).—The author has determined the most important physical constants of acetylene. The sublimation temperature of solid acetylene is  $-83.6^{\circ}$ , m. p.  $-81.5^{\circ}$  (under a pressure of 895 mm.). From Clausius' equation the heat of vaporisation of the liquid is calculated to be  $21.3 \times 10^{10}$  ergs., that of the solid,  $23.0 \times 10^{10}$  ergs. Direct measurement of the former quantity gave  $21.0 \times 10^{10}$  ergs. The specific heat of liquid acetylene between  $-78.5^{\circ}$  and  $-73^{\circ}$  is equivalent to  $4.4 \times 10^7$  ergs. The liquid has  $D_{-80} 0.613$ ; solid,  $D_{-80} 0.72$ . Critical temperature,  $36.5^{\circ}$ ; critical pressure, 61.6 atmospheres; critical volume, 83 c.c. The constants  $a$  and  $b$  of van der Waals' equation are 0.0880 and 0.00230 respectively.

From the high value of the molecular volume of acetylene (42) the author concludes that acetylene contains a bivalent carbon atom, and has the constitution of acetylidene,  $C:CH_2$ . The atomic volume of bivalent carbon in acetylene is therefore about 20, which agrees with the value obtained from the molecular volume of liquid carbon monoxide.

Acetylene forms crystalline compounds with ethyl ether, ethyl alcohol, acetone, and with the halogen hydrides (?) at low temperatures. The great solubility of the hydrocarbon in many organic liquids is probably connected with this property. Liquid acetylene is a non-conducting and non-ionising solvent.

Incidentally, an electrically controlled Dewar tube thermostat is described by means of which temperatures from  $-70^{\circ}$  to  $-95^{\circ}$  can be readily maintained constant to between  $0.3^{\circ}$  and  $0.4^{\circ}$ . H. M. D.

**Determination of Melting Points at Low Temperatures.**

II. LEO F. GUTTMANN (*J. Amer. Chem. Soc.*, 1907, 29, 345—347).—The following m. p.'s. have been determined by the method described previously (*Trans.*, 1905, 87, 1037). Methyl alcohol,  $-97.8^{\circ}$ ; ethyl alcohol,  $-117.3^{\circ}$ ; methyl acetate,  $-98.7^{\circ}$ ; ethyl acetate,  $-82.8^{\circ}$ ; propyl acetate,  $-92.5^{\circ}$ ; pentane,  $-147.5^{\circ}$ ; hexane,  $-93.5^{\circ}$ ; octane,  $-98.2^{\circ}$ ; ethyl ether,  $-117.6^{\circ}$ ; ethyl bromide,  $-117.8^{\circ}$ ; methyl iodide,  $-64.4^{\circ}$ ; ethyl iodide,  $-108.5^{\circ}$ ; *n*-propyl iodide,  $-98.8^{\circ}$ ; isopropyl iodide,  $-89^{\circ}$  to  $-91.8^{\circ}$ ; isobutyl iodide,  $-90.7^{\circ}$ ; ethyl formate,  $-78.9^{\circ}$ ; ethyl propionate,  $-72.6^{\circ}$ ; ethyl butyrate,  $-93.3^{\circ}$ ; acet-aldehyde,  $-124.6^{\circ}$ ; acetone,  $-94.6^{\circ}$ ; and methyl ethyl ketone,  $-85.9^{\circ}$ .

The results of these determinations show the value of the m. p. as a criterion of purity. Of the alcohols, methyl and ethyl alcohols give a m. p., but with propyl, isobutyl, and isoamyl alcohols no definite m. p. is obtainable, owing probably to their being composed of mixtures of various isomerides. The esters and alkyl iodides are more readily obtainable in a pure state. It is noteworthy that ethyl alcohol, ethyl ether, and ethyl bromide have almost the same m. p. E. G.

**Direct Hydrogenation of Allyl Compounds.** PAUL SABATIER (*Compt rend*, 1907, 144, 879—881. Compare this vol., i, 488, 490).—Of the reactions of direct hydrogenation in presence of reduced nickel the one most easily effected is the addition of hydrogen to an ethylenic

linking, and in an ethylenic compound, capable of hydrogenation in a second manner, it is possible to effect the reduction of the ethylenic bond alone (compare Haller and Martine, *Abstr.*, 1905, i, 533; Darzens, *Abstr.*, 1905, i, 172; this vol., i, 277; Sabatier and Senderens, *Abstr.*, 1905, i, 333). When allyl alcohol vapour mixed with hydrogen is passed over reduced nickel at 130—170°, it is completely reduced to propyl alcohol containing a small quantity of propaldehyde. The same reaction is effected, much less rapidly, by means of reduced copper at above 180°. Allyl oxide is similarly reduced by nickel at 135—140° to propyl oxide, but the allyl halides are decomposed with separation of the haloid acid. E. H.

**Addition of Hydrogen Chloride to *iso*Butylene Oxide.** K. KRASSUSKY (*J. pr. Chem.*, 1907, [ii], 75, 238—247. Compare *Abstr.*, 1901, i, 246; 1902, i, 8).—A criticism of the work of Henry (*Abstr.*, 1906, i, 228; this vol., i, 7) and of Michael and Leighton (*Abstr.*, 1906, i, 551, 781). The results obtained on reinvestigation of the action of hypochlorous acid and of hydrogen chloride on *isobutylene oxide* are in agreement with the author's previous statements. The product of the action of hydrogen chloride on *isobutylene oxide* consists of chlorotrimethylcarbinol, traces of condensation products of *isobutaldehyde*, and an *oil*, b. p. 132—136°, which is insoluble in water and is not a chlorohydrin, since it does not yield an oxide when distilled over potassium hydroxide. An insoluble, white, amorphous *substance*, m. p. 142—144°, is obtained if the turbid liquid, formed by saturating *isobutylene oxide*, cooled by ice-water, with hydrogen chloride, is treated with ether. The chloro-compound,  $C_4H_7Cl$ , obtained by distilling the chlorohydrin over phosphoric oxide, forms a *dibromide*,  $C_4H_7ClBr_2$ . G. Y.

***tert.*-Pinacolyl Alcohol.** MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 455—461. Compare *Abstr.*, 1906, i, 476, 551, 784, 921, and Henry, *Abstr.*, 1906, i, 329).—*tert.*-Pinacolyl alcohol (dimethyl-*isopropylcarbinol*),  $CHMe_2 \cdot CMe_2 \cdot OH$ , b. p. 118—118.6°, m. p. -12°, obtained by the action of magnesium *isopropyl bromide* on acetone, on treatment with acetic anhydride furnishes an *acetate*, b. p. 139—143°, which, when warmed with powdered potassium hydroxide, regenerates the alcohol unchanged. The latter is not reduced by metallic sodium, and, when treated with bromine in presence of ice or cold water, furnishes a *substance*, b. p. 115—119°. If cold water or ice is not employed the principal product is a crystalline bromide, m. p. 132—133°. The alcohol yields a crystalline *urethane*, m. p. 65—66°.

***sec.*-Pinacolyl alcohol** (methyl-*tert.*-butylcarbinol),  $CMe_3 \cdot CHMe \cdot OH$ , on treatment with acetyl chloride, furnishes an *acetate*, b. p. 135—143°, and this, when warmed with powdered potassium hydroxide, regenerates the *sec.*-alcohol unchanged, b. p. 117—121°, which, on treatment with bromine in presence of ice, furnishes pinacolin, b. p. 107—110°, but if ice is not employed the principal product is a crystalline *bromide*, m. p. 132—133°, closely resembling that obtained from the *tert.*-alcohol under similar conditions. The *sec.*-alcohol furnishes a crystalline *urethane*, m. p. 76—77°. T. A. H.

**Preparation of Alkyloxyglycols.** AUGUSTE BÉHAL and MARCEL SOMMELET (D.R.-P. 180202. Compare this vol., i, 275).—The process now described is a modification of the method formerly employed in the production of the alkyloxyglycols. It consists in subjecting halogenated methyl alkyl ethers to the action of ketones, nitriles, or acid amides in the presence of metals or organo-metallic compounds.

*β-Hydroxy-α-ethoxy-β-methyldecane*,  $C_8H_{17} \cdot CMe(OH) \cdot CH_2 \cdot OEt$ , b. p. 140—150°/20 mm., is produced by slowly adding chloromethyl ethyl ether to a mixture of pelargonitrile and magnesium in dry ether.

*β-Hydroxy-α-ethoxy-β-methylundecane*,  $C_9H_{19} \cdot CMe(OH) \cdot CH_2 \cdot OEt$ , b. p. 153—155°/17 mm., and *β-Hydroxy-α-ethoxy-β-methyldodecane*, b. p. 160—162°/15 mm., are obtained respectively from methyl nonyl ketone and methyl decyl ketone. G. T. M.

**Determination of the Limits of Inflammability of Explosive Mixtures of Ethyl Ether Vapour and Air.** JEAN MEUNIER (*Compt. rend.*, 1907, 144, 796—798).—The author has applied a modification of the method previously used (*Compt. rend.*, 1900, 131, 727) with mixtures of hydrocarbon vapours and air to mixtures of ethyl ether vapour and air. Air containing 0.045 gram of ethyl ether vapour per litre does not inflame; when the proportion of ether amounts to 0.09 gram per litre there is a clear ignition giving a blue flame which is rapidly propagated in the explosion vessel; with 0.135 gram of ether per litre the combustion is explosive, accompanied by a blue flame, which is very rapidly propagated; with 0.180 gram of ether per litre the combustion is explosive, but the flame is green, indicating an excess of ether vapour; air containing 0.225 gram of ether per litre is not inflammable, and extinguishes a lighted taper. One litre of air at 15° is theoretically necessary for the combustion of 0.098 gram of ether. The author concludes that the limits of inflammability of ether in air are approximately 0.075 and 0.2 gram of vapour per litre. On the results obtained is based a method for the determination of the proportion of ether vapour in mixtures with air. E. H.

**Limit of Inflammability of Mixtures of Ether Vapour and Air.** OCTAVE BOUDOUARD and HENRI LE CHATELIER (*Compt. rend.*, 1907, 144, 910—911. Compare Meunier, preceding abstract).—The authors draw attention to the fact that they have determined previously (Abstr., 1898, ii, 574) the inferior limit of inflammability of ether vapour in air to be 0.06 gram per litre. E. H.

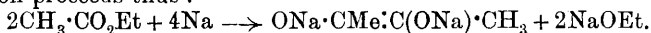
**Formation of Double Salts in Solvents other than Water.** LIVIO CAMBI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 403—408).—The author describes double salts having the compositions:  $CuCl_2, LiCl, HCO_2H$ ;  $CuCl_2, LiCl, CH_3 \cdot CN$ ;  $CdI_2, 2NaI, 9COMe_2$ ;  $CoI_2, 2NaI, 9COMe_2$ ;  $CdI_2, 2NaI, 6Ac_2O$ ;  $CoI_2, NaI, 6Ac_2O$ , and  $CoI_2, NaI, 3Ac_2O$ . The formulæ of the two salts crystallising with acetone are indicated by that of the salt  $CoI_2, 9H_2O$  (Bolschakoff, Abstr., 1899, ii, 427), as it is often found, for example, with the carnalites, that the number of mols. of water of crystallisation in the double salt is the same as in the crystalline hydrate of the salt of the

bivalent metal. That acetone mols. can replace an equal number of water mols. is rendered probable by our knowledge of oxonium salts (Schmidt, *Basische Eigenschaften des Sauerstoffs und Kohlenstoffs*, 1904, 23). No hydrated double salt is known corresponding with the salt  $\text{CoI}_2, \text{NaI}, 3\text{Ac}_2\text{O}$ , although the compound  $\text{CdI}_2, \text{HI}, 3\text{H}_2\text{O}$  (Dobroserdoff, Abstr., 1900, ii, 654) has been obtained. The difference in colour between the two salts,  $\text{CoI}_2, \text{NaI}, 3\text{Ac}_2\text{O}$  and  $\text{CoI}_2, 2\text{NaI}, 6\text{Ac}_2\text{O}$ , which are green and reddish-brown respectively, recalls the colour phenomena observed in aqueous solutions of cobalt iodide, bromide and chloride when the concentration and temperature are varied. T. H. P.

**Behaviour of Sodium and Sodium Alkyl oxides towards Various Esters of Acetic Acid.** LOUIS ALLEN HIGLEY (*Amer. Chem. J.*, 1907, 37, 293—324).—Nef has shown (Abstr., 1902, i, 6) that the alkylation of anilines by sodium alkyl oxides is due to the alkylidene dissociation of the latter. Thus, in the alkylation of acetyl-ethylaniline the alkylidene residue unites directly with the anilide,  $\text{R}\cdot\text{CH}< + \text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NPhEt} \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NPhEt}$ . It is evident, however, from the work of Geuther and Claisen with ethyl acetate and sodium ethoxide that these reactions might be due to an intermediate formation of ethyl acetoacetate. This compound would unite immediately with the alkylidene present to form mono- and di-alkylacetoacetic esters, which in the presence of the sodium hydroxide would give rise to mono- and di-alkylacetic acids. It has now been proved that this intermediate formation of ethyl acetoacetate does actually occur when acetethylaniline is heated with sodium alkyl oxides at  $100^\circ$ . There are cases, however, where the alkylation must take place directly. Thus in the alkylation of the formyl group and in the replacement of the tertiary hydrogen atom in the *isobutyl* group, the formation of an acetoacetic acid derivative is impossible.

It has been shown by Nef (Abstr., 1898, i, 112) that the reaction between ethyl acetate and sodium ethoxide proceeds as follows and is reversible:  $\text{CH}_3\cdot\text{CO}_2\text{Et} + \text{NaOEt} \rightarrow \text{CH}_3\cdot\text{C}(\text{OEt})_2\cdot\text{ONa} \rightarrow \text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{ONa} + \text{EtOH}$ .  $\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{ONa} + \text{CH}_3\cdot\text{CO}_2\text{Et} \rightarrow \text{CH}_3\cdot\text{C}(\text{OEt})(\text{ONa})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \rightarrow \text{CH}_3\cdot\text{C}(\text{ONa})\cdot\text{CH}\cdot\text{CO}_2\text{Et} + \text{EtOH}$ . Experiments have proved that this reaction proceeds with measurable velocity at  $20^\circ$ , and that equilibrium is not reached until after about twenty-five days. Meyer and Friessner (Abstr., 1902, i, 657) have found that at  $100^\circ$  equilibrium is attained in two hours.

Michael's conclusion (Abstr., 1901, i, 123; 1905, i, 506) that metallic sodium reacts directly with ethyl acetate with formation of hydrogen and ethyl sodioacetoacetate is untenable for the following reasons. (1) When ethyl acetate in dry ether is treated with sodium, neither hydrogen nor ethyl sodioacetoacetate is produced, but the reaction proceeds thus:



On treating the product with dilute acid, dimethylketol,



is produced. Acetyl dimethylketol *semicarbazone*, m. p.  $162^\circ$ , forms white needles. (2) Ethyl butyrate and ethyl hexoate react with sodium with production of nearly quantitative yields of ketol deriv-

atives of the type  $\text{ONa}\cdot\text{CR}\cdot\text{CR}\cdot\text{ONa}$  (Bouveault and Locquin, Abstr., 1905, i, 560). (3) Propionyl, butyryl, and isovaleryl chlorides, on treatment with sodium, yield compounds of the butyroin type,  $\text{OH}\cdot\text{CHPr}^a\cdot\text{COPr}^a$  (Klinger and Schmitz, Abstr., 1891, 890).

By the action of sodium ethoxide on acetethylanilide at  $100^\circ$  in a sealed tube, ethyl acetoacetate was obtained in a yield of 37% of the theoretical. When dry sodium benzyloxide is heated at  $180^\circ$ , various products are obtained, but the main reaction evidently consists in the conversion of the compound into benzoic acid and hydrogen. By the oxidation of sodium benzyloxide in dry air, sodium benzoate and sodium peroxide are produced.

A study was made of the behaviour of sodium benzyloxide towards benzyl acetate, acetethylanilide, formethylanilide, and benzyl sodioacetoacetate under various conditions. In the alkylation of benzyl acetate by sodium benzyloxide, only a 2% yield of benzyl acetoacetate was obtained, whilst in the reaction between ethyl acetate and sodium ethoxide, 36.5% of ethyl sodioacetoacetate is produced when the equilibrium point is reached. Conrad and Hodgkinson (Abstr., 1877, i, 590) found that when benzyl acetate is treated with sodium, benzyl acetoacetate is not formed, but that at  $135^\circ$  hydrogen is evolved and benzyl  $\beta$ -phenylpropionate produced. Bacon (Abstr., 1905, i, 204) has shown that benzyl ether is also produced in this reaction. Experiments have been carried out with a view to ascertain whether the production of the benzyl  $\beta$ -phenylpropionate takes place through an intermediate formation of benzyl acetoacetate, or whether it is due to a direct alkylation of the benzyl acetate by phenylmethylene, thus,  $\text{CHPh} < + \text{H}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_7\text{H}_7 \rightarrow \text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_7\text{H}_7$ . The results show that the alkylation takes place directly without intermediate formation of the acetoacetate, and the same has been found true of the alkylation of benzyl propionate and butyrate. The copper derivative of benzyl acetoacetate, m. p.  $156^\circ$ , forms green, feathery crystals.

E. G.

**Hydrolysis of Esters of Polyacid Alcohols.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1907, 13, 186—190).—The rate of hydrolysis of glycol monoacetate dissolved in 0.01 and 0.02 *N*-hydrochloric acid at  $25.2^\circ$  is measured. The reaction is of the first order, the velocity constants being  $2.85 \times 10^{-3}$  and  $5.65 \times 10^{-3}$ . The diacetate is also studied in the same way. In this case the hydrolysis takes place in two stages,  $\text{C}_2\text{H}_4(\text{OAc})_2 + \text{H}_2\text{O} = \text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{OAc} + \text{C}_2\text{H}_4\text{O}_2$  and  $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{OAc} + \text{H}_2\text{O} = \text{C}_2\text{H}_4(\text{OH})_2 + \text{C}_2\text{H}_4\text{O}_2$ .

The velocity constant of the second reaction being known, it is possible to calculate that of the first from measurements of the rate of hydrolysis of the diacetate. The values of the constant found are  $5.72 \times 10^{-3}$  in 0.01 *N* hydrochloric acid and  $9.78 \times 10^{-3}$  in 0.02 *N* acid.

T. E.

**Synthesis of Fats. I. Symmetrical Glycerides.** ADOLF GRÜN and P. SCHACHT (*Ber.*, 1907, 40, 1778—1791. Compare Abstr., 1905, i, 562).—The yield of diglyceride obtained by the action of glyceryl disulphate on a fatty acid decreases as the molecular weight of the acid diminishes. Triglycerides of the type  $\beta$ -lauro- $\alpha$ -distearin,



obtained by the action of an acid anhydride or chloride on the diglyceride, exist in two forms (compare Duffy, *Jahresb.*, 1852, 507). The one form dissolves readily and has a low m. p., whereas the other is sparingly soluble, and has either a higher m. p. or a double m. p. The glycerides of low m. p. can be crystallised from various solvents without undergoing transformation, but when such a solution is impregnated with a crystal of higher m. p., molecular transformation into the latter form occurs. The reverse change has not been accomplished so far. When melted and solidified, the compounds with double m. p. melt quite sharply at a fixed temperature. Laurodistearin and myristodilaurin give the higher m. p. and myristodistearin and oleodistearin the lower m. p. In the latter cases, however, the compounds after recrystallisation again have two melting points (compare Kreis and Hafner, *Abstr.*, 1903, ii, 190).

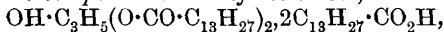
*Barium glyceroldisulphate*,  $\text{OH}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{SO}_2)_2\text{Ba}\cdot 2\text{H}_2\text{O}$ , crystallises from dilute alcohol. The *potassium* salt is anhydrous and sparingly soluble.  $\beta$ -*Aceto- $\alpha$ -distearin*,  $\text{OAc}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35})_2$ , obtained by heating distearin with an excess of acetic anhydride, forms colourless crystals, m. p.  $56\cdot5^\circ$ ; it is sparingly soluble in alcohol and is not decomposed when exposed to bright light for some months in a vacuum.

$\beta$ -*Oleo- $\alpha$ -distearin* (Kreis and Hafner, *Abstr.*, 1903, i, 788) melts at  $42^\circ$  when freshly prepared, but after a year has the double m. p.  $41^\circ$  and  $55^\circ$ , and after solidifying melts again at  $42^\circ$ .

$\beta$ -*Lauro- $\alpha$ -distearin*,  $\text{C}_{51}\text{H}_{98}\text{O}_6$ , exists in two forms, which can be separated by some 30—35 crystallisations from ether. The labile form has m. p.  $53\cdot5^\circ$  when freshly prepared and  $52\cdot5^\circ$  after solidifying. The stable form, after crystallising, melts at  $56\cdot5^\circ$  and  $68\cdot5^\circ$ , but after solidifying it has a single m. p.  $66\cdot5^\circ$ .

$\beta$ -*Myristo- $\alpha$ -distearin*,  $\text{C}_{53}\text{H}_{102}\text{O}_6$ , exists in two forms. The labile compound has m. p.  $57^\circ$  when freshly prepared and  $55\cdot5^\circ$  after solidifying. The stable form crystallises in slender, glistening needles practically insoluble in alcohol, m. p.  $58\cdot5^\circ$  and  $65^\circ$ , and after solidifying,  $58\cdot5^\circ$ .

*Dimyristin*,  $\text{C}_{31}\text{H}_{60}\text{O}_5$ , forms colourless crystals sparingly soluble in light petroleum, m. p. (from ether)  $63^\circ$ , (from amyl alcohol)  $65^\circ$ . It yields an additive compound with myristic acid,



in the form of colourless crystals, m. p.  $53\cdot5^\circ$  or  $55^\circ$ , which are more readily soluble than dimyristin in all organic solvents.  $\beta$ -*Aceto- $\alpha$ -dimyristin*,  $\text{C}_{33}\text{H}_{62}\text{O}_6$ , crystallises from ether partly in the form of glistening needles, m. p.  $41\cdot5^\circ$ , and partly as nodular masses, m. p.  $46\cdot5^\circ$ . The needles, when kept for some months, also melt at  $46\cdot5^\circ$ .

$\beta$ -*Lauro- $\alpha$ -dimyristin*,  $\text{C}_{43}\text{H}_{82}\text{O}_6$ , forms a microcrystalline powder, m. p.  $46\cdot5^\circ$ , and also exists in a second form, m. p.  $36\cdot5^\circ$ .

*Dilaurin*,  $\text{C}_{27}\text{H}_{52}\text{O}_5$ , has been obtained in a liquid form only from glyceroldisulphuric acid, but from  $\alpha$ -dichlorohydrin and potassium laurate in the form of nodular masses of needles, m. p.  $55^\circ$ .

$\beta$ -*Myristodilaurin*,  $\text{C}_{41}\text{H}_{78}\text{O}_6$ , exists in two forms, a labile compound crystallising in colourless plates, m. p.  $32^\circ$ , and a stable, micro-

crystalline powder, m. p.  $39.5^{\circ}$  (indefinite). An oily laurodimyristin is formed in the preparation of the two  $\beta$ -myristodilaurins.

$\beta$ -*Stearodilaurin*,  $C_{45}H_{86}O_5$ , has m. p.  $37.5^{\circ}$  and, after solidifying,  $42.5^{\circ}$ , and is accompanied by  $\alpha$ -*lauro- $\alpha\beta$ -distearin*,  $C_{51}H_{98}O_6$ , which has m. p.  $52.5^{\circ}$  and, after being kept for some time,  $49.5^{\circ}$ . J. J. S.

**Synthesis of Fats. II. Unsymmetrical Glycerides and their Decomposition.** ADOLF GRÜN and E. THEIMER (*Ber.*, 1907, 40, 1792—1801. Compare preceding abstract).—Unsymmetrical diacyl derivatives of glycerol  $\alpha$ -monochlorohydrin of the type  $CH_2Cl \cdot CH(OCOR) \cdot CH_2 \cdot O \cdot COR$  have been prepared by the action of fatty acids on the disulphate of the monochlorohydrin. As a rule they are accompanied by small amounts of *s*-diglycerides.

$\alpha$ -*Chloro- $\alpha\beta$ -distearin*,  $C_3H_5Cl(O \cdot CO \cdot C_{17}H_{35})_2$ , crystallises from ether or alcohol and has m. p.  $56^{\circ}$ , or after solidifying,  $41^{\circ}$ . The chlorine is not readily replaced by hydroxyl, but when heated with silver nitrite at  $120^{\circ}$  in a current of hydrogen it yields  $\beta$ -distearin, m. p.  $78.2^{\circ}$ .

$\alpha$ -*Aceto- $\alpha\beta$ -distearin*,  $C_{41}H_{78}O_6$ , has m. p.  $43^{\circ}$ , but after several weeks this has risen to  $48^{\circ}$ , but after resolidifying has again fallen to  $43^{\circ}$ .

$\alpha$ -*Lauro- $\alpha\beta$ -distearin*,  $C_{51}H_{98}O_6$ , has m. p.  $49^{\circ}$ , or after solidifying,  $47^{\circ}$ .  $\alpha$ -*Myristo- $\alpha\beta$ -distearin*,  $C_{63}H_{102}O_6$ , crystallises from alcohol in short needles, m. p.  $52^{\circ}$  and  $62^{\circ}$ , or after solidifying,  $59^{\circ}$ .

$\alpha$ -*Chloro- $\alpha\beta$ -dimyristin*,  $C_3H_5Cl(O \cdot CO \cdot C_{13}H_{27})_2$ , forms colourless crystals, m. p.  $27$ — $29^{\circ}$ . The pure compound, m. p.  $29^{\circ}$ , is most readily prepared by the action of thionyl chloride on  $\alpha\beta$ -dimyristin,  $C_{31}H_{60}O_5$ , which melts at  $64.5^{\circ}$ , or when kept for some months at  $62.5^{\circ}$ . The isomeric *aa*-dimyristin has m. p.  $55^{\circ}$  and  $61^{\circ}$ , or after solidifying,  $61^{\circ}$ .  $\alpha$ -*Lauro- $\alpha\beta$ -dimyristin*,  $C_{43}H_{82}O_6$ , crystallises in needles from alcohol and has m. p.  $45^{\circ}$ , or after some weeks,  $43.5^{\circ}$ .  $\alpha$ -*Chloro- $\alpha\beta$ -dilaurin*,  $C_3H_5Cl(O \cdot CO \cdot C_{11}H_{23})_2$ , has m. p.  $24^{\circ}$ .  $\alpha$ -*Myristo- $\alpha\beta$ -dilaurin*,  $C_{41}H_{78}O_6$ , has m. p.  $41^{\circ}$ , or after solidifying,  $36.5^{\circ}$ .  $\alpha$ -*Stearo- $\alpha\beta$ -dilaurin*,  $C_{45}H_{86}O_6$ , has m. p.  $46^{\circ}$ , or after solidifying,  $44^{\circ}$ .

$\alpha$ -*Chloro- $\alpha\beta$ -distearin* can be progressively hydrolysed by heating it for two hours at  $70^{\circ}$  with 10 mols. of 98% sulphuric acid. The products are stearic acid, monostearin, and monostearochlorohydrin.

J. J. S.

**Theory of Saponification. III.** MILAN J. STRITAR and RICHARD FANTO (*Monatsh.*, 1907, 28, 383—396. Compare Abstr., 1904, i, 843; this vol., i, 277; Kremann, Abstr., 1905, ii, 630; 1906, ii, 731).—This is in part a reply to Kremann (*loc. cit.*) and Lewkowitsch (this vol., i, 10). The authors' view that the saponification of glycerides by means of alcoholic alkalis takes place chiefly by direct hydrolysis of the triglyceride, the displacement of the glycerol by the solvent alcohol and subsequent hydrolysis of the ester so formed being minor reactions, is in opposition to that of Kremann, according to which direct hydrolysis of the triglyceride does not take place. Whilst the displacement of the glycerol is almost instantaneous in presence of much alkali, if the amount of the latter is limited the reaction takes place much more slowly and can be followed quantitatively, in the case of triacetin when about 3% of the alkali required for total saponifica-

tion is employed, or in that of rape-seed oil when the amount of alkali present has diminished from 16% to 7%.

A number of experiments with rape-seed oil, in which the hydrolysis was stopped by addition of a known amount of acetic acid in the manner previously described (this vol., i, 277), the excess of acetic acid titrated, the soap decomposed by acetic acid, and the alcohol and glycerol determined in the washed and dried fat, are described and the results tabulated. It is found that the sum of the hydroxyl ions consumed ( $s$ ) and the hydroxyl equivalents of the alcohol ( $a$ ) and of the glycerol ( $g$ ) found is greater than the ester number ( $e$ ) of the original, neutral fat. One at least of the two reactions, direct hydrolysis of the triglyceride and displacement of the glycerol, must take place in more than one stage, since if both reactions were to take place directly,  $s + a + g$  must equal  $e$ . An approximate calculation of the composition of the residue shows that the amount of ester formed is 36—37% in excess of that required by the direct reaction. The amount of glycerol found points to the presence of a diacin. It is argued that the reaction taking place in more than one stage is the displacement of the glycerol.

Further light can be thrown on the course of the saponification only by isolation of the intermediate products, which will be attempted.

G. Y.

**Reagent in the Chemistry of Fats. II.** ERNEST TWITCHELL (*J. Amer. Chem. Soc.*, 1907, 29, 566—571. Compare Abstr., 1906, i, 331).—In the earlier paper it was pointed out that sulphophenyl- and sulphonaphthyl-stearic acids act as catalytic agents in the hydrolysis of fats. It is now found that these acids are also capable of accelerating the esterification of the higher fatty acids under conditions in which the process would otherwise be scarcely noticeable. The reaction only takes place completely when the water produced is removed; the use of these sulphostearic acids is therefore especially applicable to the esterification of the higher fatty acids and alcohols which are not readily volatile at 100°, since the action occurs rapidly at this temperature and the water can be eliminated by evaporation.

Experiments are described in which the quantitative esterification of glycerol and other alcohols by commercial stearic acid (a mixture of stearic and palmitic acids) has been effected by means of sulphonaphthylstearic acid. From the results obtained, the "hydroxyl value" (milligrams of potassium hydroxide containing the same amount of hydroxyl as 1 gram of the alcohol) of the alcohols has been calculated. The reaction has been extended to the estimation of the alcoholic hydroxyl value of hydroxy-acids of the fatty series and their glycerides. The following hydroxyl values have been obtained: lard, 1.8; fatty acids of lard, 8.3; tallow fatty acids, 2.3; olive oil, 6.4 and 5.0; cotton-seed oil, 7.8 and 8.2; fatty acids of cotton-seed oil, 12.8; castor oil, 149.0; and fatty acids of castor oil, 161.4.

Experiments have also been made which show that the higher fatty acids can be quantitatively esterified by alcohols, such as glycerol, ceryl alcohol, and amyl alcohol, in presence of sulphonaphthyl-stearic acid,

E. G.

**Optical Activity of Mineral Oil.** JULIUS MARCUSSEN (*Chem. Zeit.*, 1907, 31, 419—422).—On fractionally distilling the unsaponifiable portion of an olein, obtained from tallow and palm fat, it was found that the rotatory power of the fractions increased as their boiling points rose. This is in agreement with Engler's observations on mineral oil. Determinations of the iodine number of the various fractions gave widely different results, according as they were made by the Wys or Hübl-Waller method. This phenomenon is also exhibited by cholesterol, but not by ordinary fats. A further point of resemblance between artificial and natural mineral oils lay in the fact that the optical activity of both is diminished by concentrated sulphuric acid. In reply to Neuberg's objection (*Abstr.*, 1906, i, 923) that the amount of cholesterol in fat is too small to account for the high optical activity of some mineral oils, it is pointed out that the fats of marine animals, which, according to Engler, probably form the chief source of these oils, contain a much larger percentage of cholesterol than ordinary fat, and that, moreover, cholesterol or phytosterol form normal constituents of almost every part of the animal or vegetable organism. The author also criticises the theories of Neuberg and Walden. P. H.

**Diacetylcarboxylic Acid.** CARL D. HARRIES and KARL KIRCHER (*Ber.*, 1907, 40, 1651—1652).—*Diacetylcarboxylic acid*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is obtained as a yellow, viscous oil by treating a chloroform solution of  $\beta$ -benzylidenelævulic acid with ozone and decomposing the product with water. It is stable to boiling water, and forms a green copper salt,  $\text{C}_{10}\text{H}_{10}\text{O}_8\text{Cu}$ . The *bisphenylhydrazone*,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_4$ , m. p.  $175^\circ$ , forms yellow prisms, and the *bis-semicarbazone* a white powder, m. p.  $240^\circ$ . The *ethyl ester*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , has b. p.  $79\text{—}80.5^\circ/10\text{ mm.}$ , and its *phenylhydrazone* has m. p.  $115^\circ$ .

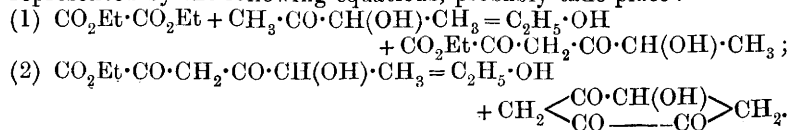
C. S.

**Condensation of Ethyl Oxalate with Dimethylketol.** OTTO DIELS and MAX STERN (*Ber.*, 1907, 40, 1622—1629).—The work of Diels and Plant (*Abstr.*, 1905, i, 509) has been continued with the view of utilising 1 : 2-diketones for the synthesis of cyclic polyketones.

Diacetylmonoxime methyl ether,  $\text{COMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{OMe}$ , is readily obtained by the action of methyl sulphate on diacetylmonoxime, and, when condensed with ethyl oxalate, forms the *compound*,  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}\cdot\text{N}\cdot\text{OMe}$ , which separates from acetone in felted needles, m. p.  $88^\circ$ . The *acid* has m. p.  $114^\circ$ . Attempts to convert these substances into cyclic compounds by elimination of alcohol or water failed.

The *compound*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CMe}\cdot\text{N}\cdot\text{OMe}$ , obtained by condensing diacetylmonoxime methyl ether with benzaldehyde, crystallises in prisms, m. p.  $82^\circ$ , and has b. p.  $165\text{—}167^\circ/14\text{ mm.}$

When dimethylketol is condensed with ethyl oxalate, the actions, represented by the following equations, probably take place :



The resulting compound,  $C_6H_6O_4$ , is acid in character, and can be titrated like a monobasic acid. With phenylhydrazine, it forms a *dihydrazone*,  $C_{18}H_{18}O_2N_4$ , with m. p.  $114\cdot5^\circ$  (decomp.) ; when methylated with diazomethane it forms a *methyl* derivative,  $C_7H_8O_4$ , which separates from alcohol in glistening leaflets, m. p.  $91^\circ$ , and which reduces Fehling's solution.

The compound,  $C_6H_6O_4$ , combines with *o*-phenylenediamine to form a characteristic *quinoxaline* derivative,  $C_{12}H_{12}O_8N_2$ , which forms bright red needles, m. p.  $237^\circ$  (decomp.).  
A. McK.

**Double Cobalt Malonates.** RICHARD C. LORD (*J. Physical Chem.*, 1907, 11, 173—200).—Cobalt malonate and a series of double cobalt malonates have been prepared. Denoting the malonic acid radicle by *M*, the composition of these is represented by the following formulæ. In most cases the specific gravity has been determined, this being indicated by the figures in brackets.  $CoM, 2H_2O$  (2·279),  $H_2CoM_2, 2H_2O$ ,  $(NH_4)_2CoM_2, 4H_2O$  (1·804),  $K_2CoM_2, 4H_2O$  (2·234),  $Rb_2CoM_2, 4H_2O$  (2·131),  $Cs_2CoM_2, 4H_2O$  (2·682),  $K_2CoM_2$ .

Solubility measurements at  $18^\circ$  gave the following numbers, which express the number of grams of anhydrous salt in 100 grams of solution:  $CoM$ , 1·353 ;  $(NH_4)_2CoM_2$ , 10·61 ;  $K_2CoM_2$ , 4·26 ;  $Cs_2CoM_2$ , 14·23.

The electrical conductivity of the solutions of the double cobalt malonates is very much smaller than the sum of the conductivities of corresponding solutions of cobalt malonate and the alkali malonates. The difference between these values also increases considerably with the dilution. From this, in conjunction with the fact that the addition of an alkali malonate to a solution of cobalt malonate causes a change in colour from a bright red to a purple-red, the conclusion is drawn that the double cobalt malonates are in reality complex salts, which dissociate electrolytically with the formation of complex cobalt malonyl ions of considerable stability. Migration experiments are described which support this conclusion. On electrolysing solutions of the complex cobalt malonates, acidified with malonic acid, the colour of the anode solution changes to green. The author supposes that cobalt-malonates are formed in these circumstances, but attempts to separate crystalline malonates containing trivalent cobalt were unsuccessful.  
H. M. D.

**Esterification of Succinic Acid.** ISAAC K. PHELPS and J. L. HUBBARD (*Amer. J. Sci.*, 1907, 23, 368—374).—It was shown (this vol., ii, 297) that pure succinic acid is obtained best by hydrolysis of ethyl succinate ; in the present paper the preparation of the pure ester, and the conditions under which its formation takes place almost quantitatively, are described.

The results of a number of experiments show that whilst the yield of ethyl succinate depends to some extent on the purity of the succinic acid and the alcohol employed, on the proportion of hydrogen chloride (compare Fischer and Speier, *Abstr.*, 1896, i, 201), and the time of the reaction, it is affected to a more considerable extent by the removal of the water formed during the esterification. This is accomplished by passing alcohol vapour charged with hydrogen chloride into a mixture

of succinic acid, alcohol, and hydrogen chloride, distilling continuously at 100—110°. In this manner, a 97% yield of ethyl succinate is obtained from 50 grams of succinic acid in five hours, whilst the yield may be increased to 97.7% in two and a half hours if after one and a half hours the whole of the alcohol, water, and hydrogen chloride in the distilling flask is removed by distillation at 60°/15 mm. and the esterification process repeated. Only small amounts of ethyl succinate are found in the alcoholic-acid distillate. G. Y.

**Ester-, Amide-, Anilide-, and *p*-Toluidide-Acids of Mesaconic Acid.** RICHARD ANSCHÜTZ [and, in part, JULIEN DRUGMAN, FERDINAND HAAS, OSWALD SCHARFENBERG, and OTTO SIEPLEIN] (*Annalen*, 1907, **343**, 139—208. Compare *Abstr.*, 1890, 368; 1898, i, 128; Cloëz, *Abstr.*, 1890, 739).—Hydrogen  $\beta$ -ethyl mesaconate,  
 $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Et}$ ,

m. p. 67—68°, was prepared by Cloëz (*loc. cit.*) by the action of barium carbonate and water on ethyl dibromomethylacetoacetate. On partial esterification of mesaconic acid, Anschütz and Drugman (*Abstr.*, 1898, i, 128) obtained a hydrogen ethyl mesaconate, m. p. 42°, which they considered to be the  $\alpha$ -ethyl ester,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , and, by partial hydrolysis of ethyl mesaconate, a hydrogen ethyl mesaconate, m. p. 67—68°, which they assumed to be identical with Cloëz's  $\beta$ -ethyl ester. Certain observations made in the preparation of mesaconamic and mesaconanilic acids having thrown doubt on the constitution of Anschütz and Drugman's esters, the partial hydrolysis of methyl mesaconate and partial methylation of mesaconic acid have been studied. It is found that whilst the product of the partial hydrolysis is almost pure hydrogen  $\alpha$ -methyl mesaconate, that of the partial methylation is a mixture of the  $\alpha$ - and  $\beta$ -methyl esters. The reinvestigation of the hydrogen ethyl esters led to similar results; the ester-acid obtained by partial hydrolysis of ethyl mesaconate is hydrogen  $\alpha$ -ethyl mesaconate and is isomeric with Cloëz's hydrogen  $\beta$ -ethyl ester which melts at the same temperature, whilst the product of the partial esterification is a mixture of the  $\alpha$ - and  $\beta$ -ethyl esters.

In the experimental part of the paper, the formation of these ester-acids and of the corresponding mesaconamic, mesaconanilic, and mesacon-*p*-toluidic acids, by conversion into which the ester-acids have been separated and identified, is described. It is shown that the  $\alpha$ -alkyl esters, which are formed by partial hydrolysis, are the main components of the mixtures obtained by partial esterification, from which it is concluded that the alkyl, which is the more difficult to introduce, is the first removed by hydrolysis.

The action of limited amounts of aniline and *p*-toluidine on mesaconyl chloride leads to the formation of almost pure mesaconanilyl and mesacon-*p*-toluidyl chlorides respectively, the chlorine of the more acid  $\alpha$ -carboxyl chloride group reacting more readily with bases than that of the  $\beta$ -carboxyl chloride.

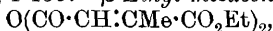
Hydrogen  $\alpha$ -methyl mesaconate, m. p. 52°, has the solubility 12.07/100 aq. at 20°, and the conductivity constant  $K=0.0353$ ; the *silver* salt was analysed; the *ammonium* salt, m. p. 153—154°. Hydrogen  $\beta$ -methyl mesaconate crystallises from light petroleum in

small needles, m. p.  $84^{\circ}$ , b. p.  $135\text{--}137^{\circ}/13$  mm., and has the solubility  $2.55/100$  aq. at  $20^{\circ}$ , and the conductivity constant  $K=0.051$ ; the *silver* and *ammonium*, m. p.  $144\text{--}146^{\circ}$ , salts were analysed. The mixture of  $\alpha$ - and  $\beta$ -methyl esters formed by partial esterification, m. p.  $36\text{--}46^{\circ}$ .

Hydrogen  $\alpha$ -ethyl mesaconate crystallises from benzene in needles, m. p.  $67\text{--}68^{\circ}$ , b. p.  $141.6\text{--}142.2^{\circ}/14$  mm., and has the solubility  $1.91/100$  aq. at  $20^{\circ}$ , and the conductivity constant  $K=0.0342$ ; the *ammonium* salt, m. p.  $127\text{--}128^{\circ}$ ; the *silver* salt was analysed. Hydrogen  $\beta$ -ethyl mesaconate crystallises from light petroleum in small, white needles, m. p.  $68^{\circ}$ , is odourless when pure, and has the solubility  $1.49/100$  aq. at  $20^{\circ}$ , and the conductivity constant  $K=0.0553$ ; the *silver* and *ammonium*, m. p.  $102\text{--}103^{\circ}$ , salts were analysed. A mixture of equal parts of the  $\alpha$ - and  $\beta$ -ethyl esters, m. p.  $46\text{--}52^{\circ}$ , whilst that, m. p.  $42\text{--}45^{\circ}$ , formed by partial esterification of mesaconic acid, contains 60% of the  $\alpha$ -ethyl ester. Mixtures of the  $\alpha$ - and  $\beta$ -esters are obtained also by heating ethyl mesaconate with mesaconic acid.

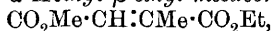
When treated with phosphorus pentachloride in chloroform solution and distilled, the mixture of hydrogen methyl mesaconates, obtained by esterification, yields a mixture of methyl mesaconyl chlorides, b. p.  $79.2^{\circ}/12$  mm.,  $D_4^{15} 1.228$ , and a mixture of the methyl-ester anhydrides, b. p.  $196^{\circ}/14$  mm. The individual ester-chlorides and ester-anhydrides are obtained by the action of phosphorus pentachloride on the pure hydrogen methyl and hydrogen ethyl esters.  $\alpha$ -Methyl mesaconyl  $\beta$ -chloride,  $\text{CO}_2\text{Me}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COCl}$ , b. p.  $80^{\circ}/13$  mm.,  $D_4^{15} 1.224$ .  $\beta$ -Methyl mesaconyl  $\alpha$ -chloride,  $\text{COCl}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Me}$ , b. p.  $79\text{--}80^{\circ}/13$  mm. or  $92\text{--}93^{\circ}/20$  mm.,  $D_{20}^{20} 1.232$ .  $\alpha$ -Ethyl mesaconyl  $\beta$ -chloride,  $\text{C}_7\text{H}_9\text{O}_3\text{Cl}$ , b. p.  $86\text{--}87^{\circ}/13$  mm.,  $D_{20}^{20} 1.173$ .  $\beta$ -Ethyl mesaconyl  $\alpha$ -chloride, b. p.  $88\text{--}90^{\circ}/13$  mm.,  $D_{20}^{20} 1.184$ . These ester-chlorides are hydrolysed by water, forming the corresponding hydrogen alkyl mesaconates from which they are obtained.

$\alpha$ -Methyl mesaconic anhydride,  $\text{O}(\text{CO}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Me})_2$ , b. p.  $190\text{--}195^{\circ}/13$  mm.,  $D_{20}^{20} 1.232$ .  $\beta$ -Methyl mesaconic anhydride, a yellow oil, b. p.  $190\text{--}195^{\circ}/13$  mm.,  $D_{20}^{20} 1.263$ .  $\alpha$ -Ethyl mesaconic anhydride, b. p.  $202\text{--}203^{\circ}/13$  mm.,  $D_{20}^{20} 1.159$ .  $\beta$ -Ethyl mesaconic anhydride,



b. p.  $200\text{--}205^{\circ}/14$  mm.,  $D_{20}^{20} 1.187$ . When treated with ammonia in ethereal solution these ester-anhydrides form the corresponding ammonium alkyl mesaconates and alkyl mesaconamates.

$\beta$ -Methyl  $\alpha$ -ethyl mesaconate,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Me}$ , formed by the action of methyl iodide on silver  $\alpha$ -ethyl mesaconate, b. p.  $95.2\text{--}95.6^{\circ}/12$  mm.,  $D_{20}^{20} 1.079$ , yields hydrogen  $\alpha$ -ethyl mesaconate on partial hydrolysis.  $\alpha$ -Methyl  $\beta$ -ethyl mesaconate,



b. p.  $97\text{--}98^{\circ}/13$  mm.,  $D_{20}^{20} 1.076$ .

$\alpha$ -Methyl mesacon- $\beta$ -amate,  $\text{CO}_2\text{Me}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}_2$ , formed by the action of ammonia on the  $\alpha$ -methyl ester-chloride or of methyl iodide on silver mesacon- $\beta$ -amate, crystallises in needles, m. p.  $103^{\circ}$ , and is converted by nitrous acid into hydrogen  $\alpha$ -methyl mesaconate.

$\alpha$ -Ethyl mesacon- $\beta$ -amate,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises in small, tetragonal prisms, m. p.  $78^\circ$ . *Mesacon- $\beta$ -amic acid*,



m. p.  $174^\circ$ , is formed by hydrolysis of its esters with potassium hydroxide at the ordinary temperature; the *ammonium*, m. p.  $144$ — $146^\circ$ , and *silver* salts are described.

$\beta$ -Methyl mesacon- $\alpha$ -amate,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Me}$ , m. p.  $117^\circ$ .  $\beta$ -Ethyl mesacon- $\alpha$ -amate forms small, hard crystals, m. p.  $96^\circ$ . *Mesacon- $\alpha$ -amic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , m. p.  $222^\circ$ ; the *ammonium*, m. p.  $183$ — $184^\circ$ , and *silver* salts are described.

Mesaconanilic and mesacon-*p*-toluidic esters are formed by the action of aniline and *p*-toluidine respectively on the ester-chlorides, or of alkyl iodides on the silver mesaconanilates and *p*-toluidates. The anilic and *p*-toluidic acids are obtained by hydrolysis of their esters with the calculated amount of potassium hydroxide at the ordinary temperature. The mesaconanilic acids, obtained from the product of the partial methylation of mesaconic acid, can be separated by fractional crystallisation from water.

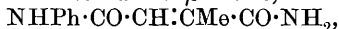
*Mesacon- $\beta$ -anilic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NHPh}$ , crystallises in glistening leaflets, m. p.  $163^\circ$ , is readily soluble in hot water, and when heated with an excess of potassium hydroxide at  $100^\circ$  yields aniline and mesaconic acid; the *silver* salt was analysed.  $\alpha$ -Methyl mesacon- $\beta$ -anilate, m. p.  $91$ — $92^\circ$ .  $\alpha$ -Ethyl mesacon- $\beta$ -anilate crystallises in needles, m. p.  $72^\circ$ .

*Mesacon- $\alpha$ -anilic acid*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , crystallises in microscopic needles, m. p.  $202^\circ$ , is sparingly soluble in hot water, and yields aniline and mesaconic acid when heated with potassium hydroxide at  $100^\circ$ ; the *silver* salt was analysed.  $\beta$ -Methyl mesacon- $\alpha$ -anilate forms long needles, m. p.  $92^\circ$ ; a mixture of this with the  $\alpha$ -methyl  $\beta$ -anilate, m. p.  $65^\circ$ .  $\beta$ -Ethyl mesacon- $\alpha$ -anilate, m. p.  $92^\circ$ .

*Mesacon- $\beta$ -p-toluidic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , crystallises in small needles, m. p.  $184^\circ$ ; the *silver* salt was analysed.  $\alpha$ -Methyl mesacon- $\beta$ -p-toluidate,  $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}$ , m. p.  $105^\circ$ .  $\alpha$ -Ethyl mesacon- $\beta$ -p-toluidate crystallises in white needles, m. p.  $99^\circ$ .

*Mesacon- $\alpha$ -p-toluidic acid*,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , white needles, m. p.  $196^\circ$ ; the *silver* salt was analysed. The *methyl* ester crystallises from methyl alcohol in needles, or from acetic acid in leaflets, m. p.  $135^\circ$ . The *ethyl* ester, white needles, m. p.  $103^\circ$ .

*Mesacon- $\alpha$ -anilyl chloride*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COCl}$ , formed by the action of 2 mols. of aniline on mesaconyl chloride in ethereal solution, crystallises from benzene in light yellow needles, m. p.  $107^\circ$ , and yields on hydrolysis mesacon- $\alpha$ -anilic acid, or with methyl alcohol the  $\beta$ -methyl  $\alpha$ -anilate. *Mesacon- $\alpha$ -anil- $\beta$ -amide*,

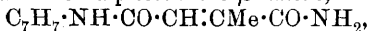


formed by the action of ammonia on the  $\alpha$ -anilyl chloride in ethereal solution, crystallises in needles, m. p.  $165^\circ$ . *Mesacon- $\alpha$ -anil- $\beta$ -p-toluidide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , from *p*-toluidine and the  $\alpha$ -anilyl chloride, crystallises from alcohol in white needles, m. p.  $189^\circ$ .

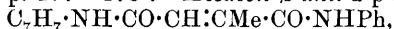
*Mesacon- $\alpha$ -p-toluidyl chloride*,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COCl}$ , crystallises in sulphur-yellow needles, m. p.  $115^\circ$ , and yields the correspond-



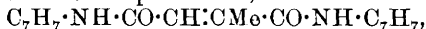
ing toluidic acid and its esters on treatment with alkalis, or methyl or ethyl alcohol. *Mesacon- $\alpha$ -p-toluidide- $\beta$ -amide*,



white needles, m. p. 177—178°. *Mesacon- $\beta$ -anil- $\alpha$ -p-toluidide*,



white needles, m. p. 183°; a mixture of this with its isomeride, m. p. 172—174°. *Mesacon-p-toluidide*,



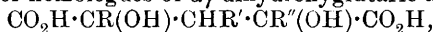
white needles, m. p. 212°.

Pebal's silver hydrogen mesaconate (*Annalen*, 1851, 78, 139), which, contrary to that author's statement, crystallises from a solution of silver mesaconate in a concentrated, aqueous solution of an excess of mesaconic acid, is the  $\beta$ -silver salt, since on treatment with methyl and ethyl iodides it yields almost pure hydrogen  $\beta$ -methyl and hydrogen  $\beta$ -ethyl mesaconates. The solution of silver mesaconate in an excess of mesaconic acid, before crystallisation of the  $\beta$ -silver salt, contains the  $\alpha$ - and  $\beta$ -silver salts in equilibrium, the  $\alpha$ -salt preponderating, since the action of ethyl iodide on the solution leads to the formation of a mixture of hydrogen ethyl mesaconates, of which the  $\alpha$ -ethyl ester is the chief component. G. Y.

**r-Dilactylic Acid.** ÉMILE JUNGLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1907, 144, 979—981).—The product formed by the action of ethyl  $\alpha$ -chloropropionate on the sodium derivative of ethyl lactate is not, as von Brüggem supposed (*Annalen*, 1868, 148, 224), ethyl ethyl-lactyl-lactate,  $\text{OEt}\cdot\text{CHMe}\cdot\text{CO}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , but ethyl dilactylate,  $\text{O}(\text{CHMe}\cdot\text{CO}_2\text{Et})_2$ , b. p. 110—112°/15 mm.,  $D^{20}_D$  1.051, identical with that obtained by Wurtz and Friedel (*Ann. Chem. Pharm.*, 1861, 63, 114) and Tanatar and Tschelebéeff (*Abstr.*, 1891, 177). The free acid, m. p. 106°, crystallises from benzene in lamellæ and from water in prisms, and on distillation, even under reduced pressure, yields dilactylic anhydride,  $\text{O}\langle\begin{smallmatrix} \text{CO}\cdot\text{CHMe} \\ \text{CO}\cdot\text{CHMe} \end{smallmatrix}\rangle\text{O}$ , b. p. 110°/20 mm., a colourless liquid which, in contact with water, slowly regenerates the acid.

T. A. H.

**Dilactones. II.** RUDOLF FITTIG (*Annalen*, 1907, 353, 1—64. Compare *Abstr.*, 1901, i, 120).—This investigation has been continued with the object of determining the influence of the position of the lactone rings in the molecule on the chemical properties of the dilactones and of the corresponding hydroxy-lactonic acids. The substances examined are chiefly those containing the annexed groupings. The simplest of these, the dilactone (pentadilactone) and monolactone (pentoxylactonic acid) of  $\alpha\gamma$ -dihydroxyglutaric acid, have been prepared and will be described later; in the present paper, the derivatives of homologues of  $\alpha\gamma$ -dihydroxyglutaric acid,

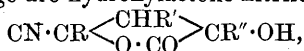


are described.

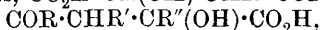
The work of Zelinsky on the derivatives of  $\alpha\gamma$ -dihydroxy- $\alpha\gamma$ -dimethyl-

glutaric acid (Abstr., 1892, 436. Compare Auwers and Kauffmann, Abstr., 1893, i, 72; Michael and Lamb, this vol., i, 134) has been repeated; it is found that that author's supposed stable  $\alpha\gamma$ -dihydroxy- $\alpha\gamma$ -dimethylglutaric acid is a monobasic hydroxy-lactonic acid, which nullifies the arguments as to the stereo-configuration of the supposed isomeric dihydroxydimethylglutaric acids and their relation to dimethyltartaric acid.

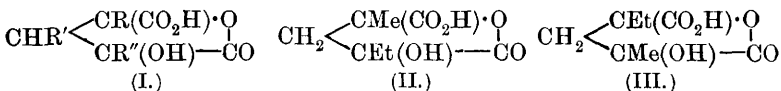
The  $\alpha\gamma$ -dihydroxyglutaric acids are obtained from the corresponding diketones, which, when shaken with cold saturated aqueous potassium cyanide, develop heat and form potassium derivatives yielding the dihydroxy-dinitriles,  $\text{OH}\cdot\text{CR}(\text{CN})\cdot\text{CHR}'\cdot\text{CR}''(\text{CN})\cdot\text{OH}$ , on treatment with carbon dioxide; the potassium derivatives readily decompose, and only one,  $\text{OK}\cdot\text{CMe}(\text{CN})\cdot\text{CH}_2\cdot\text{CPr}^a(\text{CN})\cdot\text{OK}$ , has been isolated. The dihydroxy-dinitriles undergo hydrolysis in two stages; the products of the first stage are hydroxylactone-nitriles,



which, when boiled with water, lose hydrogen cyanide, forming hydroxy-ketonic acids,  $\text{CO}_2\text{H}\cdot\text{CR}(\text{OH})\cdot\text{CHR}'\cdot\text{COR}''$ , or

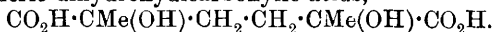


but are hydrolysed by concentrated hydrochloric acid at the ordinary temperature, yielding the hydroxy-lactonic acids (I). It is found that with R and R'' = Me, and R' = H, the hydroxy-lactonic acid, obtained from the nitrile, is not identical with that formed by partial hydrolysis of the dilactone, whereas the same hydroxy-lactonic acid is obtained by both methods if R and R' are different alkyls and R'' = H; the constitution of the hydroxy-lactonic acid, which may be II or III, has not been determined.



The tendency to formation of isomerides is much greater if R' is an alkyl group, the dinitrile,  $\text{OH}\cdot\text{CMe}(\text{CN})\cdot\text{CHEt}\cdot\text{CMe}(\text{CN})\cdot\text{OH}$ , being obtained in two modifications, one of which behaves as described above, whilst the *iso*-compound, when treated with concentrated hydrochloric acid at the ordinary temperature, forms a hydroxy-lactone-amide which is further hydrolysed by hot concentrated hydrochloric acid, yielding the same acid as is obtained directly from the first modification of the dinitrile.

A dihydroxy-dinitrile has been obtained in the same manner from acetonylacetone (Zelinsky and Isaieff, Abstr., 1896, i, 413). On hydrolysis with concentrated hydrochloric acid, it yields a  $\delta\delta$ -dilactone and two isomeric dihydroxydicarboxylic acids,



The  $\delta\delta$ -dilactone,  $\begin{array}{c} \text{O} \text{---} \text{CO} \\ | \qquad \qquad | \\ \text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe} \\ | \qquad \qquad | \\ \text{CO} \text{---} \text{O} \end{array}$ , is more stable than the

$\gamma\gamma$ -dilactones described above.

*Derivatives of  $\alpha\gamma$ -dihydroxy- $\alpha\gamma$ -dimethylglutaric acid.*—[With PAUL

KRAUS.]—The *calcium*, *barium* ( $3\text{H}_2\text{O}$ ), and *silver*,  $\text{C}_7\text{H}_9\text{O}_5\text{Ag}$ , salts of the hydroxylactone acid, m. p.  $186^\circ$ , are described. The *barium*,  $\text{C}_7\text{H}_{10}\text{O}_6\text{Ba}$ , and *calcium* ( $\frac{1}{2}\text{H}_2\text{O}$ ) salts of the dibasic acid were analysed; on liberation from its salts, the dibasic acid changes into the hydroxy-lactonic acid, m. p.  $186^\circ$ . The *isohydroxy-lactonic acid*,  $\text{C}_7\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$ , formed by the action of water on the dilactone, is identical with Zelinsky's dihydroxydimethylglutaric acid, loses  $\text{H}_2\text{O}$  at  $95-100^\circ$ , and when anhydrous crystallises from ether in prisms, m. p.  $107^\circ$ ; the *calcium* ( $9\text{H}_2\text{O}$ ), *barium* ( $\text{H}_2\text{O}$ ), and *silver*,  $\text{C}_7\text{H}_9\text{O}_5\text{Ag}$ , salts are described.

*$\alpha$ -Methylpentenolactone*,  $\text{CHMe} \begin{array}{c} \diagup \text{O} \cdot \text{CO} \\ \diagdown \text{CH} \end{array} \text{CMe}$ , is formed, together with the dilactone, by distillation of the hydroxy-lactonic acid, as an oil, b. p.  $205-207^\circ$ , and, with bases, forms salts of  *$\alpha$ -methylævulic acid*. The *calcium* and *barium* salts and the *phenylhydrazone*,  $\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}_2$ , white needles, decomposing on exposure to air, are described.

(Béhal, Abstr., 1901, i, 278, obtained a lactone, b. p.  $205-206^\circ$ , by distilling  *$\alpha$ -methylævulic acid*.)

*Derivatives of  $\alpha\gamma$ -dihydroxy- $\alpha$ -methyl- $\gamma$ -ethyl- and  $\alpha\gamma$ -dihydroxy- $\alpha$ -methyl- $\gamma$ -n-propyl-glutaric acids*.—[With JOSEPH VON PANAYEFF.]—The *dihydroxy-dinitrile*,  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{Et}$ , prepared from propionyl-acetone, crystallises from a mixture of alcohol and ether in small leaflets, m. p.  $145^\circ$  (decomp.). The *hydroxy-lactonic nitrile*,  $\text{C}_8\text{H}_{11}\text{O}_3\text{N}$ , crystallises in monoclinic prisms, m. p.  $114^\circ$ , distils at the ordinary temperature with slight decomposition, and when boiled with water yields the *keto-acid*,  $\text{C}_7\text{H}_{12}\text{O}_4$ . This is obtained as a viscid liquid, b. p.  $160-165^\circ/100$  mm.; the *calcium* salt,  $(\text{C}_7\text{H}_{11}\text{O}_4)_2\text{Ca}\cdot\text{H}_2\text{O}$ , was analysed; the *phenylhydrazone*,  $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2$ , crystallises in colourless plates, m. p.  $121^\circ$  (decomp.). The *hydroxy-lactonic acid*,  $\text{C}_8\text{H}_{12}\text{O}_5\cdot\text{H}_2\text{O}$ , crystallises in rhombic plates, m. p.  $84^\circ$ , or, when anhydrous, forms small, flat crystals, m. p.  $122^\circ$ ; the *calcium* and *silver* salts were analysed. The *calcium*,  $\text{C}_8\text{H}_{12}\text{O}_6\text{Ca}\cdot 6\text{H}_2\text{O}$ , and *silver* salts of  *$\alpha\gamma$ -dihydroxy- $\alpha$ -methyl- $\gamma$ -ethylglutaric acid* are described. The *dilactone*,  $\text{C}_8\text{H}_{10}\text{O}_4$ , crystallises in small leaflets, m. p.  $55^\circ$ , and yields the hydroxy-lactonic acid on recrystallisation from water.

The *potassium* derivative of the dinitrile of  *$\alpha\gamma$ -dihydroxy- $\alpha$ -methyl- $\gamma$ -n-propylglutaric acid*,  $\text{C}_9\text{H}_{12}\text{O}_2\text{N}_2\text{K}_2$ , crystallises in nacreous leaflets, decomposes on exposure to air, losing hydrogen cyanide, and blues moistened, red litmus paper. The *dinitrile*,  $\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2$ , crystallises in prisms, m. p.  $137^\circ$  (decomp.) The *hydroxy-lactonic nitrile*,  $\text{C}_9\text{H}_{13}\text{O}_3\text{N}$ , forms monoclinic prisms, m. p.  $125^\circ$ .

*Derivatives of  $\alpha\gamma$ -dihydroxy- $\alpha\gamma$ -dimethyl- $\beta$ -ethylglutaric acid*.—[With WALTER PETERS.]—The action of potassium cyanide on ethylacetyl-acetone leads to the formation of two products which are separated by recrystallisation from ether or chloroform. The *dihydroxydinitrile*,  $\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2$ , crystallises in small, monoclinic plates, m. p.  $139^\circ$  (decomp.). The *iso-compound* crystallises in thin, tetragonal needles, m. p.  $124^\circ$  (decomp.), and is more soluble in ether or chloroform than its isomeride. The *hydroxy-lactonic nitrile*,  $\text{C}_9\text{H}_{13}\text{O}_3\text{N}$ , crystallises in rhombic plates [ $a:b:c = 0.8760:1:0.8103$ ], m. p.  $109^\circ$ , has piezoelectrical properties when powdered, is decomposed by boiling water, and when treated

with cold concentrated hydrochloric acid is gradually converted into the *hydroxy-lactonic acid*,  $C_9H_{14}O_5$ , which crystallises in prisms, m. p.  $140^\circ$ , and is hygroscopic; the *calcium*,  $(C_9H_{13}O_5)_2Ca$ , *barium*, and *silver* salts were analysed. The *isohydroxy-lactonic nitrile*,  $C_9H_{13}O_3N$ , formed from the *isodinitrile*, crystallises in monoclinic or triclinic plates, m. p.  $72^\circ$ , and is converted by cold concentrated hydrochloric acid into the corresponding *amide*,  $C_9H_{15}O_4N$ , which crystallises in rhombic plates, m. p.  $223^\circ$ , sublimes above  $250^\circ$ , and on hydrolysis with alkalis or hot hydrochloric acid yields the hydroxy-lactonic acid, m. p.  $140^\circ$ . The *barium*,  $C_9H_{14}O_6Ba$ , and *calcium* salts of dihydroxy-dimethylethylglutaric acid were analysed. The *dilactone*,  $C_9H_{12}O_4$ , crystallises from light petroleum in rhombohedra, m. p.  $52^\circ$ , and when shaken with cold water gradually forms the hydroxy-lactonic acid.

*Derivatives of  $\alpha\delta$ -dihydroxy- $\alpha\delta$ -dimethyladipic acid*.—[With FRITZ LENTZ.]—The *dinitrile*, formed by the action of potassium cyanide on acetylacetone, was not isolated.  $\alpha\delta$ -Dihydroxy- $\alpha\delta$ -dimethyladipic acid,  $C_8H_{14}O_6$ , crystallises in monoclinic prisms, m. p.  $206$ — $208^\circ$ ; the *calcium* ( $6H_2O$ ), *barium* ( $5H_2O$ ), and *silver* salts were analysed. When heated at  $160^\circ$ , the dihydroxy-acid yields the *hydroxy-lactonic acid*,  $C_8H_{12}O_5$ , stout crystals, m. p.  $139$ — $140^\circ$ , or on distillation the hydroxy-lactonic acid together with the *dilactone*,  $C_8H_{10}O_4$ . This separates from ether in large crystals, m. p.  $95$ — $96^\circ$ , sublimes above  $100^\circ$ , and is hydrolysed by boiling water, forming  $\alpha\delta$ -dihydroxy- $\alpha\delta$ -dimethyladipic acid.

*iso- $\alpha\delta$ -Dihydroxy- $\alpha\delta$ -dimethyladipic acid*, formed in small quantity from the dinitrile, crystallises in needles, m. p.  $189^\circ$  (decomp.); the *calcium* ( $5H_2O$ ) and *barium* ( $5H_2O$ ) salts were analysed. When boiled with water, the *iso-acid* is converted partially into its isomeride, whilst the action of concentrated hydrochloric acid and ether converts it slowly and partially into the dilactone; when distilled the *iso-acid* yields the dilactone, but at  $160^\circ$  is converted into an *isohydroxy-lactonic acid*,  $C_8H_{12}O_5$ , which crystallises in leaflets, m. p.  $153^\circ$ , and on recrystallisation from water yields dihydroxydimethyladipic acid. G. Y.

**Esters of Orthotrithioformic Acid.** BROR HOLMBERG (*Ber.*, 1907, 40, 1740—1743).—Simple mercaptans can be condensed by means of anhydrous hydrogen chloride with derivatives of formic acid to form esters of orthotrithioformic acid of the type  $CH(SR)_3$ .

Ethyl orthotrithioformate is a colourless oil, b. p.  $133^\circ/21$  mm.,  $119^\circ/12$  mm.,  $116^\circ/10$  mm., of characteristic, unpleasant odour;  $D_4^{20}$  1.053. Phenyl orthotrithioformate, prepared from phenyl mercaptan and formic acid, m. p.  $40^\circ$ , is identical with that prepared by Gabriel (*Ber.*, 1877, 186) from chloroform and sodium phenyl mercaptide. E. F. A.

**Carbithionic Acids. III. The Dithio, Propionic, Butyric, isoValeric, and isoHexoic Acids.** JOSEF HOUBEN and H. POHL (*Ber.*, 1907, 40, 1725—1730. Compare Abstr., 1903, i, 42; 1906, i, 847; this vol., i, 382).—The action of carbon disulphide on organo-magnesium compounds is a general one, and has been extended to acids of the aliphatic series. The acids,  $R \cdot CS_2H$ , are reddish-yellow oils of un-

pleasant odour, the salts of the alkalis and alkaline earths are soluble in water, the salts of the heavy metals are, as a rule, unstable.

*Ethylcarbithionic* [dithiopropionic] acid,  $\text{Et}\cdot\text{CS}_2\text{H}$ , has b. p.  $48^\circ/17$  mm.,  $D^{20}$  1.12; its lead salt is stable. When oxidised by iodine, thiopropionyl disulphide,  $\text{CSEt}\cdot\text{S}\cdot\text{S}\cdot\text{CSEt}$ , is obtained. *Propylcarbithionic* [n-dithiobutyric] acid,  $\text{CH}_2\text{Et}\cdot\text{CS}_2\text{H}$ , has b. p.  $59^\circ/13$  mm.,  $D^{19}$  1.08; *isobutylcarbithionic* [dithioisovaleric] acid,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CS}_2\text{H}$ , b. p.  $84^\circ/33$  mm.,  $D^{19}$  1.008, and *isoamylcarbithionic* [dithioisohexic] acid,  $\text{CHMe}_2\cdot[\text{CH}_2]_2\cdot\text{CS}_2\text{H}$ , b. p.  $84^\circ/10$  mm.,  $D^{22}$  0.98.

The yields of acid obtained vary from 12% to 4.4% of the theoretical.

W. R.

**Mercaptal Acids.** BROR HOLMBERG and KARL MATTISSON (*Annalen*, 1907, 353, 123—130. Compare Holmberg, *Abstr.*, 1905, i, 323; Bongartz, *Abstr.*, 1888, 478; Jonsson, *Svensk kemisk tidskrift*, 1904, 22).—Mercaptal acids are formed by the condensation of aldehydes with thiol acids. The authors have prepared such substances by condensation of formaldehyde and benzaldehyde with thiolacetic and thiolpropionic acids.

*Methylenedi-thiolacetic acid*,  $\text{CH}_2(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , is prepared with development of heat by the action of formaldehyde on thiolacetic acid; the velocity of the reaction is increased by addition of hydrochloric or sulphuric acid. It crystallises in white, prismatic leaflets, m. p.  $128.5$ — $129^\circ$ , has the affinity constant  $K=0.0461-0.0586$  with  $v=16-512$ , is hydrolysed only slowly by hot concentrated hydrochloric acid, and on oxidation with potassium permanganate yields methylenedimethyldisulphone,  $\text{CH}_2(\text{SO}_2\text{Me})_2$ . The sodium, sodium hydrogen ( $\text{H}_2\text{O}$ ), and calcium ( $\text{H}_2\text{O}$ ) salts are analysed; the ethyl ester is a colourless oil.

*Benzylidenedi-thiolacetic acid*, m. p.  $126$ — $127^\circ$  ( $123$ — $124^\circ$ : Bongartz, *loc. cit.*), is sparingly soluble in water, and has the affinity constant  $K=0.0575-0.0697$  with  $v=128$ — $512$ . The sodium, sodium hydrogen, and barium ( $1\frac{1}{2}\text{H}_2\text{O}$ ) salts were analysed; the ethyl ester is an oil.

*Methylenedi- $\alpha$ -thiolpropionic acid*,  $\text{CH}_2(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$ , m. p.  $130$ — $131^\circ$ , is prepared by the action of  $\alpha$ -thiolpropionic acid on 40% formaldehyde in presence of sulphuric acid.

*Benzylidenedi- $\alpha$ -thiolpropionic acid*,  $\text{CHPh}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$ , is obtained as a white, crystalline mass, m. p.  $138$ — $140^\circ$ . G. Y.

**Methenyltri-thiolacetic Acid.** BROR HOLMBERG (*Annalen*, 1907, 353, 131—138. Compare preceding abstract).—Formic acid reacts with thiolacetic acid in presence of anhydrous zinc chloride, hydrogen chloride, or sulphuric concentrated acid with development of heat, forming *methenyltri-thiolacetic acid*, which is formed also by the action of thiolacetic acid on ethyl formate or formamide saturated with hydrogen chloride.

*Methenyltri-thiolacetic acid*,  $\text{CH}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_3$ , crystallises from water in thin, white leaflets, m. p.  $173^\circ$  evolving gas, has the molecular conductivity  $\mu=58.50$  and  $210.6$ , and the affinity coefficient  $K=0.090$  and  $0.140$  with  $v=32$  and  $512$ , and is stable towards dilute acids, but

is hydrolysed slowly when boiled with alkali hydroxides or concentrated hydrochloric acid. The *sodium*, *calcium* ( $6\text{H}_2\text{O}$ ), and *lead* salts are described; the *ethyl* ester forms a colourless oil. The acid is oxidised by bromine in aqueous solution cooled by ice, forming sulphoacetic acid (Stillich, Abstr., 1906, i, 552). G. Y.

**Cystine Occurring in Urinary Calculi.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1907, 51, 391—393).—The data adduced show that the cystine obtained from urinary calculi is in the highest probability identical with that obtained from proteins. W. D. H.

**Action of Trimethylenetrissulphone on Formaldehyde.** ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 417—422).—When trimethylenetrissulphone (Baumann and Camps, Abstr., 1890, i, 478; 1892, i, 591) is dissolved in a known quantity of *N*-sodium hydroxide solution and this mixture is titrated with *N*-acid in presence of phenolphthalein, the trimethylenetrissulphone exerts no influence on the reaction, although it is precipitated to some extent towards the end. When formaldehyde is added to such a solution, gelatinisation occurs, unless the solution is dilute, and the author has investigated this action by adding known quantities of the aldehyde to such solutions and determining after an interval of three hours (1) the alkalinity of the system, and (2) the amount of free formaldehyde, by Seyewetz and Gibello's method (Abstr., 1904, ii, 521). The results show that the quantity of formaldehyde absorbed by a molecule of the trissulphone does not increase in proportion with the quantity of aldehyde employed. The principal reaction may be represented by the following equation:  $\text{C}_3\text{H}_6\text{O}_6\text{S}_3 + 2\text{CH}_2\text{O} = (\text{C}_3\text{H}_2\text{O}_6\text{S}_3)\text{H}_2(\text{CH}_2\cdot\text{OH})_2$ , but the compounds  $(\text{C}_3\text{H}_4\text{O}_6\text{S}_3)\text{H}(\text{CH}_2\cdot\text{OH})$  and  $(\text{C}_3\text{O}_6\text{S}_3)\text{H}_3(\text{CH}_2\cdot\text{OH})_3$  are probably also formed in addition to multimolecular compounds having a nucleus such as  $\begin{array}{c} \text{—O}_2\text{S—} \\ \text{—O}_2\text{S—} \end{array} > \text{C} < \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} > \text{C} < \begin{array}{c} \text{SO}_2\text{—} \\ \text{SO}_2\text{—} \end{array}$ .

The addition of electrolytes to the solutions causes gelatinisation or the formation of gelatinous precipitates, and opalescence is produced by the addition of much alcohol, but the solutions are not affected by boiling. T. A. H.

**Preparation of Acyclic Aldehydes. II.** P. BAGARD (*Bull. Soc. chim.*, 1907, [iv], 1, 346—365. Compare this vol., i, 384).—Decoic acid was prepared by reducing ethyl nonoate by Bouveault and Blaise's method (Abstr., 1903, i, 597, 673) and converting the alcohol obtained into the acid through the bromide and cyanide.

*α*-Bromodecoic acid, m. p.  $4^\circ$ , prepared by treating decoic acid with phosphorus trichloride and bromine, is a colourless liquid at atmospheric temperature, and separates from ether in crystals at  $-80^\circ$ . The *ethyl ester*, b. p.  $163\text{—}164^\circ/21\text{ mm.}$ , is a colourless liquid. The bromo-acid, on treatment with a solution of sodium hydroxide, furnishes *α*-hydroxydecoic acid, m. p.  $70\cdot5^\circ$ , which crystallises from chloroform or light petroleum. The *methyl ester*, m. p.  $30^\circ$ , separates in lamellæ from light petroleum on cooling. The *anilide*, m. p.  $79^\circ$ ,

crystallises from a mixture of benzene and light petroleum, and the *p-toluidide*, m. p. 100°, crystallises from ethyl acetate. *α-Acetoxydecoic acid*, m. p. 40°, crystallises with difficulty by cooling its solution in light petroleum with methyl chloride. When *α*-hydroxydecoic acid is heated under the conditions already described (*loc. cit.*) it gives a yield of about 71% of nonaldehyde (Schimmel & Co., Abstr., 1902, i, 345), in addition to small quantities of a polymeride of the aldehyde, an *αβ*-olefinic acid, and carbon monoxide. No ethylenic hydrocarbon or carbon dioxide is formed in this decomposition (compare this vol., i, 385).

*Nonaldehyde semicarbazone*, m. p. 100°, separates in small crystals from a mixture of benzene and light petroleum. The *oxime*, m. p. 64°, crystallises from light petroleum and the *azine* is liquid at atmospheric temperature, but crystallises from light petroleum when cooled in methyl chloride. The corresponding naphthacinchonic acid has m. p. 238—240° (Schimmel & Co., *loc. cit.*). The *diethylacetal*, b. p. 130°/20 mm., is a colourless liquid.

Undecoic acid was prepared by treating undecenoic acid with hydriodic acid and reducing the iodoundecoic acid so formed with zinc turnings in presence of hydrochloric acid. The *anilide*, m. p. 68°, crystallises from a mixture of light petroleum and ethyl acetate and the *p-toluidide*, m. p. 75°, is purified in the same manner as the anilide.

*α-Hydroxyundecoic acid*, m. p. 69°, was prepared by hydrolysing with an aqueous solution of potassium hydroxide the *α*-bromo-acid obtained by treating undecoic acid with phosphorus trichloride and bromine. It separates in small, brilliant needles from a mixture of light petroleum and chloroform. The *ethyl ester*, m. p. 33°, crystallises from chloroform; the *anilide*, m. p. 80°, crystallises from a mixture of light petroleum and ethyl acetate, and the *p-toluidide*, m. p. 92°, crystallises from ethyl acetate.

When heated, *α*-hydroxyundecoic acid furnishes about 52% of decaldehyde, small quantities of  $\Delta^a$ -decylene (Grossjean, Abstr., 1892, i, 691), and of a polymeride of the aldehyde and a mixture of carbon monoxide and dioxide. *Decaldoxime*, m. p. 69°, separates in large lamellæ from a mixture of alcohol and water; the *azine*, m. p. 34°, crystallises from benzene, and the corresponding *diethylacetal* has b. p. 133·5°/14 mm.

*β-Ethylnonoic acid*, b. p. 170°/28 mm., was prepared by condensing  $\gamma$ -iodononane with ethyl malonate, hydrolysing the ester of the dibasic acid formed, and distilling the latter. On treatment with phosphorus trichloride and bromine and hydrolysis of the bromo-acid so formed, it furnishes *α-hydroxy-β-ethylnonoic acid*, m. p. 47°, which crystallises from light petroleum, on cooling the solution in methyl chloride, and yields an *ethyl ester*, b. p. 148—150°/15 mm. When distilled, the hydroxy-acid gives in addition to *α*-ethyloctaldehyde, considerable quantities of an ethylenic hydrocarbon, which may have the constitution  $C_6H_{13} \cdot C(Et) \cdot CH_2$ , and leaves a yellow residue, which is probably an *αβ*-olefinic acid.

*α-Ethyloctaldehyde*, b. p. 92°/16 mm., is colourless, mobile, and possesses a penetrating odour. The *semicarbazone*, m. p. 53°, is a

crystalline powder; the *oxime*, b. p. 131—132°/13 mm., is a colourless liquid, and the corresponding naphthacinchonic acid, m. p. 190—195°, crystallises from formic acid on the addition of methyl alcohol.

T. A. H.

**Preparation of Stable Compounds from Aldehydes and Hyposulphites.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 180529).—By the interaction of 2 mols. of a saturated aldehyde and 1 mol. of a hyposulphite in neutral or acid solution, aldehyde-hyposulphites,  $2RCHO \cdot X_2S_2O_4$ , are obtained, which are very stable substances, exhibiting the characteristic property of reducing indigotin only on warming. It has now been found that when molecular proportions of an aldehyde and a hyposulphite are mixed in the presence of a compound which will convert an acid sulphite into a normal sulphite, then one half of the sulphur present is eliminated as sulphite, whilst the other half is present in an aldehydesulphoxylate of the type  $RCH_2 \cdot SO_3X$ , R being an organic group and X a univalent metal. The aldehydesulphoxylate is distinguished from the aldehydehyposulphite by the fact that the latter gives a white precipitate with calcium chloride, whilst the former does not.

*Sodium formaldehydesulphoxylate*,  $CH_3 \cdot SO_3Na$ , is obtained by mixing together in concentrated aqueous solutions molecular proportions of sodium hyposulphite, sodium hydroxide, and formaldehyde; the sodium sulphite produced is precipitated either by concentrating the solution or by adding an equal volume of alcohol, the filtrate on further concentration to a syrupy consistence yields the sulphoxylate. This substance may also be produced by the interaction of zinc hyposulphite, sodium hydroxide, and formaldehyde; the greater portion of the zinc is precipitated as sulphite and the sodium formaldehydesulphoxylate is obtained from the filtrate.

*Sodium acetaldehydesulphoxylate* resembles the preceding compound, but crystallises even with greater difficulty.

*Sodium benzaldehydesulphoxylate* is prepared from sodium hyposulphite, sodium hydroxide, and benzaldehyde; the reaction takes place with generation of heat and the new salt separates in long, rectangular prisms.

G. T. M.

**Conversion of Aldehydes into Ketones by Means of Diazomethane.** FRITZ SCHLOTTERBECK (*Ber.*, 1907, 40, 1826—1827).—Polemical. A reply to Meyer (this vol., i, 323).

G. Y.

**Keten.** NORMAN T. M. WILSMORE and ALFRED W. STEWART (*Nature*, 1907, 75, 510).—In contact with a strongly heated platinum wire, acetic anhydride yields a pungent-smelling gas, b. p. about  $-65^\circ$ , which solidifies at about  $-130^\circ$ , and is obtained also from acetone or in traces by the action of phosphoric oxide or concentrated sulphuric acid on acetic anhydride. The substance, which condenses at the ordinary temperature, forming a pungent, brownish-yellow oil, is absorbed by water and all ordinary reagents, yields an additive compound with bromine and crystalline compounds with hydrogen sulphites, is charred by phosphoric oxide or concentrated sulphuric



acid, and is considered to have probably the constitution  $\text{CH}_3\text{:CO}$ , and to be the parent substance of the ketens (Staudinger, Abstr., 1905, i, 444).  
G. Y.

**Action of Sodium on Acetone.** RAYMOND FOSS BACON and PAUL C. FREER (*Philippine J. Sci.*, 1907, 2, 67—76. Compare Abstr., 1890, 956; 1891, 1181; 1894, i, 65; Beckmann and Schliebs, Abstr., 1896, i, 124).—As the result of M. Taylor's statement (Trans., 1906, 89, 1258) that acetone sodium consists chiefly of sodium hydroxide mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone, numerous experiments on the action of sodium on pure acetone in the presence of dry ethyl ether or light petroleum have been repeated and the formation of a sodium derivative of acetone is confirmed. The percentage of sodium is too high, owing to the presence of other sodium compounds, but at least 50% of the original acetone can be recovered from the sodium derivative. It is essential that the materials should be dry and that air should be excluded.  
J. J. S.

**Condensation of Sodium Derivatives of the Acyloins [Hydroxyketones] with Esters of the Acetic Series.** LOUIS BOUEVAULT and RENÉ LOCQUIN (*Compt. rend.*, 1907, 144, 851—853. Compare Abstr., 1906, i, 782).—Since the sodium derivative,  $\text{ONa}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{ONa}$ , which gives rise to acetoin on treatment with water, is produced by treating ethyl acetate dissolved in ether with sodium in the cold, it seemed likely that this substance occurs as an intermediate product in the formation of ethyl acetoacetate and that consequently the higher homologues of this ester might be obtained by a direct condensation, which may be represented by the following equation:  $\text{ONa}\cdot\text{CR}\cdot\text{CR}\cdot\text{ONa} + 2\text{EtO}\cdot\text{Ac} = 2\text{R}\cdot\text{C}(\text{ONa})\cdot\text{CH}\cdot\text{CO}_2\text{Et} + 2\text{H}_2$ . It is found, however, that when the sodium derivatives of the acyloins are condensed with either ethyl or amyl acetate, by heating a mixture of the two substances during four or five hours at  $100^\circ$ , a series of acids is formed, provisionally represented by the following typical formula,  $\begin{array}{c} \text{CR} \\ | \\ \text{CHR} \end{array} = \text{C}\cdot\text{CO}_2\text{H}$ .

The acid,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , m. p.  $104\text{--}105^\circ$ , b. p.  $200\text{--}210^\circ/10\text{ mm.}$ , formed by condensing the sodium derivative of acetoin with ethyl acetate, crystallises from petroleum, combines with bromine in the cold, evolving hydrogen bromide, and changes when kept to a yellow liquid. Its methyl ester, b. p.  $142\text{--}143^\circ/8\text{ mm.}$ , on treatment with ammonia furnishes an amide, m. p.  $83^\circ$ , and on reduction with sodium in alcohol yields a saturated alcohol,  $\text{C}_{10}\text{H}_{20}\text{O}$ , b. p.  $97\text{--}99^\circ/10\text{ mm.}$ , which possesses a pleasant odour of mint and furnishes an acetate, b. p.  $114\text{--}115^\circ/16\text{ mm.}$ , and a pyruvate the semicarbazone of which, m. p.  $97\text{--}98^\circ$ , crystallises from light petroleum.

The acid,  $\text{C}_8\text{H}_{12}\text{O}_2$ , b. p.  $190\text{--}195^\circ/12\text{ mm.}$ , obtained by the action of ethyl acetate on the sodium derivative of propionin is a paste. Its methyl ester, b. p.  $145\text{--}150^\circ/20\text{ mm.}$ , yields on reduction the alcohol,  $\text{C}_8\text{H}_{16}\text{O}$ , b. p.  $90^\circ/15\text{ mm.}$ , which furnishes a pyruvate semicarbazone, m. p.  $114^\circ$ .

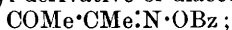
The *product*,  $C_{12}H_{20}O_2$ , b. p. 205—215°/12 mm., m. p. 151—152°, derived from the sodium derivative of *isovaleroin* gives a *methyl ester*, b. p. 155—160°/12 mm.

The *substance*,  $C_{14}H_{24}O_2$ , b. p. 230—235°/12 mm., derived from the sodium derivative of *hexonoin* furnishes a *methyl ester*, b. p. 195—200°/20 mm. T. A. H.

**Diacetylmonoxime.** Decomposition of its Benzoyl Derivative. Theory of the Beckmann Transformation. OTTO DIELS and MAX STERN (*Ber.*, 1907, 40, 1629—1633).—Diacetylmonoxime,  $COMe \cdot CMe : N \cdot OH$ , is a typical *isonitrosoketone*, colourless in the free state, and forming intensely yellow alkali salts. According to Hantzsch, such compounds are weak acids, and the degree of hydrolysis of their alkali salts is much less than corresponds with the acidity of the substances themselves; *isonitrosoketones* are *pseudo-acids* of the

type (I), whilst the salts are represented by the type (II). This conception is in accordance with the observation that alkaline solutions of *isonitrosoketones* do not unite with aldehydes, whereas the corresponding oximino-ethers do (compare preceding abstract).

The attempt was made by the authors to form condensation products from the benzoyl derivative of diacetylmonoxime,

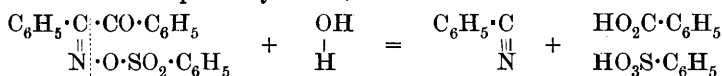


these experiments failed on account of the instability of the benzoate in question towards cold dilute alkalis, which form acetonitrile, benzoic acid, acetic acid, and the dibenzoyl derivative of dimethylglyoxime.

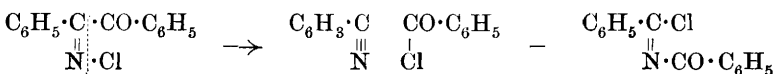
The formation of the latter compound is represented by the scheme :  $2COMe \cdot CMe : N \cdot OBz (+ H_2O - H_2O) =$

$COMe \cdot COMe + OBz \cdot N : CMe \cdot CMe : N \cdot OBz$ , whilst the decomposition into acetonitrile, acetic acid, and benzoic acid is represented by  $CH_3 \cdot CO \cdot CMe : N \cdot O \cdot CPh + H_2O = CH_3 \cdot CO_2H + CNMe + Ph \cdot CO_2H$ .

According to Werner and Piguet (*Abstr.*, 1905, i, 66),  $\alpha$ -benzilmonoxime, when treated with benzenesulphonyl chloride in alkaline or in pyridine solution, forms benzonitrile and benzoic acid. In this change, it is probable that a benzenesulphonic ester is first formed and then is decomposed by alkali, thus :



In the Beckmann rearrangement, the intermediate formation of oxime esters is assumed, and the typical nitrile formation is probably the primary action. In the transformation of  $\alpha$ -benzilmonoxime by phosphorus pentachloride, for example, the following scheme is submitted :



*Benzoyldiacetylmonoxime*,  $\text{COPh}\cdot\text{O}\cdot\text{N}\cdot\text{CMe}\cdot\text{COMe}$ , obtained by the action of benzoyl chloride on a solution of diacetylmonoxime in sodium hydroxide, separates from alcohol in needles, m. p.  $115\cdot5^\circ$ . When boiled with dilute acids, it is converted into diacetyl, benzoic acid, and hydroxylamine.

*Dimethylglyoxime dibenzoate*, obtained from the preceding compound, separates from chloroform in rhombic plates, m. p.  $223^\circ$ , and is identical with the compound obtained by the benzoylation of dimethylglyoxime. A. McK.

**Dextroses and their Phenylhydrazones and Oximes.** ROBERT BEHREND (*Annalen*, 1907, 353, 106—122. Compare Abstr., 1905, i, 173; Behrend and Roth, Abstr., 1904, i, 716).—The birotation of dextrose has been explained by the assumed existence of two stereoisomeric forms,  $\alpha$ - and  $\beta$ -dextrose, which readily undergo transformation one into the other and exist together in equilibrium in solutions with constant rotation. The possibility of the existence of an aldehyde form has also been recognised. When such equilibrium solutions are cooled or evaporated, the form crystallising out must be that the solubility limit of which is reached first. It is found now that whilst  $\alpha$ -dextrose can exist in contact with boiling ethyl or isobutyl alcoholic solutions, or, in the form of its hydrate, in contact with aqueous solutions,  $\beta$ -dextrose, m. p.  $148\text{--}150^\circ$ ,  $[\alpha]_D + 20\cdot7^\circ$ , crystallises from a solution of  $\alpha$ -dextrose in boiling pyridine, and is identical probably with Tanret's  $\gamma$ -dextrose (Abstr., 1895, i, 490). A mixture of  $\alpha$ - and  $\beta$ -dextrose has m. p.  $146\text{--}148^\circ$ .

The phenylhydrazones of dextrose have been re-examined. Skraup's phenylhydrazone (Abstr., 1889, 1130) is formed by shaking dextrose with phenylhydrazine in alcoholic or aqueous alcoholic solution; it crystallises in needles, m. p.  $106\text{--}107^\circ$ , and in 5% aqueous solution has the initial rotatory power  $[\alpha]_D - 2^\circ$ , after twenty minutes  $[\alpha]_D - 5^\circ$ , and finally  $[\alpha]_D - 50^\circ$ . Fischer's phenylhydrazone (Abstr., 1887, 567), formed in alcoholic acetic acid solution, crystallises in leaflets, m. p.  $159\text{--}160^\circ$ , and in 5% aqueous solution has the initial rotatory power  $[\alpha]_D - 70^\circ$ , and finally  $[\alpha]_D - 50^\circ$ . The transformation of the phenylhydrazones into each other takes place also in alcoholic solution, and is accelerated by addition of acetic acid. Skraup's hydrazone crystallises from alcoholic acetic acid cooled by ice, whilst Fischer's compound separates from a similar solution at the ordinary temperature.

If the oil obtained on evaporation of the aqueous solution of dextroseoxime is acetylated in pyridine solution immediately, it forms a *deca-acetyl* compound derived from a condensation product of 2 mols. of dextroseoxime,  $\text{C}_{12}\text{H}_{14}\text{O}_{11}\text{NAc}_{10}$ , which is a viscid oil or colourless, vitreous mass, has  $[\alpha]_D + 36\cdot75^\circ$  in pyridine solution, and on hydrolysis with sulphuric acid yields acetic acid, hydroxylamine, and dextrose. The condensation of the 2 mols. of dextroseoxime is shown to take place during the acetylation.

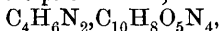
Wohl's hexa-acetyldextroseoxime (Abstr., 1893, i, 292), m. p.  $110\text{--}111^\circ$ , is formed by the action of acetic anhydride on the oxime, m. p.  $138^\circ$ , in pyridine solution cooled by ice. Acetylation in hot

pyridine solution leads to the formation of the hexa-acetyl derivative, together with the deca-acetate and penta-acetylgluconitrile, in amounts varying with the conditions.

On hydrolysis with bromine, freshly prepared solutions of the oxime and solutions with constant rotation yield almost identical mixtures of  $\alpha$ - and  $\beta$ -dextrose. G. Y.

**Action of Ammonia-Zinc Hydroxide on *d*-Galactose and *l*-Arabinose.** KATSUJI INOUE (*Ber.*, 1907, 40, 1890—1892. Compare Windaus and Knoop, *Abstr.*, 1905, i, 381, 509; Windaus, this vol., i, 90, 288).—This work was undertaken to determine if methylglyoxaline is formed by the action of a solution of zinc hydroxide in ammonia on sugars other than dextrose.

4 (or 5)-Methylglyoxaline, obtained from *d*-galactose or *l*-arabinose, forms a crystalline mass, m. p. 55—56°; the *picrolonate*,



crystallises in yellow needles, m. p. 287—288·5°. The action of benzoyl chloride and aqueous sodium hydroxide on 4-methylglyoxaline leads to the formation of a *substance*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$ , crystallising in needles, m. p. 142°, which the author refers to as dibenzoyldiaminoethylene [*dibenzoyldiaminopropylene*,  $\text{NHBz}\cdot\text{CMe}\cdot\text{CH}\cdot\text{NHBz}$ ] (compare Bamberger and Berlé, *Abstr.*, 1892, 632). G. Y.

**Scyllitol.** JOHANNES MÜLLER (*Ber.*, 1907, 40, 1821—1826).—In continuation of his studies of naturally occurring alicyclic compounds, the author has undertaken the investigation of scyllitol, discovered by Staedeler and Frerichs (*J. pr. Chem.*, 1858, [i], 73, 48) in various organs of the *Plagiosomi*. • No analysis of scyllit has been published previously.

Scyllitol,  $\text{C}_6\text{H}_{12}\text{O}_6$ , crystallises in hard, glistening, monoclinic prisms, m. p. above 339°, is only sparingly soluble in water, is optically inactive, after careful evaporation with nitric acid gives a red coloration with calcium chloride, and forms a *hexa-acetyl* derivative,  $\text{C}_6\text{H}_6(\text{OAc})_6$ . It is concluded that scyllitol is *cyclohexan-1:2:3:4:5:6*-hexaol and is an *i*-inositol. G. Y.

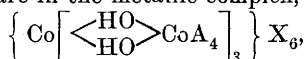
**Inequality of the Resistance of Natural Starch and Artificial Amylose towards Extract of Barley.** JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1907, 144, 645—646).—Pure amylose is acted on to a practically equal extent by extract of barley and extract of malt, whilst natural amylose is far more resistant towards barley extract than towards malt extract.

The results show that non-germinated barley contains a diastase which acts on amylose and not on amylopectin. N. H. J. M.

**Complex Metal Ammonias. III. Dodecamminehexoltetracobalt and Hexaethylenediaminehexoltetracobalt Salts.** ALFRED WERNER [and, in part, E. BERL, GUSTAV JANTSCH, and E. ZINGGELER] (*Ber.*, 1907, 40, 2103—2125. Compare *Abstr.*, 1898, ii, 223; 1899, ii, 658).—Two series of salts are described having the

general formula  $\left\{ \text{Co} \left[ \begin{smallmatrix} \text{HO} \\ \text{HO} \end{smallmatrix} \text{CoA}_4 \right]_3 \right\} \text{X}_6$ ; in one series, the ammonia series, A represents  $\text{NH}_3$ , whilst in the other, the ethylenediamine series, A represents  $\text{C}_2\text{H}_4(\text{NH}_2)_2$ .

These salts represent a second class of basic salts, differing in properties from the hydroxo-compounds described previously. The HO groups have a share in the metallic complex, thus:

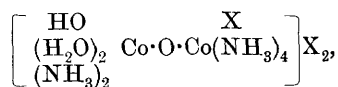


and for such compounds the designation "ol" is suggested.

Members of the ammonia series have been obtained by Jörgensen (Abstr., 1898, ii, 226), who termed them anhydrobasic tetrammine-diaquodiammine salts. They are prepared readily in several ways. *Dodecamminehexoltetracobalt sulphate*,  $\text{Co}_4\text{H}_{42}\text{O}_{18}\text{N}_{12}\text{S}_3 \cdot 9\text{H}_2\text{O}$ , is obtained by heating dibromotetramminecobalt bromide with a little water until bromine is evolved, and treating the solution of the product with a solution of ammonium sulphate; it is also obtained by adding pyridine to a hot dilute acetic acid solution of diaquodiamminecobalt sulphate. The *dithionate*,  $\text{Co}_4\text{H}_{42}\text{O}_{24}\text{N}_{12}\text{S}_6 \cdot 4\text{H}_2\text{O}$ , is prepared by adding sodium dithionate and pyridine to a solution of diaquodiamminecobalt chloride in very dilute acetic acid and heating to boiling. The majority of the salts of this series form glistening, brownish-black, well-formed crystals.

The most characteristic salt of the ethylenediamine series is the *nitrate*,  $\left[ \text{Co} \left( \begin{smallmatrix} \text{HO} \\ \text{HO} \end{smallmatrix} \text{Co en}_2 \right)_3 \right] (\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$ , which is formed when a solution of cobalt nitrate and of ethylenediamine is submitted to atmospheric oxidation; it crystallises in long, dark brown needles, yields *cis*-diaquodiethylenediaminecobalt halide by solution in concentrated hydrochloric or hydrobromic acid, 1 : 6-dichlorodiethylenediaminecobalt chloride by evaporation with dilute hydrochloric acid, and *cis*-hydroxo-aquodiethylenediaminecobalt nitrate by treatment with potassium hydroxide. The *bromide*, *iodide*, and *thiocyanate* of the ethylenediamine series are obtained from the nitrate by precipitation, the *chloride* in a similar manner to the nitrate.

The author rejects Jörgensen's formula for salts of the ammonia series for the following reasons: (1) the salts cannot contain HO directly attached to cobalt, since they do not yield aquo-salts by treatment with mineral acids; (2) in the chloride the presence of chlorine directly attached to cobalt is contrary to the fact that this salt is converted into a halogen-free sulphate by the action of soluble sulphates; (3) the estimation of the products of decomposition of these salts by hydrochloric or hydrobromic acid leads to results contrary to Jörgensen's formula. Thus, the sulphate of the ammonia series yields 81.1% of diaquodiamminecobalt chloride, and the nitrate of the ethylenediamine series, 80.71% of 1 : 6-dichlorodiethylenediaminecobalt nitrate, whereas the amounts calculated from Jörgensen's formula are 68.1% and 54.6% respectively. If the molecular formulæ of these complex salts are doubled and the author's constitutional formula is adopted, the



observed percentages in the preceding decompositions agree well with the calculated values ; (4) the estimation of the chlorine evolved by the action of cold concentrated hydrochloric acid on salts of either series agrees well with the theory that in the molecule of these salts four cobalt atoms are present, one of which passes from the trivalent to the bivalent state during the decomposition. According to Jörgensen's formula, the products of decomposition must contain one cobalt atom in the form of a tetrammine salt and one cobalt atom as a diammine salt ; the latter, in spite of numerous attempts, cannot be detected ; (5) the sulphate of the ammonia series is decomposed by dilute sulphuric acid, yielding oxygen, and by concentrated sulphuric acid, evolving oxygen and nitrogen in quantities which agree with those calculated from the author's formula.

The author points out that his formula is the only one which explains satisfactorily the chemical behaviour of these complex salts, particularly with reference to the amount of water, 3 mols., retained by them in the dried state.

C. S.

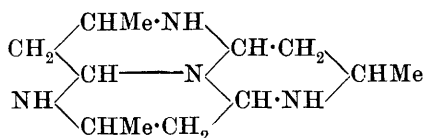
**$\alpha$ -Amino- and Imino-acids.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1907, 40, 1801—1802. Compare this vol., i, 19).—Polemical. A reply to Stadnikoff (this vol., i, 393). J. J. S.

**Ethylideneimine (Aldehyde-ammonia) and Hexaethylidene-tetramine.** MARCEL DELÉPINE (*Compt. rend.*, 1907, 144, 853—856. Compare Abstr., 1898, i, 462 ; 1899, i, 326).—Further evidence that aldehyde-ammonia may be regarded as the hydrate of triethylidene-triamine (trimeric ethylideneimine),  $\text{CHMe} \begin{smallmatrix} \text{NH} \cdot \text{CHMe} \\ \text{NH} \cdot \text{CHMe} \end{smallmatrix} \text{NH}$ , has

been obtained by the preparation of the *trinitroso*-derivative of the latter. This may be obtained by mixing solutions of ethylideneimine and nitrous anhydride in chloroform, or by passing a current of nitrous anhydride into ethylideneimine dissolved in chloroform and cooled by means of methyl chloride. The small yield of the trinitroso-derivative (4—6% of the theoretical) obtained is due to (1) the liberation of water, which transforms part of the imine into the hydrate which is decomposed by nitrous anhydride, and (2) to the production, from impurities contained in the nitrous anhydride, of nitric acid, which reacts with the aldehyde-ammonia, forming ammonium nitrate and aldehyde. The trinitroso-derivative,  $\text{CHMe} \begin{smallmatrix} \text{N(NO)} \cdot \text{CHMe} \\ \text{N(NO)} \cdot \text{CHMe} \end{smallmatrix} \text{N} \cdot \text{NO}$ , m. p.  $161^\circ$ ,

crystallises from alcohol in opaque, yellowish-white needles, and from benzene or chloroform in transparent, sulphur-yellow, orthorhombic prisms, which are truncated at the acute angle. It is stable in the dark, but when exposed to light slowly forms traces of brown material insoluble in chloroform. It gives the usual reactions of nitroso-compounds, and is decomposed by warm acetic acid into aldehyde and nitrogen. Hydrochloric acid liberates the nitrogen partly free and partly in the form of nitrous vapours with the formation of some nitrosoparalidine,  $\text{CHMe} \begin{smallmatrix} \text{O} \cdot \text{CHMe} \\ \text{O} \cdot \text{CHMe} \end{smallmatrix} \text{N} \cdot \text{NO}$  (Curtius and Jay, Abstr., 1890, 735).

The hexaethylidenetetramine, described by Kudernatsch (Abstr.,



1900, i, 377), is shown to be identical with the tri-crotonylidenetetramine, obtained by Wurtz by the action of crotonaldehyde on ammonia at 100°

(Abstr., 1879, 780), to which the annexed formula is now assigned.

Crotonaldehyde has  $D_4^0$  0.8715 and  $D_4^{25}$  0.8593 (compare Bauer, *Compt. rend.*, 1860, 51, 55, and Henninger, Abstr., 1884, 897).

T. A. H.

**Occurrence of *l*-Serine in Silk.** EMIL FISCHER (*Ber.*, 1907, 40, 1501—1505. Compare Abstr., 1906, i, 807).—The presence of derivatives of *l*-serine in the products obtained on hydrolysis of silk has been overlooked in consequence of the much greater solubility in water of the active than of the racemic substances. The residue obtained, on distilling at 140°/0.2—0.5 mm. the esters of the amino-acids formed by hydrolysis of silk or silk fibroin with hydrochloric acid, contains *i*-serine anhydride (Fischer and Suzuki, Abstr., 1906, i, 73) and *l*-serine anhydride. On recrystallisation of the mixture from water, the *l*-anhydride remains in the filtrate and is precipitated on addition of alcohol and cooling with ice as long needles, m. p. 247° (corr.) (decomp.),  $[\alpha]_D^{25} - 58.8^\circ$ , which cannot be freed from the racemic compound. When heated with 20% hydrobromic acid at 100°, the *l*-anhydride is converted into *l*-seryl-*l*-serine,  $\text{C}_6\text{H}_{12}\text{O}_5\text{N}_2$ , which crystallises in colourless leaflets, m. p. 234° (corr. decomp.),  $[\alpha]_D^{19} + 3.8^\circ$  in aqueous or +12° in *N*-hydrochloric acid solution, and dissolves with difficulty in boiling water, but does not crystallise out on cooling.

On more prolonged heating with 48% hydrobromic acid at 100°, *l*-serine anhydride yields *l*-serine, which is identical with synthetical *l*-serine in all its properties except the rotatory power, which is smaller,  $[\alpha]_D + 11.6^\circ$  in hydrochloric acid solution, pointing to the presence of 20% of racemic serine in the natural product.

G. Y.

**Synthesis of Polypeptides. XVII.** EMIL FISCHER (*Ber.*, 1907, 40, 1754—1767. Compare Proc., 1907, 23, 82; this vol., i, 295).—The coupling together of amino-acids has been carried to an octa-decapeptide, composed of 15 glycine and 3 *l*-leucine residues. Starting from triglycylglycine and *d*-α-bromoisohexoyldiglycylglycyl chloride, which were condensed in the cold in presence of sodium hydroxide, glass pearls being added to obviate the violent frothing, *d*-α-bromoisohexoylhexaglycylglycine was obtained. This has  $[\alpha]_D^{20} + 3.55^\circ$ , becoming 0 after eighteen hours, turns yellow at 246° (corr.) and decomposes above this, and shows a marked biuret coloration. With anhydrous liquid ammonia, it undergoes a Walden rearrangement, forming *l*-leucylhexaglycylglycine,

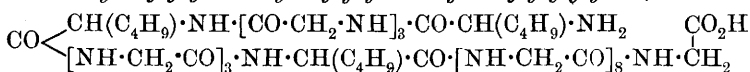
$\text{NH}_2\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_6\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $[\alpha]_D^{20} + 6.34^\circ$ , which turns yellow at 200°, brown at 250°, and decomposes at 300°. The *nitrate*, *sulphate*, and *hydrochloride* form microscopic crystals without definite structure; it shows a marked biuret reaction, and forms a sparingly soluble *copper* salt.

*d*- $\alpha$ -Bromoisohexyloctaglycylglycine is a colourless, indefinitely crystalline powder, which turns brown at 250° (corr.) and decomposes about 300° (corr.). 1-Leucyloctaglycylglycine,

$\text{NH}_2 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO} \cdot [\text{NH} \cdot \text{CH}_2 \cdot \text{CO}]_8 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , becomes brown at 260° and black at 300°, and gives a red biuret coloration. It condenses with *d*- $\alpha$ -bromoisohexoyldiglycylglycyl chloride to *d*- $\alpha$ -bromoisohexoyltriglycyl-leucyloctaglycylglycine, a colourless solid which turns brown at 255° and decomposes at 305°. Liquid anhydrous ammonia converts it into 1-leucyltriglycyl-1-leucyloctaglycylglycine,  $\text{NH} \left\langle \begin{array}{l} \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \\ \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO} \cdot [\text{NH} \cdot \text{CH}_2 \cdot \text{CO}]_8 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array} \right\rangle \cdot \text{CO} \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{NH}_2$  which becomes brown at 235° and decomposes without melting; it shows a cherry-red biuret coloration, is precipitated by ammonium sulphate, tannin and phosphotungstic acid, and the nitrate forms large, almost crystalline granules.

*d*- $\alpha$ -Bromoisohexoyltriglycyl-1-leucyltriglycyl-1-leucyloctaglycylglycine is obtained by repeating the condensation of the tetradecapeptide with the bromo-compound as a granular precipitate, which turns brown at 240° and froths and decomposes at 310° (corr.).

1-Leucyltriglycyl-1-leucyltriglycyl-1-leucyloctaglycylglycine,



forms a colourless powder which dissolves in 100 parts of boiling water; the aqueous solution froths considerably, and gives precipitates with ammonium sulphate, phosphotungstic acid, or tannin.

These four polypeptides closely resemble the natural proteins; they do not show the colour reactions of Millon and Adamkiewicz, or the xanthoprotein and sulphur reactions, since they do not contain tyrosine, tryptophan, or cystine. The octadecapeptide has a molecular weight of 1213, and is thus the substance of highest molecular weight of which the constitution is known.

*d*-Bromopropionyl-1-leucine crystallises in narrow needles aggregated in bundles, m. p. 50—51° (corr.),  $[\alpha]_D^{20} - 5.8^\circ$ . *d*-Alanyl-1-leucine forms narrow-pointed plates from water or lens-like, four-sided plates from alcohol; m. p. 255—256° (corr.),  $[\alpha]_D^{20} - 17^\circ$ . E. F. A.

**Synthesis of Polypeptides. XVIII. Derivatives of Aspartic Acid.** EMIL FISCHER and ERNST KOENIGS (*Ber.*, 1907, 40, 2048—2061. Compare Abstr., 1905, i, 31).—The two isomeric leucylasparagines, previously obtained as a mixture, have been prepared in larger quantity and separated. By hydrolysis of one of them with acid and examination of the leucine obtained, the constitution of the dipeptides and the corresponding  $\alpha$ -bromoisohexylasparagines is established.

The separation of the active bromo-derivatives was effected by means of the fractional precipitation of the alkaline solution with normal hydrochloric acid, the *l*- $\alpha$ -bromoisohexoxic acid derivative being sparingly soluble. *l*- $\alpha$ -Bromoisohexoyl-*l*-asparagine has  $[\alpha]_D^{20} - 30.1^\circ$ , and is soluble in 200—300 parts of water; *d*- $\alpha$ -bromoisohexoyl-*l*-asparagine crystallises with  $\text{H}_2\text{O}$  in stellar aggregates of long,

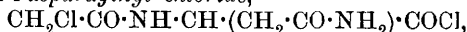


narrow prisms, m. p. 146—148°, has  $[\alpha]_D^{20} + 15.7^\circ$ , and is soluble in 100—150 parts water at 25°.

*d-Leucyl-l-asparagine* crystallises in colourless prisms and domes, m. p. 230° (corr. decomp.), and has  $[\alpha]_D^{20} - 53.6^\circ$ ; *l-leucyl-l-asparagine* forms needles or prisms, m. p. 228° (corr.), has  $[\alpha]_D^{20} + 17.8^\circ$ , and gives a bluish-violet coloration with alkali and a copper salt; it yields *l-leucine* when hydrolysed.

$\alpha$ -Bromoisohehexoyl-*l*-asparagine, when shaken with acetyl chloride, yields a compound,  $C_{10}H_{16}O_4N_2$ , m. p. 128—130° (corr.), which is optically inactive, soluble in alkali, and yields ammonia on boiling. It gives complicated decomposition products with sulphuric acid, and is of, as yet, unknown constitution.

*Chloroacetyl-l-asparaginyll chloride*,

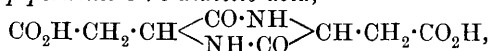


prepared by the action of acetyl chloride on chloroacetyl-*l*-asparagine, can be coupled with *l-leucine ester* to *ethyl chloroacetyl-l-asparaginyll-l-leucine* crystallising in microscopic needles, m. p. 166—167° (corr.); it tastes bitter. *Chloroacetyl-l-asparaginyll-l-leucine* forms bunches of centimetre long, pointed prisms, m. p. 167° (corr., red coloration), and does not taste bitter. The tripeptide, *glycyl-l-asparaginyll-l-leucine*,

$NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CH_2 \cdot CO \cdot NH_2) \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO_2H$ , obtained by the action of liquid ammonia on the foregoing, crystallises in nodular aggregates of microscopic needles and has  $[\alpha]_D^{20} - 46.5^\circ$ .

*Methyl l-aspartate* is a colourless liquid, b. p. 119—120°/15 mm., which on heating for three days at 100° forms *methyl 2:5-diketopiperazine-3:6-diacetate*, crystallising in bunches of microscopic needles or long, thin prisms.

*2:5-Diketopiperazine-3:6-diacetic acid*,



forms small, oblique plates or prisms decomposing at 300°. When left in the cold with barium hydroxide, it forms a compound,  $C_8H_{12}O_7N_2$ , probably *asparagylaspartic acid*,



this decomposes at 120°.

E. F. A.

### Method of Synthesis of $\beta$ -Ketonic Non-substituted Amides.

CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1907, 144, 806—808. Compare *Bull. Soc. chim.*, 1906 [iii], 35, 523).—By heating the alcoholic solution of an acetylenic amide with a small quantity of a secondary amine (preferably piperidine) for some hours, under a reflux condenser, the corresponding  $\beta$ -ketonic amide is formed. With aliphatic amides only a few drops of piperidine are necessary, but with phenylpropiolamide an equal molecular quantity is required. The piperidine appears to act catalytically by the formation of an intermediate compound, and a compound,  $C_5NH_{10} \cdot CPh \cdot CH \cdot CO \cdot NH_2$ , m. p. 135—136°, has actually been isolated from phenylpropiolamide, and when treated with oxalic acid in ether-alcoholic solution gives piperidine oxalate and benzoylacetamide. The  $\beta$ -ketonic amides are soluble in aqueous alkali hydroxide solutions, and their alcoholic

solutions give an intense reddish-violet coloration with ferric chloride. The constitution is confirmed by condensation with hydrazine hydrate to the corresponding pyrazolones with elimination of ammonia:

$$R \cdot CO \cdot CH_2 \cdot CO \cdot NH_2 + N_2H_4 \rightarrow R \cdot C(:CH \cdot CO \cdot NH_2) \cdot NH \cdot NH_2 \rightarrow$$

$$\begin{array}{c} CO \cdot NH \\ CH : CR \end{array} \rightarrow NH + NH_3.$$

*Hexoylacetamide*,  $C_5H_{11} \cdot CO \cdot CH_2 \cdot CO \cdot NH_2$ , has m. p. 99—100°; *heptoylacetamide*,  $C_6H_{13} \cdot CO \cdot CH_2 \cdot CO \cdot NH_2$ , has m. p. 106—107°. Benzoylacetamide, previously obtained by Obrégia (Abstr., 1892, 324) and Guareschi (Abstr., 1904, i, 891), was also prepared.

E. H.

**Direct Hydrogenation of Carbimides.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, 144, 824—826).—When a current of hydrogen impregnated with the vapour of ethylcarbimide is passed over nickel heated at 180—190° the issuing gas contains ammonia and carbon dioxide, but is free from methane and carbon monoxide, and when passed into a cooled receptacle deposits a liquid containing small quantities of mono-, di-, and tri-ethylamine, but chiefly constituted by methylethylamine. The principal reaction may be represented by the equation:  $Et \cdot N : CO + 3H_2 = H_2O + NHMeEt$ . The secondary products are due to the formation of some diethylcarbamide by the action of the water produced on a portion of the ethylcarbimide, with the subsequent reduction of the diethylcarbamide to methylethylamine and ethylamine, the latter then giving rise in contact with the nickel to some di- and tri-ethylamine (compare Sabatier and Senderens, Abstr., 1905, i, 267; Mailhe, Abstr., 1905, i, 571, 635). When phenylcarbimide is reduced under similar conditions, the issuing gas contains methane and carbon dioxide; the tube containing the nickel becomes coated with crystals of diphenylcarbamide, and the liquid product obtained when the gas is cooled consists of water and aniline. The principal reaction may be represented by the equation:  $Ph \cdot N : CO + 4H_2 = NH_2Ph + CH_4 + H_2O$ . Most of the water formed reacts with some of the phenylcarbimide to produce diphenylcarbamide. The tendency of phenylcarbimide to produce aniline on reduction has already been observed by Gumpert (Abstr., 1885, 656).

T. A. H.

**Trichloroacetimido-methyl Ether.** WILHELM STEINKOPF (*Ber.*, 1907, 40, 1643—1646).—*Trichloroacetimido-methyl ether*,



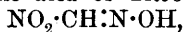
b. p. 148—149°, is a colourless oil of terpene-like odour, obtained by heating trichloroacetonitrile and methyl alcohol on the water-bath. Hydrogen chloride decomposes it in ethereal or alcoholic solution with the separation of ammonium chloride. Attempts to prepare the hydrochloride by Pinner's method lead to the formation of trichloroacetamide. When the methyl ether is heated with aniline, *trichloroacetophenylamidine*,  $CCl_3 \cdot C(NH) \cdot NHPh$ , m. p. 101°, is obtained, which is not changed by water at 100°, and evolves the odour of phenylcarbamine when treated with warm dilute sodium hydroxide; the

*hydrochloride*,  $C_8H_7N_2Cl_3 \cdot HCl$ , sinters and darkens at  $171^\circ$  and has m. p.  $183^\circ$ ; the *platinichloride*,  $C_{16}H_{14}N_4Cl_6 \cdot H_2PtCl_6 \cdot H_2O$ , is mentioned.  
C. S.

**Remarkable Additive Reaction of Fulminic Acid.** F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 545—552).—The author discusses Nef's carbyloxime formula,  $C:N \cdot OH$ , for fulminic acid and shows that Jovitschitsch's objections to it (*Abstr.*, 1906, i, 732) are invalid. His own investigations are then described.

Fulminic acid yields a hydrobromide resembling the hydrochloride in being extremely volatile and disagreeable to work with. The *hydriodide*, m. p.  $65^\circ$ , however, is more stable, and, with aniline in ethereal solution, gives phenylisourethane and, with aqueous silver nitrate, quantitative yields of silver iodide and fulminate; its aqueous solution is strongly acid.

One of the products of the action of nitrous acid on fulminic acid is found to be methylnitrolic acid or nitroformoxime,



which supports Nef's carbyloxime structure for fulminic acid.

T. H. P.

**Anhydrous Thiocyanic Acid.** ARTHUR ROSENHEIM and RICHARD LEVY (*Ber.*, 1907, 40, 2166—2169).—When concentrated sulphuric acid is allowed to drop slowly on to a mixture of dry potassium thiocyanate and phosphoric oxide in an atmosphere of hydrogen at 40—60 mm. pressure, pure thiocyanic acid, m. p. about  $5^\circ$ , is obtained and condenses in a cooled receiver in the form of white crystals. It has a corrosive action on the skin, is soluble in water at  $0^\circ$  without decomposition, but at higher temperatures changes rapidly to a yellow polymeride.  
C. S.

**Comparisons of Nitriles and *iso*Nitriles in their Behaviour towards Metallic Salts. Constitution of Double Cyanides.** KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1907, 40, 1772—1778).—The behaviour of nitriles and carbylamines towards certain metallic salts has been examined in order to determine which of these two groups of compounds resembles potassium cyanide in its power of forming complex cyanides. No stable compounds of nitriles or carbylamines with silver cyanide have been isolated. The compound  $AgCN, EtNC$  (E. Meyer, *J. pr. Chem.*, 1856, [i], 67, 147; A. W. Hoffmann, *Annalen*, 1867, 144, 118) is extremely unstable.

Platinous chloride readily forms the additive compound, *platinous chloride bisphenylcarbylamine*,  $PtCl_2 \cdot 2PhNC$ , which crystallises in purple-coloured prisms almost insoluble in ether and other organic solvents. It is extremely stable towards water and dilute alkalis, and potassium sulphide acts but slowly on a hot solution. The chlorine is also difficult to remove from the molecule.

An isomeric compound, *platinous chloride bisbenzonitrile*, is slowly deposited when an ethereal solution of the nitrile is mixed with an aqueous solution of potassium platinochloride. It forms pale yellow crystals showing double refraction, dissolves in hot sodium hydroxide

solution or in warm potassium cyanide solution, liberating the nitrile. It does not react with silver nitrate. A similar compound of acetonitrile and platinous chloride has been obtained.

Phenylcarbylamine forms the unstable compound  $2\text{AgCN}, \text{PhNC}$ , which gradually gives up the carbylamine. Cuprous cyanide forms an unstable compound,  $\text{CuCN}, 2\text{EtNC}$ . Benzonitrile combines with neither silver nor mercurous cyanide.

J. J. S.

**Direct Hydrogenation of Aliphatic *iso*Cyanides [Carbylamines].** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, 144, 955—957. Compare Abstr., 1905, i, 267, this vol., i, 458, 488).—When a current of hydrogen, impregnated with an aliphatic carbylamine, is passed over a column of reduced nickel, heated at  $160\text{--}180^\circ$ , the carbylamine is reduced, for the most part, to the corresponding *sec.*-amine, but a portion is converted into the isomeric cyanide, which in turn is reduced, whilst a third portion is polymerised with the formation of tarry matter, which is deposited on the nickel and impedes its reducing action so that ultimately a portion of the carbylamine escapes unchanged. If the reduction is conducted at  $220\text{--}250^\circ$ , the *sec.*-amine formed suffers decomposition with the production of hydrogen, hydrocarbons, and ammonia, especially in the case of the more complex carbylamines.

Methylcarbylamine furnishes principally dimethylamine together with small quantities of ethylamine and diethylamine. Ethylcarbylamine similarly yields methylethylamine accompanied by smaller quantities of propylamine and dipropylamine. *tert.*-Butylcarbylamine,  $\text{CMe}_3\text{NC}$ , furnishes on reduction methyl-*tert.*-butylamine accompanied by dimethylpropylamine, b. p.  $83^\circ$ , and a small quantity of an amine of higher b. p. *Methyl-tert.-butylamine*,  $\text{CMe}_3\text{NHMe}$ , b. p.  $58\text{--}60^\circ$ , is a colourless, mobile liquid with a penetrating, but not disagreeable, odour. It yields an oily *nitroso*-derivative. The *carbonate* becomes yellow on keeping; the *hydrochloride* is deliquescent; the *oxalate* has m. p.  $160^\circ$  (decomp.). With phenylcarbylamine the amine furnishes  $\beta$ -*phenyl- $\alpha$ -methyl  $\alpha$ -tert.-butylcarbamide*, m. p.  $118^\circ$ , which crystallises from alcohol in needles or rhombic lamellae.

T. A. H.

**Attempts to Synthesise Nitroacetonitrile. II. Halogenated Amino-oximes.** WILHELM STEINKOPF and LUDWIG BOHRMANN (*Ber.*, 1907, 40, 1633—1643. Compare Abstr., 1905, i, 122).—Unsuccessful attempts have been made to obtain nitroacetonitrile from nitroacetamide and phosphoric oxide, from bromonitromethane and potassium cyanide, and by the nitration of ethyl cyanoacetate. Cyanoformaldehyde also could not be prepared.

A series of  $\alpha$ -halogenated amino-oximes has been prepared from  $\alpha$ -halogenated acetonitriles and hydroxylamine in neutral, aqueous solution. These compounds differ strikingly from unsubstituted amino-oximes in the rapidity of their formation and in their stability to boiling water, hydroxylamine being eliminated only in sealed tubes at  $100^\circ$ , or by the action of hot alkalis.

$\alpha$ -Chloroethenylamino-oxime,  $\text{CH}_2\text{Cl}\cdot\text{C}(\text{NH}_2)\text{:NOH}$ , m. p.  $91\text{--}92^\circ$

(decomp.), obtained from chloroacetonitrile, crystallises from benzene in long needles, and reduces a boiling alkaline solution of mercuric chloride; the *hydrochloride*,  $C_2H_5ON_2Cl \cdot HCl$ , has m. p. 116—118° (decomp.).

*aa-Dichloroethenylamino-oxime*,  $CHCl_2 \cdot C(NH_2) : N \cdot OH$ , m. p. 103—104° (decomp.), prepared from dichloroacetonitrile, gives a violet coloration with ferric chloride, yellow precipitates with sodium or ammonium hydroxides, a white silver salt, and a bluish-green copper salt; the *hydrochloride*,  $C_2H_4ON_2Cl_2 \cdot HCl$ , has m. p. 135° (decomp.), and the *acetyl* derivative,  $CHCl_2 \cdot C(N \cdot OH) \cdot NHAc$ , obtained by evaporating a solution in acetic anhydride over potassium hydroxide in a vacuum, has m. p. 114—115°. *Oximinoethenylamino-oxime*,  $OH \cdot N : CH \cdot C(NH_2) : N \cdot OH$ , m. p. 148—152° (decomp.), is obtained by treating the preceding amino-oxime or dichloroacetonitrile with an excess of neutral hydroxylamine at 60°; it reduces solutions of silver, copper, and mercury salts, and is precipitated from its concentrated aqueous solution by nickel acetate in the form of a reddish-brown *nickel* salt,  $C_4H_8O_4N_6Ni$ , which dissolves in dilute sulphuric acid to a colourless solution. By evaporating the solution of oximinoethenylamino oxime in acetic anhydride in a vacuum over potassium hydroxide, the *diacetyl* compound,  $OAc \cdot N : CH \cdot C(N \cdot OH) \cdot NHAc$ , m. p. 142—150°, is obtained, which is identical with the product obtained by treating Söderbaum's acetylisonitrosoacetonitrile (Abstr., 1892, 815) with hydroxylamine and acetylating the resulting amino-oxime.

*Trichloroethenylamino-oxime*,  $CCl_3 \cdot C(NH_2) : N \cdot OH$ , m. p. 128—129° (decomp.), crystallises in glistening leaflets; the *hydrochloride* has m. p. 149° (decomp.). By treating trichloroacetonitrile with 2 mols. of hydroxylamine at 65°, *α-chloro-oximinoethenylamino-oxime*,  $CCl(N \cdot OH) \cdot C(NH_2) : N \cdot OH$ , m. p. 109° (decomp.), is obtained, which gives a deep reddish-brown coloration with ferric chloride.

*Iodoethenylamino-oxime*,  $CH_2I \cdot C(NH_2) : N \cdot OH$ , m. p. 123—124° (decomp.), is prepared from iodoacetonitrile and hydroxylamine in methyl-alcoholic solution; the *acetyl* derivative,  $CH_2I \cdot C(N \cdot OH) \cdot NHAc$ ,

has m. p. 103—105°.

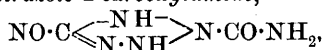
C. S.

**Cyanogen Bromide and Hydroxylamine.** III. HEINRICH WIELAND and HUGO BAUER (*Ber.*, 1907, 40, 1680—1691. Compare Abstr., 1904, i, 628; 1905, i, 420; this vol., i, 494).—The azoxydicarboxylamidedioxime, produced by the action of alkali on dihydroxyguanidine, results probably from the condensation of unchanged substance with aminomethylnitrosolic acid,  $OH \cdot N : C(NH_2) \cdot NO + OH \cdot N : C(NH_2) \cdot NH \cdot OH =$

$OH \cdot N : C(NH_2) \cdot ON_2 \cdot C(NH_2) : N \cdot OH + H_2O$ , the nitrosolic acid being derived from the hydrolysis of the azo-derivative,  $OH \cdot N : C(NH_2) \cdot N : N \cdot C(NH_2) : N \cdot OH$ . In alkaline solution this compound undergoes isomeric change into the hydrazone, *amino-azaurolic acid*,  $ON \cdot C(NH_2) : N \cdot NH \cdot C(NH_2) : N \cdot OH$ , which crystallises from hot water in long, orange-red needles with a blue reflex, exploding at 184°. In preparing this substance, the temperature and concentra-

tion exert a great influence. The *silver* salt is brick-red, the *copper* salt is dark reddish-brown. On reduction with hydrogen sulphide, *hydrazodicarboxylamideoxime*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NOH}$ , is obtained quantitatively in colourless needles from water decomposing at  $220^\circ$ ; the *silver* salt is colourless. As distinguished from hydrazodicarboxylamide (Thiele, Abstr., 1892, 1298, 1429), this hydrazo-derivative is easily oxidised by chromic acid or nitric acid to an unstable azo-compound. It is, however, very stable towards acids, no elimination of hydroxylamine occurring.

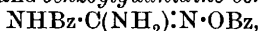
5-Nitrosodihydrotetrazole-2-carboxylamide,



results from the interaction of hydrazodicarboxylamideoxime and nitrous acid, mixed probably with an azo-compound, as a red, explosive substance. The above constitution is assigned to the substance, as nitrous acid is obtained on hydrolysis by acids.

When aminoazaurolic acid is boiled with 18% hydrochloric acid, the solution suddenly changes to a dark green colour and finally becomes honey-yellow, nitrogen and carbon dioxide being evolved at the same time. On cooling, orange-yellow crystals of the *hydrochloride* of isonitrosoaminohydrotetrazine,  $\text{NH}_2 \cdot \text{C} \begin{array}{c} \nwarrow \text{N} = \text{N} \\ \nearrow \text{N} \cdot \text{NH} \end{array} \text{C} \cdot \text{NOH}, \text{HCl}$ , are obtained, which do not decompose at  $350^\circ$ . In addition to the tetrazine being a mono-acid base, it gives a dark red *silver* salt,  $\text{C}_2\text{H}_3\text{O}_6\text{N}_6\text{Ag}$ .

*Benzoylation of Dihydroxyguanidine.*—Experiments made to methylate or benzoylate azodicarboxylamidedioxime by means of methyl sulphate or benzoyl chloride either in sodium carbonate or sodium hydrogen carbonate solution, were without result. When dihydroxyguanidine and benzoyl chloride interact in the presence of sodium hydrogen carbonate, a chrome-yellow mass first separates and afterwards colourless crystals. The yellow material consists largely of *azoxydicarboxylamidedioxime dibenzoate*,  $\text{ON}_2[\text{C}(\text{NH}_2) \cdot \text{NOBz}]_2$ , purified by repeated shaking with acetone until it is completely soluble in dilute sodium hydroxide, which quickly causes decomposition into benzoic acid, nitrogen, and hydroxycarbamide. At  $155^\circ$  it decomposes explosively. The colourless crystalline portion consists of dibenzhydroxamic acid and *benzoylguanidine benzoate*,



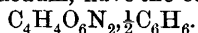
crystallising from alcohol in needles decomposing at  $162$ – $163^\circ$ . When warmed with alkalis or acids, benzoylguanidine benzoate gives benzoic acid and *aminophenylazoxime*,  $\text{NH}_2 \cdot \text{C} \begin{array}{c} \nwarrow \text{N} \cdot \text{O} \\ \nearrow \text{N} \cdot \text{CPh} \end{array}$ , crystallising in needles, m. p.  $164^\circ$ . Alkaline permanganate is without action on the substance, which forms a *silver* salt. W. R.

**Acethydroxamic Chloride.** HEINRICH WIELAND (*Ber.*, 1907, 40, 1676–1680. Compare Piloty and Steinbock, Abstr., 1902, i, 735).—A method for preparing acethydroxamic chloride in nearly quantitative yield directly from acetaldoxime and chlorine is described; its derivatives from amines and phenols are well-defined, crystalline sub-

stances, and the chloride is therefore a suitable reagent for characterising these classes of compounds.

The interaction of the chloride and hydrazine results in the formation, not of a hydrazo-compound, but of aminodimethyltriazole; aniline gives acetanilide-oxime (Nordmann, Abstr., 1885, 238), and phenylhydrazine, phenylhydrazoacetaldoxime (Bamberger, Abstr., 1902, i, 247). *Acet-p-phenetide-oxime*,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CMe} \cdot \text{NOH}$ , from the acethydroxamic chloride and the corresponding amine, crystallises in large, colourless plates from alcohol, m. p.  $148^\circ$ , and forms a *hydrochloride*. Ferric chloride gives a very intense, carmine-red coloration. The *acetate*,  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$ , crystallises in prisms, m. p.  $117$ – $118^\circ$ . The *oxime* of *o*-acetoxybenzoic acid,  $\text{C}_9\text{H}_9\text{O}_4\text{N}$ , crystallises in plates, m. p.  $100^\circ$ , and gives a red coloration with ferric chloride. W. R.

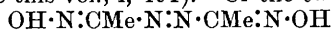
**Isomeric Dioximinosuccinic Acids.** ANDRÉ WAHL (*Compt. rend.*, 1907, 144, 922–924. Compare Abstr., 1906, i, 624).—By application of Söderbaum's method (Abstr., 1891, 825) to sodium dihydroxytartrate, extraction of the product with ether, and evaporation of the ethereal solution, a viscid liquid is obtained which, in a vacuum, is completely converted into a pale yellow, crystalline mass. The latter on repeated fractional crystallisation gives (1) a small quantity of oxalic acid; (2) transparent crystals of *isonitrosocyanoacetic acid*, and (3) hemispherical aggregates of crystalline prisms, which, after drying in a vacuum, have the composition



The benzene of crystallisation is lost at  $190^\circ$ , leaving a residue having the composition of dioximinosuccinic acid. The latter forms very hard, white crystals, m. p.  $168$ – $170^\circ$  (decomp.), of which the aqueous solution gives white precipitates with silver nitrate and calcium acetate, and with cupric acetate a green precipitate which is transformed into a bluish-green, crystalline substance on heating or keeping. The two isomeric acids described by Söderbaum have m. p.  $145$ – $150^\circ$ , and of these the  $\beta\beta$ -acid with cupric acetate gives a dirty green precipitate becoming brown.

If a current of dry hydrogen chloride is passed through a solution of ethyl dioximinosuccinate in anhydrous ether and the solution is evaporated in a vacuum over potash, the product is a white, crystalline substance having the same composition as the original ester, but different properties. It crystallises from water in fine, felted needles, m. p.  $140^\circ$ , and can be purified through the *silver salt*. The latter, obtained by adding silver nitrate to an aqueous solution of the acid, forms explosive, white crystals, which blacken in air, have a composition corresponding with the formula  $\text{C}_8\text{H}_{12}\text{O}_6\text{N}_2, \text{AgNO}_3$ , and are decomposed by an equivalent amount of sodium chloride, liberating the ester in a pure state. The latter has the same composition and molecular weight as the original ester, but differs from it in melting point ( $143^\circ$ ), solubility, and reaction with silver nitrate. This isomeric transformation is also effected by acetyl chloride, but not by acetic anhydride, which gives the *diacetate* of the ester in the form of colourless prisms, m. p.  $105^\circ$ . E. H.

**Aliphatic Azo- and Nitroso-compounds. I. Constitution of Azaurolic Acids. II. Ethylnitrosolic and Ethylhydroxy-azaurolic Acids.** HEINRICH WIELAND (*Annalen*, 1907, 353, 65—105. Compare this vol., i, 491).—Of the two possible structures,



and  $\text{NO}\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ , suggested for ethylazaurolic acid by Meyer and Constam (Abstr., 1883, 40), the former was preferred by these authors. In view of the results obtained by Wieland (Abstr., 1905, i, 420), and Wieland and Bauer (Abstr., 1906, i, 412), it seemed probable that the alkaline reduction of ethylnitrosolic acid would lead to the formation of *acethydroxylamino-oxime*,  $\text{OH}\cdot\text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ , which would be converted by the action of the alkali into the azaurolic acid. It is now found that the reduction product of ethylnitrosolic acid contains considerable amounts of *acethydroxylamino-oxime*, which undergoes the conversion into the azaurolic acid only slowly at the low temperature of the reduction. It is shown further that when treated with cooled 40% aqueous alkalis, *acethydroxylamino-oxime*, prepared by the action of hydroxylamine on acethydroxamyl chloride, yields ethylazaurolic acid, which is formed thus in the absence of a reducing agent.

As an aliphatic azo-compound, ethylazaurolic acid was expected to undergo hydrolysis in the same manner as the azo-compound derived from dihydroxyguanidine (Wieland, *loc. cit.*), forming ethylnitrosolic acid and acetamino-oxime,  $\text{OH}\cdot\text{N}:\text{CMe}\cdot\text{NO} + \text{NH}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ ; this expectation was not realised, the azaurolic acid, as shown by Meyer and Constam, being stable towards alkalis. On the other hand, in agreement with the second or hydrazone constitution, ethylazaurolic acid is decomposed by moderately concentrated acids, evolving nitrous acid, and by boiling water, with loss of  $\text{NOH}$  ( $2\text{NOH} = \text{N}_2\text{O} + \text{H}_2\text{O}$ ), reactions which are characteristic of the grouping  $\cdot\text{N}:\text{CR}\cdot\text{NO}$ , as contained in benzylnitrosolic acid (Wieland and Bauer, *loc. cit.*). The products, nitrous acid, hydrazine, hydroxylamine, nitrogen, and acetic acid, obtained by the action of acids on the azaurolic acid, point to the decomposition taking place partly directly, partly after intermediate change into the isomeric azo-form. Acetaldehyde, which would be expected in both cases, could not be detected. Traces of nitrous oxide and of leucazone are also formed.

Leucazone, which is formed from ethylazaurolic acid by the action of boiling water, or together with ammonia by reduction of the azaurolic acid with hydrogen sulphide, is considered to have the constitution  $\text{CMe}\begin{smallmatrix} \text{O} \\ \diagup \text{N} \diagdown \\ \text{N} \end{smallmatrix} \text{NH} \text{CMe}$ .

In the stability of its hydrazone form, ethylazaurolic acid is in opposition to Bamberger's nitroso-derivatives of aldehydephenylhydrazones (Abstr., 1903, i, 283), which are stable in the azo-form,  $\text{OH}\cdot\text{N}:\text{CR}\cdot\text{N}:\text{NPh}$ . This difference in the stabilities of such azo- and hydrazone compounds appears to be a characteristic difference of aromatic and aliphatic compounds.

Similarly to dihydroxyguanidine and benzenylhydroxylamino-oxime, *acethydroxylamino-oxime* can be converted, by the action of



15% aqueous sodium carbonate at 30° and by way of the unstable azo-compound, into acetamino-oxime and ethylnitrosolic acid,



which is formed also by careful oxidation of acethydroxylamino-oxime, or by the decomposition of nitrosoacethydroxylamino-oxime in neutral solution. Ethylnitrosolic acid is converted by hydrochloric acid into acethydroxamyl chloride, or by reduction with hydrogen sulphide into acethydroxylamino-oxime.

The mechanism of the formation of the azo-compound and its transformations is discussed. The reaction is complicated by the interaction of one of the products, ethylnitrosolic acid, and unchanged acethydroxylamino-oxime; the resulting *azoxy*-compound,  $\text{ON}_2(\text{CMe}\cdot\text{N}\cdot\text{OH})_2$ , is unstable, decomposing, on the one hand, into acethydroxamic acid and nitrogen, and, on the other, into acetaldoxime and nitrosoacethydroxylamino-oxime, but in concentrated alkaline solution undergoes transformation into the stable *ethylhydroxyazaurolic acid*,  $\text{NO}\cdot\text{CMe}\cdot\text{N}\cdot\text{N}(\text{OH})\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ , which on reduction yields ethylazaurolic acid, and is decomposed by boiling water, forming *hydroxy-leucazone*.

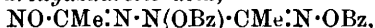
*Dibenzoyl ethylazaurolic acid*,  $\text{NO}\cdot\text{CMe}\cdot\text{N}\cdot\text{NBz}\cdot\text{CMe}\cdot\text{N}\cdot\text{OBz}$ , crystallises in orange-red needles, m. p. 210° (decomp.).

*Acethydroxylamino-oxime hydrochloride*,  $\text{C}_2\text{H}_6\text{O}_2\text{N}_2\cdot\text{HCl}$ , forms long, colourless needles, m. p. 156° (decomp.), gives a blue coloration with ferric chloride, reduces ammoniacal silver nitrate, and with Fehling's solution forms a red *copper* derivative. The dark brown, crystalline *copper* derivative,  $\text{C}_2\text{H}_4\text{O}_2\text{N}_2\text{Cu}\cdot 2\text{H}_2\text{O}$ , formed by the action of copper acetate on the hydrochloride, decomposes when heated with its mother liquor, yielding nitrogen, nitrous acid, acetic acid, and cuprous chloride. The free *hydroxylamino-oxime* is unstable; on oxidation it yields acetic acid, or with bromine water, ethylnitrosolic acid.

*Ethylnitrosolic acid* is stable only in its bluish-green solution; it gives a brownish-green coloration with ferric chloride, liberates iodine slowly from acidified potassium iodide solution, and decomposes when warmed. It gives coloured precipitates with salts of the heavy metals in neutral solution; the *silver*,  $\text{C}_2\text{H}_3\text{O}_2\text{N}_2\text{Ag}$ , and *potassium* salts are described.

*Ethylhydroxyazaurolic acid*,  $\text{C}_2\text{H}_8\text{O}_3\text{N}_4$ , crystallises in yellow needles, decomposes at 106—108°, gives with ferric chloride a reddish-brown coloration and Liebermann's nitroso-reaction, and when treated with hydrochloric acid is transformed into the isomeric *azoxy*-compound which immediately decomposes, forming nitrogen and acethydroxamic acid.

*Sodium nitrosoacethydroxylamino-oxime*,  $\text{C}_2\text{H}_4\text{O}_3\text{N}_3\text{Na}$ , formed by the action of ethylnitrosolic acid on acethydroxylamino-oxime in cooled dilute sodium hydroxide solution, crystallises in nacreous scales, decomposes with detonation above 250°, is decomposed slowly by boiling water, and on acidification yields acethydroxamyl chloride, acethydroxamic acid, and hydroxylamine. The free *nitroso* compound is unstable.

*Dibenzoyl ethylhydroxyazaurolic acid*,

crystallises in golden needles, m. p.  $157^\circ$  (decomp.), is stable towards aqueous alkalis, but is decomposed by alcoholic alkalis, evolving gas.

*Hydroxyleucazone*,  $\text{CMe} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{N}(\text{OH}) \end{smallmatrix} \text{CMe}$ , forms colourless, crystalline, spherical aggregates, m. p.  $150^\circ$  (decomp.), gives a red coloration with ferric chloride, is oxidised by potassium permanganate, forms hygroscopic salts with alkalis and acids, and is stable towards reducing agents, yielding leucazone only in one experiment with stannous chloride and hydrochloric acid. G. Y.

**Condensation of Formaldehyde with Hydrazine Hydrate.**

ROBERT STOLLÉ (*Ber.*, 1907, 40, 1505—1507. Compare Pulvermacher, *Abstr.*, 1894, i, 12; Duden and Scharff, *Abstr.*, 1895, i, 122).—This is an account of an unsuccessful attempt to prepare triaminotrimethylene-triamine. The action of 4 mols. of formaldehyde on 5 mols. of hydrazine hydrate leads to the formation of a white, amorphous product, which is obtained also when trioxymethylene is heated with hydrazine hydrate under pressure at  $100^\circ$ , and is probably a polymeric *methylenehydrazine*,  $(\text{CH}_2 \cdot \text{N} \cdot \text{NH}_2)_3$  (compare Curtius and Pflug, *Abstr.*, 1892, 456; Curtius and Lublin, *Abstr.*, 1900, i, 700). When heated it detonates without melting, is converted partially into methyleneazine when boiled with water, reacts with benzaldehyde, yielding under certain conditions the mixed aldazine,  $\text{CHPh} : \text{N} \cdot \text{N} : \text{CH}_2$ , under others, benzylideneazine and methyleneazine, reduces Fehling's and ammoniacal silver nitrate solutions, and with silver nitrate in aqueous solution forms the *additive* compound,  $(\text{CH}_2 \cdot \text{N} \cdot \text{NH}_2)_3 \cdot 2\text{AgNO}_3$ , which is obtained as a white powder, detonates when heated, and gradually decomposes, evolving the odour of impure acetamide.

*m*-Nitrobenzylidenehydrazine (Curtius and Lublin, *loc. cit.*), which is unimolecular, forms an *additive* compound with silver nitrate,  $\text{C}_7\text{H}_7\text{O}_2\text{N}_3 \cdot \text{AgNO}_3$ ; this is obtained as a white, crystalline powder, detonates when heated, and yields the aldazine when suspended in alcohol and treated with hydrogen sulphide. G. Y.

**Additive Products of Trialkyl-phosphines, -arsines and -stibines.** ARTHUR HANTZSCH and HAROLD HIBBERT (*Ber.*, 1907, 40, 1508—1519. Compare Hibbert, *Abstr.*, 1906, i, 153).—Co-ordination isomerides,  $[\text{RMe}_3\text{X}]\text{Y}$  and  $[\text{RMe}_3\text{Y}]\text{X}$ , corresponding with hydroxy-trimethylammonium bromide and trimethylbromoammonium hydroxide (*Abstr.*, 1905, i, 576), are not obtained if  $\text{R} = \text{P}$ ,  $\text{As}$ , or  $\text{Sb}$ , since these three elements differ from nitrogen in being truly quinquevalent even in their simplest halogen derivatives. The dibaloids and dithiocyanates,  $\text{RMe}_3\text{X}_2$ , behave as salts of very weak bases, being hydrolysed in aqueous solution, not only completely to the hydroxy-salts,



but also further to the hydrate and free acid,  $\text{RMe}_3(\text{OH})_2$ . This

hydrolysis is still more marked in the case of the derivatives,  $\text{SMe}_2\text{Br}_2$  and  $\text{OH}\cdot\text{SMe}_2\cdot\text{NO}_3$ , of dimethylsulphoxide,  $\text{SMe}_2\text{O}$ , which is an even more feeble base than are the oxides of trialkyl-phosphines, -arsines or -stibines.

The sulphides of the trialkyl-bases,  $\text{RMe}_3\text{S}$ , form *additive* compounds with methyl iodide, which are most stable in the phosphorus and least so in the antimony series, being hydrolysed by alkalis and water respectively according to the equation  $\text{RMe}_3\text{S}\cdot\text{MeI} + \text{H}_2\text{O} = \text{RMe}_3\text{O} + \text{HI} + \text{SHMe}$ . The constitution of the phosphorus derivative as a sulphonium,  $\text{PMe}_3\cdot\text{SMeI}$ , or a phosphonium,  $\text{SMe}\cdot\text{PMe}_3\text{I}$ ,

compound has not been established.

Contrary to Hofmann's statement (*Proc. Roy. Soc.*, 1860, 10, 186, 616; 1862, 11, 291), the action of tetrachloromethane on triethylphosphine leads to the formation of the derivative  $\text{CCl}(\text{PEt}_3\text{Cl})_3$  only and not to that of the compound,  $\text{C}(\text{PEt}_3\text{Cl})_4$ .

The constitution of the red, *additive* compound of triethylphosphine and carbon disulphide is discussed, and the conclusion is drawn that the most probable formula is that suggested by Jacobson,  $\text{PEt}_3\begin{smallmatrix} \text{CS} \\ | \\ \text{S} \end{smallmatrix}$ , which represents the substance as an intramolecular anhydride of the acid  $\text{OH}\cdot\text{PEt}_3\cdot\text{CS}\cdot\text{SH}$ , and is in agreement with its conversion by hydrogen chloride into the hygroscopic, colourless chlorotriethylphosphonium dithiocarboxylic acid,  $\text{PEt}_3\text{Cl}\cdot\text{CS}\cdot\text{SH}$ . This is stable in concentrated acid solution, but is decomposed by water, forming sulphur and hydrogen sulphide. The red, *additive* compound forms a red methiodide in which the ring structure must remain; its constitution is considered to be most probably  $\text{PEt}_3\begin{smallmatrix} \text{CS} \\ | \\ \text{SMeI} \end{smallmatrix}$ . The additive compound of triethyl-

phosphine and carbon disulphide is readily decomposed by heating with anhydrous fatty acids, forming triethylphosphine sulphide, carbon oxysulphide, and derivatives of thio-fatty acids.

The additive compounds of the trialkylphosphines and halogens are hygroscopic, and are readily decomposed by water, forming the hydrogen haloid. *Trimethylstibine oxybromide anhydride*,  $(\text{SbMe}_3\cdot\text{Br})_2\text{O}$ , formed by mixing aqueous solutions of the dibromide and oxide, crystallises in needles. *Trimethylarsine dibromide*,  $\text{AsMe}_3\text{Br}_2$ , is obtained by treating the perbromide with acetone.

These dihaloid and oxyhaloid derivatives behave towards sodium hydroxide and phenolphthalein as the free hydrogen haloids. The hygroscopic oxides are neutral to litmus, in agreement with which are the high values obtained for the molecular conductivities of the dihaloid derivatives: trimethylstibine dibromide,  $\mu = 500-521$ ; trimethylarsine dibromide,  $\mu = 496.8-559.6$ , and trimethylphosphine dibromide,  $\mu = 513.6-565.9$ , with  $v = 64-1024$ . As the conductivity of 1 mol. of hydrogen bromide at similar dilutions is  $\mu = 402-406$ , the hydrolysis of the dihaloid derivatives leads chiefly to the formation of the oxyhaloid compounds, which are hydrolysed to a smaller extent; thus trimethylstibine oxybromide has  $\mu = 201.2-243.9$  with  $v = 80-1280$ .

*Trimethylstibine dithiocyanate*,  $\text{SbMe}_3(\text{CNS})_2$ , formed by heating the

dichloride with potassium thiocyanate in alcoholic solution, is obtained in white crystals.

Triethylphosphine forms unstable *additive* compounds with cyanogen iodide and bromide. The *additive* compound of trimethylstibine and cyanogen iodide, formed in ethereal solution at  $-20^{\circ}$ , decomposes readily, and on solution in water or alcohol yields *trimethylstibine oxyiodide*,  $(\text{SbMe}_3\text{I})_2\text{O}$ . The colourless *triphenylstibine iodocyanide* is slightly more stable, but decomposes partially even when rapidly dried in a desiccator.

*Dimethylsulphide dibromide*,  $\text{SMe}_2\text{Br}_2$ , forms yellow crystals; it yields a colourless aqueous solution in which it is completely hydrolysed. The *oxynitrate* has similar properties. The extremely feeble basic properties of dimethylsulphoxide induced the authors to determine the conductivity of solutions of ethylene oxide in hydrochloric acid; the results show that the oxide has no basic properties in aqueous solution.

The sulphides of the trialkyl-phosphines, -arsines, and -stibines are formed by the action of sulphur on the trialkyl bases or by that of hydrogen sulphide on the oxides. *Trimethylstibine sulphide*,  $\text{SbMe}_3\text{S}$ , m. p.  $168^{\circ}$  (decomp.). The methiodides of the sulphides are colourless, neutral salts. *Triethylphosphonium sulphide methiodide*,  $\text{PEt}_3\text{S}\cdot\text{MeI}$ , m. p.  $123^{\circ}$ , is decomposed slowly by boiling water, and is normally dissociated in aqueous solution, having almost the same conductivity as triethylsulphonium iodide,  $\mu = 89\cdot7-105\cdot7$ , with  $\nu = 32-512$ , at  $25^{\circ}$ . The methiodide is decomposed by alkalis below  $0^{\circ}$ , the free *base* decomposing immediately into mercaptan and triethylphosphine oxide.

*Trimethylarsine sulphide methiodide*,  $\text{AsMe}_3\text{S}\cdot\text{MeI}$ , crystallises in white needles, m. p. about  $180^{\circ}$  (decomp.), and is decomposed by water. *Trimethylstibine sulphide methiodide* is formed in solution, but cannot be isolated.

The action of carbon tetrabromide on triethylphosphine leads to the formation of *bromomethenyltri-triethylphosphonium bromide*,  $\text{CBr}(\text{PEt}_3\text{Br})_3$ . The corresponding chlorine compound is hydrolysed by water, forming chlorotriethylphosphonium chloride, triethylphosphonium oxide, and hydrogen chloride.

The molecular weight of the *additive* compound of triethylphosphine and carbon disulphide,  $\text{CS}_2\text{PEt}_3$ , has been determined cryoscopically in nitrobenzene solution. The *methiodide*, m. p.  $96-97^{\circ}$ , forms a red, neutral, aqueous solution having the conductivity  $\mu_{38} = 93\cdot8$ , or  $\mu_{512} = 98\cdot6$ , and is decomposed by sodium hydroxide. The free *base* decomposes immediately on liberation, forming mercaptan, sulphur, hydrogen sulphide, triethylphosphonium oxide, and carbon dioxide.

G. Y.

**Influence of Solvents in the Claisen Condensation Catalytic Action of Ether and of Tertiary Bases in this Reaction, and also in the Formation of the Grignard Reagent.** J. BISHOP TINGLE and ERNEST E. GOESLINE (*Amer. Chem. J.*, 1907, 37, 483-494).—The authors have examined the effect of the solvent in the Claisen and Grignard reactions and find a complete parallelism of the two reactions in this respect.

It is possible to accelerate or to retard a given condensation by adding or withdrawing ether from the solution. In the cases examined, the yield of condensation product is essentially the same, whether the sodium compound dissolves in the liquid, is suspended in it, or forms a crust over the sodium wire.

The rapidity with which the magnesium is attacked in the preparation of the Grignard reagent by the halide compound depends on the nature of the alkyl or aryl halide, provided that other conditions remain constant; the presence of ether is not essential to the reaction, nor is a high temperature necessary, provided that sufficient time is allowed. Light petroleum (b. p.  $36^{\circ}$ ) may be used as a solvent. The views of Tschelinzeff regarding the function of the ether in the Grignard reaction are discussed.

A. McK.

**Conversion of Individual Organo-magnesium Compounds into Amine Complexes and the Thermochemical Investigation of the Reaction.** WLADIMIR TSCHELINZEFF (*Ber.*, 1907, 40, 1487—1496. Compare *Abstr.*, 1905, ii, 803; 1906, i, 241, 489; ii, 334, 335; this vol., i, 199).—A number of organo-magnesium ammonium compounds have been prepared by various authors by the action of nitrogen compounds on organo-magnesium ether complexes. This method may lead to the formation of mixtures, a disadvantage which is avoided by acting with the amine directly on the individual organo-magnesium compound; this second method has the further advantage that it allows of the preparation of amine complexes having a smaller heat of formation than the corresponding ether complex. In the present paper, the formation of amine complexes, which are considered to have the structure  $C_3H_7 \cdot Mg \cdot NRR'R''I$  by the action of magnesium propyl iodide on simple aliphatic and aliphatic-aromatic tertiary amines,  $NRR'R''$ , is described.

The values found for  $Q$  in the thermochemical equation:  $NRR'R'' + Mg(C_3H_7)I = NRR'R''I \cdot Mg \cdot C_3H_7 + Q$ , are with triethylamine, 11.70 cal.; tripropylamine, 10.32 cal.; triisobutylamine, 9.0 cal.; dimethylaniline, 3.81 cal.; dimethyl-*o*-toluidine, 0.98 cal., and diethylaniline, 0.78 cal. These values are compared with the heats of formation of the corresponding ether complexes formed from magnesium propyl iodide and ethyl ether, 6.63 cal.; ethyl propyl ether, 6.15 cal.; ethyl amyl ether, 5.91 cal., and methyl and ethyl phenoxide, about 0 cal. In agreement with the known properties of ammonium and oxonium compounds, the amine complexes are found to have the greater heats of formation.

G. Y.

**Optical Behaviour of Some Styrenes.** AUGUST KLAGES (*Ber.*, 1907, 40, 1768—1772. Compare *Abstr.*, 1904, i, 567).—The refractive indices for  $H_a$ ,  $N_a$ ,  $H_\beta$ , and  $H_\gamma$ , also  $N_a$ ,  $N_{Na}$ ,  $N_\gamma$ , and  $N_\gamma - N_a$ , as well as the molecular refraction  $\alpha$ ,  $N_a$ ,  $\gamma$ , and  $\gamma - \alpha$ , have been measured accurately for a number of styrenes. The calculated molecular refractions and the excess of observed over calculated values are also recorded. For the full details of the physical measurements the original must be consulted.

The homologous series of  $\Delta^{\alpha\gamma}$ -styrenes all agree in showing an

increase in molecular refraction for the red hydrogen and sodium *D* lines of about 4.5 units above the calculated values, and further show an abnormally high dispersion.

$\alpha$ -Phenyl- $\Delta^{\alpha\gamma}$ -butadiene (compare von der Heide, Abstr., 1904, i, 583) has  $D_4^{16}$  0.9309,  $n_{Na}^{16}$  1.61283, excess mol. ref.<sub>Na</sub> 4.64.

$\alpha$ -Phenyl- $\Delta^{\alpha\gamma}$ -pentadiene,  $CHPh:CH:CH:CHMe$ , is a mobile, colourless oil, b. p. 116°/16 mm., m. p. -4°; it polymerises when kept to a viscid liquid, and has  $D_4^{13}$  0.9384,  $n_{Na}^{13}$  1.61114, excess mol. ref.<sub>Na</sub> 4.63. With sodium and boiling ethyl alcohol it yields phenyl- $\Delta^{\beta}$ -pentene, a colourless, fruity oil, b. p. 111°/30 mm., 201°/760 mm.

$\alpha$ -Phenyl- $\Delta^{\alpha\gamma}$ -hexadiene,  $CHPh:CH:CH:CHEt$ , prepared from magnesium propyl iodide and cinnamaldehyde, contains a carbinol, from which it is freed by treatment with hydrogen chloride and heating with pyridine at 125°. The hydrocarbon is a colourless oil, b. p. 128°/16 mm.,  $D_4^{12}$  0.9253,  $n_{Na}^{12}$  1.60252, excess mol. ref.<sub>Na</sub> 5.35. On reduction it yields  $\alpha$ -phenyl- $\Delta^{\beta}$ -hexene,  $CH_2Ph:CH:CH:CH_2Et$ , b. p. 108°/16 mm.,  $D_4^{16}$  0.8898,  $n_D^{16}$  1.5058, mol. ref. 53.4.

$\alpha$ -Phenyl- $\epsilon$ -methyl- $\Delta^{\alpha\gamma}$ -hexadiene,  $CHPh:CH:CH:CH:CHMe_2$ , has b. p. 143°/22 mm., 136°/16 mm.,  $D_4^{20}$  0.9248,  $n_{Na}^{20}$  1.58727, excess mol. ref.<sub>Na</sub> 4.66.

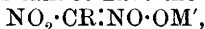
$\alpha$ -Phenyl- $\xi$ -methyl- $\Delta^{\alpha\gamma}$ -heptadiene,  $CHPh:CH:CH:CH:CH_2:CHMe_2$ , has b. p. 146—147°/15 mm.,  $D_4^{20}$  0.9508,  $n_{Na}^{20}$  1.58547, excess mol. ref.<sub>Na</sub> 3.15.

E. F. A.

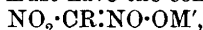
**Yellow, Red, Green, Violet, and Colourless Salts from Dinitro-compounds.** ARTHUR HANTZSCH [and, in part, ERICH BORCHERS, A. H. SALWAY, and E. HEDLEY] (*Ber.*, 1907, 40, 1533—1555).—Whilst the mononitro-compounds,  $CH_2R:NO_2$ , yield only colourless *aci*-nitro-salts,  $CHR:NO:OM'$ , the dinitro-compounds,  $CHR(NO_2)_2$ , form salts which exist in yellow and red modifications, thus resembling the *chromo*-salts of the nitrophenols and nitro-ketones (compare this vol., i, 513, 555). These yellow and red salts are convertible into each other with varying, but mostly great, ease, depending on the temperature, the solvent, the nature of the metal, and the nature of the dinitro-compound, so that only in a few cases can both modifications be isolated. The aqueous solutions of the yellow and red salts are identical, containing the two forms in equilibrium; at low temperatures the yellow, but at higher temperatures the red, form preponderates. It is shown that the salts are unimolecular in solution and that the degree of dissociation varies with the temperature independently of the change in colour, hence neither form is a polymeride of the other. Since, moreover, both yellow and red salts are obtained in the anhydrous state, the difference in colour must result from isomerism. Coloured ethers of *aci*-dinitroethane have not been obtained.

Dinitroethane on neutralisation behaves as a  $\psi$ -acid, the gradual change which takes place in the conductivity of the solutions, formed by mixing dinitroethane and alkalis in molecular proportions, being accompanied by a corresponding change in colour.

The yellow and red salts cannot have the constitution



since the salts of other *aci*-nitro-compounds,  $\text{CRX}:\text{NO}\cdot\text{OM}'$ , in which  $\text{X}=\text{Br}$  or  $\text{CN}$ , are colourless, as is also nitrodiazobenzene methyl ether; moreover, under certain conditions, almost colourless salts of *aci*-dinitro-compounds, which are probably colourless salts containing traces of yellow salts and must have the constitution



have been obtained. Hence the constitution of the dinitroethane ion must be changed still further in the yellow and red salts; the constitutions of these and the question as to their structural or stereoisomerism are discussed, but left undecided.

If the two nitro-groups are situated differently in the molecule, as in the nitrophenylnitromethanes,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NO}_2$ , four coloured salts can be formed, yellow and red salts derived from the colourless *aci*-nitro-salt,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{NO}\cdot\text{OM}'$ , and green and violet salts derived from the colourless *aci*-salt,  $\text{OM}'\cdot\text{NO}:\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NO}_2$ . Of the colourless salts, only one, the mercuric salt formed from *m*-nitrophenylnitromethane, has been isolated. The stability of the *chromo*-salts depends on the nature of the metal and of the dinitro-compound and on the presence or absence of water of crystallisation; the complete series of four coloured salts has been isolated only in the case of the potassium and caesium salts of the *p*-nitro-compound.

The *methyl ether* of nitrocyanophenylmethane,  $\text{CN}\cdot\text{CPh}:\text{NO}\cdot\text{OMe}$ , formed by the action of methyl iodide on the silver derivative at the laboratory temperature, crystallises in colourless needles, m. p.  $38-39^\circ$ , and is hydrolysed only slowly by boiling water, distilling almost unchanged in a current of steam.

The solutions of phenyldinitromethane (Ponzio, Abstr., 1906, i, 735) in non-ionising solvents are colourless, whilst those in alcohol or water are intensely yellow, especially when heated; if an excess of hydrochloric acid is added to the aqueous solution of the alkali salt at  $0^\circ$ , the resulting yellow solution becomes colourless only gradually. The *leuco*-salts have not been isolated in the perfectly colourless state; on addition of a concentrated alkali hydroxide to the finely-powdered dinitro-compound, a colourless salt is formed, but rapidly becomes yellow. On addition of sodium or potassium ethoxide to the alcoholic solution of the dinitro-compound at  $-75^\circ$  or at the laboratory temperature, a pale yellow salt is precipitated, sometimes together with the ordinary dark lemon-yellow salt. The aqueous solutions of these pale yellow salts are dark yellow at the ordinary temperature and become red when heated. The lemon-yellow salts form the stable modification at the ordinary temperature. Of the red isomerides, the most stable is the *sodium* salt, which is formed from the dinitro-compound by the action of concentrated aqueous sodium hydroxide on the solid, or by addition of sodium ethoxide and ether to the alcoholic solution, or of sodium ethoxide alone to the benzene solution, or from the yellow salt on evaporation of the aqueous solution, or, as green leaflets, by addition of propyl alcohol to the boiling, concentrated solution. It is stable when rapidly dried in presence of ether vapour, but changes into the yellow salt when dissolved, or in contact with the liquids from which it is precipitated, or when acted on by

alcohol vapour. When heated with a small amount of alcohol, the yellow salt changes into the red, but is reformed as the alcohol cools. On slow evaporation, the aqueous solution of the yellow salt deposits a mixture of the yellow and red isomerides, occasionally together with the colourless salt. The red salts of the other alkali metals and of ammonium are less stable and, when formed, change rapidly into the yellow modifications.

When freshly prepared, the yellow salts, formed by the action of alkali ethoxides on phenyldinitromethane in ethereal or toluene solution, are much less stable than when obtained from aqueous solutions, and change much more readily into the red modifications at the ordinary temperature; these unstable, yellow salts gradually lose their reactivity, changing into the ordinary, stable, yellow modifications.

The leuco-*potassium* salt of piperonyldinitromethane (Ponzio, *loc. cit.*),  $C_8H_5O_6N_2K$ , formed by the action of potassium ethoxide on the dinitro-compound in presence of much ether, is straw-coloured, becomes dark-yellow at  $60-70^\circ$ , and dissolves in water, forming the orange solution which is obtained also from the yellow and red *chromo*-salts. The yellow *silver* salt crystallises in orange needles. Of the deep Bordeaux-red salts, the most stable is the *sodium* salt, which when pure remains unchanged for months in a desiccator, and resembles the red salt of phenyldinitromethane. Cryoscopic and ebullioscopic molecular weight determinations show that the pale yellow solution at  $0^\circ$  and the orange solution at  $100^\circ$  contain the normally dissociated, unimolecular salt.

The *lithium* salt ( $3H_2O$ ) of *p*-nitrophenylnitromethane is obtained only in the yellow modification. The *red sodium* salt ( $3H_2O$ ), formed by the action of sodium ethoxide in benzene solution, crystallises in prismatic needles; the *green* isomeride separates from the aqueous solution at  $-14^\circ$ , and in contact with ice below  $0^\circ$  undergoes transformation into the *yellow* salt ( $3H_2O$ ), which loses  $2\frac{3}{4}H_2O$  at  $100^\circ$ , changing into the red salt; this becomes anhydrous at  $130^\circ$ .

The *yellow potassium* salt of *p*-nitrophenylnitromethane ( $2H_2O$ ), formed in aqueous solution at the ordinary temperature, crystallises in leaflets, m. p.  $160^\circ$  (decomp.), and at  $100^\circ$  loses  $1\frac{1}{2}H_2O$ , changing into the red salt (Holleman, *Abstr.*, 1897, i, 409), which at  $130^\circ$  loses the remaining  $\frac{1}{2}H_2O$ , forming the *violet* salt. The anhydrous red salt is formed by the action of potassium ethoxide in absolute alcohol on the dinitro-compound in benzene solution. The *green* isomeride ( $2H_2O$ ) is formed when the violet salt or the red salt, obtained from the yellow isomeride by loss of  $H_2O$  in a desiccator, is exposed to moist air.

The *rubidium* salt of *p*-nitrophenylnitromethane is formed as the *yellow* modification ( $2H_2O$ ), which loses  $2H_2O$  at  $100^\circ$ , yielding the *violet* isomeride; this absorbs  $2H_2O$  in moist air, forming the *green* modification. *Yellow* ( $2H_2O$ ), *red* ( $H_2O$ ), *violet*, and *green caesium* salts are obtained in a similar manner. *Yellow*, m. p.  $136^\circ$ , and *green ammonium*, and *trimethylammonium*, and *yellow* and *red pyridine* salts are described. The *silver* salt is obtained as a red, gelatinous precipitate, which becomes violet and almost black when dried; the

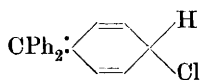


barium salt ( $2\text{H}_2\text{O}$ ) is yellow and loses  $1\frac{3}{4}\text{H}_2\text{O}$  at  $120^\circ$ , becoming red; the calcium, mercurous, mercuric, and lead salts are yellow.

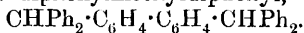
Differently coloured salts, but not differently coloured modifications of the same salt, of *o*-nitrophenylnitromethane have been obtained; the potassium (Holleman, *loc. cit.*) and sodium, m. p.  $224^\circ$  (decomp.), salts are red; the lithium, ammonium, lead, silver, and mercuric salts are yellow; the mercurous salt is olive-green. Indications of the formation of a violet potassium salt have been observed.

*m*-Nitrophenylnitromethane is formed in a 50% yield from *m*-nitrobenzyl chloride and silver nitrite. The alkali salts are orange and are probably mixtures of the yellow and red modifications. The mercuric salt,  $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NO}\cdot\text{O})_2\text{Hg}$ , is colourless and, in agreement with its formulation as a salt of an oxygen acid, yields mercuric oxide when treated with sodium hydroxide. G. Y.

**Phenylated Derivatives of 4 : 4'-Ditolyl.** ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1907, 40, 1810—1819).—If triphenylmethyl chloride,



or its tautomeric modification, has the quinonoid structure ascribed to it by many authors, the first product,  $\text{CPh}_2\cdot\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5\cdot\text{CPh}_2$ , of its reaction with metals should be obtained by isomeric change from bis-4 : 4'-diphenylmethyldiphenyl,



The formation from this of a hydrocarbon,  $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2$ , or  $\text{C}_6\text{H}_4\langle\text{CPh}_2\rangle\text{C}_6\text{H}_4$ , by removal of the two methenyl hydrogen atoms, was of special interest, as such a substance would be closely related to Gomberg's triphenylmethyl. In the present paper is described the preparation, by Grignard's reaction from ethyl diphenyl-4 : 4'-carboxylate, of the glycol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$ , the conversion of this into the dichloride,  $\text{C}_{12}\text{H}_8(\text{CPh}_2\text{Cl})_2$ , by the action of hydrogen chloride in glacial acetic acid solution, the reduction of the glycol, by hydriodic acid in glacial acetic acid solution, and of the dichloride, by means of tin and alcoholic hydrochloric acid, forming bis-4 : 4'-diphenylmethyldiphenyl, and the formation of the hydrocarbon,  $\text{C}_{38}\text{H}_{28}$ , by the action of zinc, silver, or copper on solutions of the dichloride in an atmosphere of carbon dioxide. The last substance shows its relation, on the one hand, to the diphenyl dyes by the formation of strongly-coloured solutions, and, on the other, to triphenylmethyl by its instability and the ease with which it is oxidised on exposure to air.

The glycol,  $\text{C}_{38}\text{H}_{30}\text{O}_2$ , is purified best by conversion into its dichloride, from which it is regenerated by the action of water in pyridine solution; it crystallises from benzene as a granular powder ( $\text{C}_6\text{H}_6$ ), from glacial acetic acid ( $2\text{C}_2\text{H}_4\text{O}_2$ ), from alcohol in small prisms ( $2\text{C}_2\text{H}_5\text{O}$ ), or from a mixture of ethyl acetate and light petroleum as a crystalline powder, which sinters at  $160$ — $165^\circ$ , melts on further heating to a turbid liquid, becoming more opaque, and finally clear at  $186$ — $187^\circ$ . The dichloride,  $\text{C}_{38}\text{H}_{28}\text{Cl}_2$ , crystallises as a white powder, m. p.  $219^\circ$ , and forms a turbid liquid, becoming transparent at  $223^\circ$ ; it dissolves in hot acetic acid, forming a light red, or in hot

nitrobenzene an intense red, solution, and is readily decomposed by moisture. The *dibromide*,  $C_{38}H_{28}Br_2$ , formed by the action of hydrogen bromide on the glycol in glacial acetic acid solution, is obtained as a red powder, m. p. 215—219° (decomp.), and is readily decomposed by moisture.

The glycol resembles triphenylcarbinol in forming coloured carbonium salts; similarly coloured compounds are obtained also by the action of zinc, mercuric, and stannic chlorides on the dichloride in nitrobenzene solution. Of these substances, the *compound* with stannic chloride,  $C_{38}H_{28}Cl_2 \cdot SnCl_4$ , has been isolated; it forms a red, amorphous mass, is stable in benzene or hydrochloric acid solution, but is decolorised by dilution with water, and dyes cotton wool in nitrobenzene solution, the dyed cotton wool being more stable towards water than the pure stannichloride.

*Bis-4 : 4'-diphenylmethyldiphenyl*,  $C_{38}H_{30}$ , crystallises in leaflets, m. p. 162—163°, and yields the above dibromide when acted on by bromine in carbon disulphide solution under the influence of direct sunlight.

The *hydrocarbon*,  $C_{38}H_{28}$ , separates from a mixture of benzene and light petroleum as a violet powder, is rapidly oxidised by air, especially when moist, and forms solutions resembling those of potassium permanganate; when dissolved in sulphuric acid and treated with water, it yields a white precipitate from which the dichloride is obtained by the action of hydrogen chloride in glacial acetic acid solution.

G. Y.

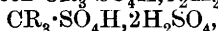
**Chlorination with Phosphorus Pentachloride.** LEE H. CONE and C. S. ROBINSON (*Ber.*, 1907, 40, 2160—2166. Compare Abstr., 1906, i, 424).—Partial replacement of bromine by chlorine occurs when *pp'*-dibromobenzophenone or *p*-bromobenzoic acid is heated with phosphorus pentachloride at 150° for five hours. Benzophenone and *p*-bromobenzophenone retain their nuclei unchanged by treatment with phosphorus pentachloride in hot benzene. Diphenylmethane and phosphorus pentachloride at 170° yield chiefly diphenylchloromethane, while *pp'*-dibromodiphenylmethane at 150° and triphenylmethane at 160° yield respectively *pp'*-dibromodiphenylchloromethane, m. p. 92°, and triphenylchloromethane. Phosphorus pentachloride reacts with *aaa*-triphenylethane at 190—200°, forming a monochlorinated product which is probably *aaa*-triphenyl- $\beta$ -chloroethane, m. p. 118°, with *aaa*-triphenylpropane at 190—200°, yielding in a few minutes *aaa*-triphenyl- $\beta$ -chloropropane (?), b. p. 240°/47 mm., with *as*-tetraphenylethane at 170—180°, forming *tetraphenylethylene*, m. p. 221° (the *s*-isomeride is not attacked at 190°), and with pentaphenylethane at 170°, yielding triphenylchloromethane as the only crystalline product isolated.

C. S.

**Triphenylmethyl. XVI. Tautomerism in the Triphenylmethane Series.** MOSES GOMBERG (*Ber.*, 1907, 40, 1847—1888. Compare Abstr., 1906, i, 822).—Triphenylmethyl chloride and its derivatives react with silver sulphate in benzene solution, forming coloured solutions and yielding the theoretical amounts of silver

chloride. Whilst, under the same conditions, *o*-bromo-, and *m*-bromotriphenylmethyl chlorides yield only 1 mol. of silver chloride, the amount of silver haloid, obtained from tri-*p*-chloro-, tri-*p*-bromo-, and 2:4':4"-trichlorotriphenylmethyl chlorides, shows that one nucleus halogen atom has been removed in addition to the chlorine of the carbinyl chloride group. This reaction takes place only partially at 20°, probably in consequence of the protection of the silver sulphate by a layer of insoluble carbinyl sulphate, more nearly quantitative results being obtained on prolonged shaking at 50°. The nucleus halogen atom reacts only when in the para-position and after formation of the carbinyl sulphate; tri-*p*-chlorotriphenylmethyl ethyl ether does not react with silver sulphate. It is argued that all coloured substances of the triphenylmethane series, and therefore the triphenylmethyl sulphates, are quinones, and that the nucleus halogen atom can react with silver sulphate only when the substance is in the quinonoid form. On hydrolysis, the red *sulphate*, formed from *p*-bromotriphenylmethyl chloride, yields a yellow, crystalline *substance* having a pronounced odour of quinone. The *sulphate*, obtained from tri-*p*-bromotriphenylmethyl chloride, separates from methyl sulphate in red crystals, m. p. 135—136°, probably contains methyl sulphate of crystallisation, and when shaken with ether and water loses sulphuric acid and forms a red, amorphous *mass*, which may be *di-p*-bromodiphenylquinomethane,  $C_6H_4O:C(C_6H_4Br)_2$ .

The acid sulphates, formed by the action of an excess of methyl sulphate on tri-*p*-bromo- and tri-*p*-chloro-triphenylmethyl chlorides, vary in composition between  $CR_3 \cdot SO_4H, 1\frac{1}{2}H_2SO_4$  and



form small, red, strongly hygroscopic crystals, are iridescent by reflected light, are insoluble in benzene, and in agreement with von Baeyer's statement (Abstr., 1905, i, 281) do not react with silver sulphate or molecular silver. The results of experiments with *p*-bromo- and tri-*p*-bromo-triphenylmethyl chlorides are quoted, showing that whilst the carbinyl chloride reacts with silver sulphate quantitatively even in presence of two and two-third mols., the reaction of the nucleus halogen atom is hindered by the presence of less than 1 mol. of free sulphuric acid, which acts as a negative catalyst. The reaction with silver sulphate is hindered similarly by the presence of sulphur dioxide. In both cases the action of the monobromo-compound is more readily affected than that of the tribromo-compound by the negative catalyst.

All triphenylmethylcarbinyl chlorides, although colourless when solid, form yellow to red solutions in liquid sulphur dioxide, the colourless chlorides being regained on evaporation. If coloured substances of the series have quinonoid structures, the solutions of the carbinyl chlorides in liquid sulphur dioxide should behave differently to the colourless solutions in solvents such as benzene. This is found to be the case in the behaviour of the *p*-bromo-derivatives towards silver chloride; in liquid sulphur dioxide solution the nucleus bromine is substituted by chlorine, silver bromide being formed, whilst the reaction takes place to only a small extent in methyl sulphate and not at all in benzene or toluene solution. The tautomerising effect

of the sulphur dioxide is diminished by dilution of the solution with methyl sulphate or, to a still greater extent, with toluene. 4:4'-*Dichloro-4''-bromotriphenylmethyl chloride*,  $C_{19}H_{12}Cl_2Br$ , formed by the action of silver chloride on tri-*p*-bromotriphenylmethyl chloride dissolved in a mixture of toluene and liquid sulphur dioxide, or from ethyl *p*-bromobenzoate and *p*-chloriodobenzene by Grignard's reaction, crystallises in white needles, m. p. 122°. Tri-*p*-chlorotriphenylmethyl chloride is formed by the action of an excess of silver chloride on tri-*p*-bromo-, 4-*chloro-4':4''-dibromo-*, m. p. 133°, and 4:4'-*dichloro-4''-bromotriphenylmethyl chlorides* in liquid sulphur dioxide. The whole reaction may be represented as taking place in stages in the following manner:  $C(C_6H_4Br)_3Cl \rightarrow C_6H_4BrCl:C(C_6H_4Br)_2 \rightarrow C_6H_4Cl_2:C(C_6H_4Br)_2 \rightarrow C_6H_4Cl:C(C_6H_4Br)_2Cl \rightarrow C_6H_4Cl:C(C_6H_4Br)_2Cl:C(C_6H_4Br)_2Cl \rightarrow$ , &c. The benzenoid compound,  $C_6H_4Cl:C(C_6H_4Br)_2Cl$ , must be formed, even if only in small amount, in equilibrium with the preceding, as also with the succeeding, quinonoid substance.

The second half of this paper contains a long, theoretical discussion of the basic properties of carbon and of the constitution of the triphenylmethane dyes and of triphenylmethyl. G. Y.

**Catalysis: Rearrangement of Acetylhalogenaminobenzene Derivatives into Halogen Acetanilide Derivatives.** SALOMON F. ACREE and J. M. JOHNSON (*Amer. Chem. J.*, 1907, 37, 410—413).—It has been shown by Blanksma (*Abstr.*, 1902, ii, 646) that the velocity of the rearrangement of acetylphenylchloroamine into *p*-chloroacetanilide in presence of hydrochloric acid is that of a unimolecular reaction, and increases as the square of the concentration of the acid increases.

It is now found that the catalytic action of the acid is not due to the hydrogen ions present, but that an intermediate compound is produced, thus:  $CH_3 \cdot CO \cdot NPhCl + HCl \rightarrow CH_3 \cdot CO \cdot NHPhCl_2 \rightarrow CH_3 \cdot CO \cdot NH \cdot C_6H_4Cl + HCl$ . Acetylphenylchloroamine and hydrobromic acid yield *p*-bromoacetanilide; acetylphenylbromoamine and hydrochloric acid yield the same product, owing to the fact that the bromine migrates to the benzene nucleus more rapidly than chlorine. Chlorine and bromine quickly convert acetylphenylchloroamine into *p*-chloroacetanilide and *p*-bromoacetanilide respectively. The reaction between acetylphenylchloroamine and hydrobromic acid is of the second order, and the velocity constant of the rearrangement is about one thousand times as great as that induced by hydrochloric acid of the same concentration. It is evident that the catalysis is not directly dependent on the concentration of the hydrogen ions, and it is shown from a consideration of the mass law that the phenomena are easily explained on the hypothesis of the formation of an intermediate compound. Since, in this case, the velocity of the reaction is not proportional to the concentration of the hydrogen ions of the catalysing agent, but to the square of that concentration, it seems possible that there may be reversible actions in which the equilibrium is changed by a change in the concentration of the catalyser. The energetic catalytic action of chromium nitride in effecting its own formation from chromium

and ammonia, whilst it has no great influence in the reverse reaction, namely, the formation of ammonia from its elements (Baur and Voerman, Abstr., 1905, ii, 715), is regarded as a case of this kind.

E. G.

**Preparation of Acyl Alkyl Compounds of Highly Halogenated Aromatic Amines.** BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 180203, 180204).—The acyl derivatives of highly chlorinated aromatic amines are readily obtained by heating the sodium derivative of the acylated base with an alkyl haloid.

*Aceto-2:3:4:6-tetrachloroethylanilide*, m. p. 73—74°, is produced by heating *aceto-2:3:4:6-tetrachloroanilide* with alcoholic sodium ethoxide and ethyl chloride for twenty-four hours at 100°.

*Aceto-2:3:4:6-tetrachloromethylanilide*, m. p. 96—97°, *aceto-2:3:4:6-tetrachlorobenzylanilide*, m. p. 97°, and *benzo-2:3:4:6-tetrachlorobenzylanilide*, m. p. 134°, are similarly prepared, and are employed as camphor substitutes in the production of celluloid.

The primary aromatic amines, containing halogen atoms in both the contiguous ortho-positions with respect to nitrogen, are acylated only with difficulty, but the corresponding monoalkyl derivatives readily undergo condensation with acid chlorides or anhydrides.

*Aceto-2:4:6-trichloromethylanilide*, m. p. 89—90°, is readily obtained by heating *2:4:6-trichloromethylaniline* with glacial acetic acid and acetyl chloride.

The employment of ethyl- and benzyl-*2:4:6-trichloroanilines* leads to the formation of *aceto-2:4:6-trichloroethylanilide*, m. p. 50—51°, and *aceto-2:4:6-trichlorobenzylanilide*, m. p. 61°. These condensations occur even more smoothly with acetic anhydride.

*Benzo-2:4:6-trichloroethylanilide*, m. p. 127—128°, is obtained by gradually heating to 150° a mixture of *2:4:6-trichloroethylaniline* and benzoyl chloride.

G. T. M.

**Nitrogen Derivatives of Trichloroacetic Acid.** LEOPOLD SPIEGEL and PERCY SPIEGEL (*Ber*, 1907, 40, 1730—1740).—Ethyl trichloroacetate is conveniently prepared by passing hydrogen chloride into a cooled molecular mixture of alcohol and the acid. *Trichloroaceto-p-phenetide*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CCl}_3$ , forms colourless, rhombic plates, m. p. 132°; the *methylanilide* forms colourless needles, m. p. 55°; the *p-nitroanilide*,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CO}\cdot\text{CCl}_3$ , separates in almost colourless, prismatic columns, m. p. 147°, whilst the *o-nitroanilide* yields long, yellow needles, m. p. 65°. *Bis-trichloroacetyl-p-phenylenediamine*,  $\text{C}_6\text{H}_4(\text{NH}\cdot\text{CO}\cdot\text{CCl}_3)_2$ , crystallises in colourless, glistening plates, m. p. 264° (decomp.), whilst the *o-phenylenediamine* derivative gives well-formed, colourless needles, m. p. 233—234° (browning and decomposition). On prolonged heating at 200°, part of the substance decomposes and part sublimes in long, silky, glistening needles. *o-Trichloroacetylaminophenol*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CCl}_3$ , forms colourless, silky, glistening needles, m. p. 161—162°. *o-Trichloroacetylaminophenyl benzoate*,  $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CCl}_3$ , forms colourless, brightly glistening, rhombic plates, m. p. 104—105°. *Bis-trichloroacetylhydrazine*,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{CCl}_3)_2$ , crystallises in colourless, quadrate pyramids, m. p. 195°; *trichloroacetyl-*

*p*-nitrophenylhydrazine,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{CCl}_3$ , prepared by heating the hydrazine in ethereal suspension with trichloroacetyl chloride, gives bright red needles from alcohol and orange-red, hexagonal plates from benzene, both of which become reddish-yellow on standing in a vacuum; m. p.  $164^\circ$  (decomp.). The compound colours the skin an intense reddish-yellow and forms a very delicate indicator for alkali.

$\beta$ -Benzoyl- $\alpha$ -trichloroacetylhydrazine,  $\text{NHBz}\cdot\text{NH}\cdot\text{CO}\cdot\text{CCl}_3$ , crystallises in large, glistening plates, m. p.  $168^\circ$ . Trichloroacetylcarbamic hydrazide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{CCl}_3$ , forms small, colourless, quadrate columns, m. p.  $175^\circ$ .  $\beta$ -Benzoyl- $\alpha$ -trichloroacetyl- $\alpha$ -phenylhydrazine,  $\text{NHBz}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CCl}_3$ , crystallises in glistening, colourless needles, m. p.  $178^\circ$ .  
E. F. A.

**$\alpha$ -Anilinoisobutyronitrile and Derivatives.** A. MULDER (*Rec. trav. chim.*, 1907, 26, [ii], 180—187).—Tiemann and Stephan have stated (Abstr., 1883, 199) that the product obtained by the condensation of aniline with acetonecyanohydrin is  $\alpha$ -anilinoisobutyronitrile, and that the acid and amide obtained from it by hydrolysis are also  $\alpha$ -derivatives. Bischoff and Mintz, on the contrary (Abstr., 1892, 1338), have found that aniline condenses with ethyl  $\alpha$ -bromoisobutyrate to furnish ethyl  $\beta$ -anilinoisobutyrate, and the acid and amide obtainable from this being identical with those prepared by Tiemann from his nitrile, they suggested that the latter must be a  $\beta$ -derivative. The author finds that Tiemann's nitrile, on reduction with sodium in boiling alcohol, furnishes isopropylaniline and is therefore an  $\alpha$ -derivative, and infers that if the acid and amide prepared by Bischoff and Mintz are  $\beta$ -derivatives (compare Bucherer and Grolée, Abstr., 1906, i, 349), transposition must occur, probably during the hydrolysis of the nitrile to the amide. Acetonecyanohydrin does not condense with methyl-aniline.

When  $\alpha$ -anilinoisobutyronitrile is gradually mixed with excess of nitric acid (D 1.4) and the mixture heated to boiling, it furnishes the 2:4-dinitro-derivative, m. p.  $157^\circ$ , which crystallises from acetic acid in yellow spangles and is decomposed by sulphuric acid, yielding 2:4-dinitroaniline and 2:4-dinitroanilinoisobutyramide, m. p.  $155$ — $156^\circ$ , which may also be obtained by direct nitration of the amide prepared by Tiemann's method (*loc. cit.*). It crystallises from alcohol in yellow plates. When heated with hydrochloric acid at  $100^\circ$ , the nitrile yields the corresponding dinitro-acid, m. p.  $190$ — $191^\circ$  (decomp.), which separates from dilute acetic acid in small, bright yellow crystals together with a small amount of 2:4-dinitroaniline.

When anilinoisobutyramide, obtained by Tiemann's method, is dissolved in hydrochloric acid and an aqueous solution of sodium nitrite is added, phenylnitrosoaminoisobutyric acid, m. p.  $141$ — $142^\circ$ , is obtained, which crystallises from water in colourless needles, gives the Liebermann reaction, and regenerates the amide on reduction with tin and hydrochloric acid.  
T. A. H.

**Hexahydroaromatic Amines.** JOHANNES GUTT (*Ber.*, 1907, 40, 2061—2070).—The author has prepared and characterised the five

possible isomeric amines of methylcyclohexane. The optical properties of the new substances described are fully given in each case as well as those of a number of others.  $\beta$ -Methylcyclohexanol yields a chloride convertible into hexahydro-*m*-toluic acid, the chloride of which with aqueous ammonia forms 3-amino-1-methylcyclohexane. This has  $[\alpha]_D -1.9^\circ$ ,  $D_4^{20}$  0.8456, b. p.  $150^\circ/747$  mm.; the urethane has b. p.  $123^\circ/12$  mm., m. p.  $60-61^\circ$ ; the *N*-benzoyl derivative forms long needles, m. p.  $163^\circ$  (corr.).

1-Methyl-2-cyclohexanol was converted into hexahydro-*m*-toluic acid, of which the chloride has b. p.  $75-76^\circ/15$  mm. and the amide, m. p.  $180^\circ$ . 2-Amino-1-methylcyclohexane has b. p.  $149^\circ/760$  mm.,  $D_4^{20}$  0.8558; the urethane, b. p.  $123^\circ/14$  mm., m. p.  $76-77^\circ$ ; aurichloride, yellow needles, m. p.  $205-207^\circ$ , and *N*-benzoate, flat needles, m. p.  $146-147^\circ$ , are described.

The amide of hexahydro-*p*-toluic acid has m. p.  $220-221^\circ$  (corr.); the urethane derived from it shows b. p.  $138^\circ/21$  mm., m. p.  $76^\circ$ . 4-Amino-1-methylcyclohexane has b. p.  $150^\circ/743$  mm.,  $D_4^{20}$  0.8472; the hydrochloride, glistening plates, m. p.  $260^\circ$ ; aurichloride, m. p.  $189^\circ$ ; platinichloride, m. p.  $260^\circ$  (decomp.), and *N*-benzoate, glistening, flat needles or plates, m. p.  $180^\circ$ , are described.

Hexahydrobenzylamine has b. p.  $163.5^\circ/760$  mm. (corr.),  $D_4^{20}$  0.8702, and forms an aurichloride, m. p.  $183^\circ$ ; platinichloride, m. p. above  $280^\circ$  (decomp.), and an *N*-benzoate, m. p.  $107^\circ$ . The urethane has b. p.  $140^\circ/15$  mm. and m. p.  $35^\circ$ . 1-Amino-1-methyl cyclohexane has b. p.  $142^\circ(750$  mm.),  $D_4^{20}$  0.8565, and forms a benzoate, m. p.  $101^\circ$ .

E. F. A.

**Action of Sulphites on Aromatic Amino- and Hydroxy-compounds.** IV. HANS TH. BUCHERER and FRANZ SEYDE (*J. pr. Chem.*, 1907, [ii], 75, 249-293. Compare Abstr., 1903, i, 627; 1904, i, 309, 395; 1905, i, 48, 585).—It has been shown in previous communications that primary and secondary aliphatic amines can be prepared by alkylation and decomposition of the resulting secondary or tertiary amine by means of sodium hydrogen sulphite, the process being rendered in a sense continuous by conversion of the phenol or naphthol, formed together with the aliphatic amine, into the original aromatic amine. In the present paper, the preparation of benzylamine and of diethylenediamine (piperazine), and unsuccessful attempts to prepare dibenzylamine by this series of reactions are described. It is found that sodium naphthionate reacts easily with 1 mol. of benzyl chloride in sodium carbonate solution, forming  $\alpha$ -benzylaminonaphthalene-4-sulphonic acid together with small amounts of benzyl alcohol, or in sodium acetate solution together with traces of dibenzyl- $\alpha$ -naphthylamine. 2-Benzylaminonaphthalene-4-sulphonic acid is decomposed by sodium hydrogen sulphite solution, slowly at the temperature of the water-bath, or more quickly at  $125^\circ$  under pressure, benzylamine hydrochloride being formed in a 70% yield. Prolonged action of an excess of benzyl chloride on naphthionic acid in boiling aqueous sodium acetate solution leads to the formation of a mixture of  $\alpha$ -benzylamino- and  $\alpha$ -dibenzylamino-naphthalene-4-sulphonic acids together with di benzyl- $\alpha$ -naphthylamine in a yield of 4.5% of the naphthionic acid

The dibenzylamino-sulphonic acid could not be isolated; the mixture of benzylated amino-sulphonic acids, when boiled with aqueous sodium hydrogen sulphite, yields 12% of benzylamine, the dibenzyl compound remaining undecomposed by the sulphite even at 150°.

Similar results are obtained on benzylating  $\alpha$ -naphthylamine-4:7-disulphonic and  $\alpha$ -naphthylamine-4:8-sulphonic acids. Of the mono- and dibenzyl derivatives, only sodium hydrogen  $\alpha$ -benzylaminonaphthalene-4:8-disulphonate has been isolated. Benzylamine is formed in 77.4%, 74.4%, and 20.3% yields from the solutions obtained by the action of 1 mol. of benzyl chloride on the 4:7- and 4:8-disulphonic acids and of 2 mols. of benzyl chloride on the 4:8-disulphonic acid respectively.

Naphthionic acid does not form a piperazine derivative with ethylene dibromide, whilst in consequence of its insolubility, di- $\alpha$ -naphthylpiperazine (Abstr., 1889, 1011) does not react with sodium hydrogen sulphite, but when rendered soluble by sulphonation it is decomposed to a small extent by the sulphite at 140—160°, yielding piperazine and a naphtholsulphonic acid.

It was observed (Abstr., 1905, i, 48) that the yields obtained in the preparation of secondary arylamines from derivatives of  $\beta$ -naphthol with anthranilic, sulphanilic, or metanilic acid by the sodium hydrogen sulphite method were the poorer the more soluble the product. In agreement with this,  $\beta$ -naphthol-6:8-disulphonic and  $\beta$ -naphthol-6-sulphonic acids are found to condense readily with *p*-phenylenediamine and *p*-aminophenol, whilst  $\beta$ -naphthol-3:6-disulphonic acid does not react with *p*-phenylenediamine or aniline in presence of sodium hydrogen sulphite. 2-Hydroxy-3-naphthoic acid and 2:8-dihydroxy-6-sulpho-3-naphthoic acid enter into the reaction more readily than does  $\beta$ -naphthol. It is found, further, that better yields are obtained by the action of derivatives of  $\beta$ -naphthol with *p*-substituted than with *o*-substituted arylamines, and that whilst  $\beta$ -hydroxynaphthoic acids are decomposed readily with loss of carbon dioxide, their esters remain unchanged on prolonged boiling with aqueous sodium hydrogen sulphite; in consequence of this stability of the carbethoxy-group, the esters of  $\beta$ -hydroxynaphthoic acids do not form amines by the sulphite reaction.

The constitutions of 2:8-dihydroxynaphthalene-6-sulphonic and 8-hydroxy-2-naphthylamine-6-sulphonic acids, formed by fusion of *G* salt and of amino-*G* salt respectively, are confirmed by the formation of these acids from nigrotic acid (2:8-dihydroxy-6-sulpho-3-naphthoic acid) by boiling with sodium hydrogen sulphite solution and by heating with ammonium sulphite and ammonia at 150° under pressure.

*$\alpha$ -Benzylaminonaphthalene-4-sulphonic acid*,  $C_{17}H_{15}O_2NS$ , crystallises from water in yellowish-white needles or separates as an amorphous powder; the sodium salt crystallises in white needles and has a blue fluorescence in dilute, aqueous solution.

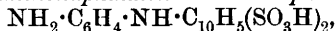
*Dibenzyl- $\alpha$ -naphthylamine*,  $C_{24}H_{21}N$ , crystallises from alcohol in white needles, m. p. 108°, and has a blue fluorescence in alcoholic solution; the hydrochloride,  $C_{24}H_{21}N \cdot HCl$ , a white powder, m. p. 186°, decomposed by water.



*Sodium hydrogen  $\alpha$ -benzylaminonaphthalene-4 : 8-disulphonate,*  
 $C_{17}H_{14}O_6NS_2Na$ ,

forms microscopic needles.

*$\beta$ -p-Aminophenylaminonaphthalene-6 : 8-disulphonic acid,*



formed from  $\beta$ -naphthol-6 : 8-disulphonic acid and *p*-phenylenediamine, crystallises in yellow, microscopic needles; the *sodium hydrogen salt*,  $C_{16}H_{18}O_6N_2S_2Na$ , was analysed.

*$\beta$ -p-Hydroxyphenylaminonaphthalene-6 : 8-disulphonic acid,* from  $\beta$ -naphthol-6 : 8-disulphonic acid and *p*-aminophenol, crystallises in yellowish-white needles; the *sodium hydrogen salt*,  $C_{16}H_{12}O_7NS_2Na$ , was analysed.

The analytical results obtained with the product of the condensation of  $\beta$ -naphthol-6-sulphonic acid and *p*-phenylenediamine point to the presence of a mixture of disulphonaphthyl-*p*-phenylenediamine and bisdisulphonaphthyl-*p*-phenylenediamine.

*$\beta$ -p-Acetylaminophenylaminonaphthalene-6-sulphonic acid,* formed together with a small amount of a sulphur-free compound, crystallising in microscopic rhomboids, was isolated in the form of its *sodium salt*,  $C_{18}H_{15}O_4N_2SNa$ , which is obtained as a bluish-white, crystalline powder.

The following new  $\beta$ -naphthylamines,  $C_{10}H_7 \cdot NHR$ , are formed by condensation of aromatic amines,  $NH_2R$ , with 3-hydroxy-2-naphthoic acid in sodium hydrogen sulphite solution.

$R = C_6H_4Me$  (*m*): white needles, m. p. 67—68°, has a blue fluorescence in alcoholic solution;  $R = C_6H_3Me_2$  ( $Me_2 = 2 : 4$ ): transparent prisms, m. p. 40°;  $R = C_6H_4 \cdot OMe$  (*p*): rhombic leaflets, m. p. 104°;  $R = C_6H_4 \cdot OMe$  (*o*): leaflets, m. p. 68°;  $R = C_6H_4 \cdot OEt$  (*p*): white leaflets, m. p. 95°, has a blue fluorescence in alcoholic solution;  $R = C_6H_4 \cdot NH_2$  (*m*): red, crystalline powder, m. p. 95°, forms a *monohydrochloride*, m. p. 205° (decomp.);  $R = C_6H_4 \cdot NH_2$  (*p*): slender needles, m. p. 94°, has a blue fluorescence in alcoholic solution, and forms a *monohydrochloride*, white needles, m. p. about 240° (decomp.), and a *dihydrochloride*, m. p. 240° (decomp.), which becomes green, and has a blue fluorescence in alcoholic solution;  $R = C_6H_4 \cdot NHAc$  (*p*): m. p. 160°. *Di- $\beta$ -naphthyl-p-phenylenediamine*,  $C_6H_4(NH \cdot C_{10}H_7)_2$ , formed in small quantity together with the mononaphthyl compound, crystallises in white needles, m. p. 228°;  $R = C_6H_4 \cdot CO_2H$  (*o*): needles, m. p. 208°, is formed together with  $R = Ph$  from anthranilic acid;  $R = C_6H_3(OH) \cdot CO_2H$  [ $OH : CO_2H = 4 : 3$ ]: tetragonal leaflets, m. p. 176°;  $R = C_6H_4 \cdot SO_3Na$  (*m*): white, prismatic needles, forms a sparingly soluble *copper salt*;  $R = C_6H_4 \cdot SO_3Na$  (*p*): white, crystalline powder, forms a green *copper salt*. The condensation product of 3-hydroxy-2-naphthoic acid with pararosanine is a mixture of mono- and dinaphthyl compounds, forms an insoluble, bluish-violet powder or green crystals, dissolves in concentrated sulphuric acid to a reddish-brown solution becoming blue on dilution, and dyes wool violet-blue. The condensation of 3-hydroxy-2-naphthoic acid with safranin leads to the formation of a mixture of *mono*- and *di-naphthyl* derivatives of safranin, which forms a green, crystalline mass, and dyes wool bluish-violet.

*2-p-Tolylamino-8-naphthol-6-sulphonic acid*,  $C_{17}H_{15}O_4NS$ , is formed in

small amount by the condensation of *p*-toluidine with nigrotic acid ; it is obtained in microscopic needles.

The action of ammonium sulphite and concentrated ammonia on ethyl 3-hydroxy-2-naphthoate in a sealed tube at 125° leads to the formation of 3-hydroxy-2-naphthoamide, m. p. 215—216° (185° : Rosenberg, Abstr., 1893, i, 221).

Technical nigrotic acid must contain 6-sulpho- $\beta$ -naphthol-3-carboxylic acid, since the formation from it of 2:8-dihydroxynaphthalene-6-sulphonic acid is accompanied by that of  $\beta$ -naphthol-6-sulphonic acid and the formation of 8-hydroxy- $\beta$ -naphthylamine-6-sulphonic acid by that of  $\beta$ -naphthylamine-6-sulphonic acid. The 6-sulpho- $\beta$ -naphthol-3-carboxylic acid cannot be removed completely by conversion of the nigrotic acid into its toluidine salt. G. Y.

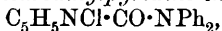
**Action of Bases, Ammonia, and Amines on *s*-Trinitrophenylmethylnitroamine.** PIETER VAN ROMBURGH and A. D. MAURENBRECHER (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 704—706).—When *s*-trinitrophenylmethylnitroamine is boiled with a 10% solution of potassium carbonate, the solution cooled, acidified, and extracted with ether, methylnitroamine is obtained, but the yield is very small. If 20% methyl- or ethyl-alcoholic ammonia is used instead of aqueous potassium carbonate, the yield is 15%, but the best result is obtained when *p*-toluidine dissolved in 96% ethyl alcohol is employed. By this method, 7 grams of methylnitroamine were obtained from 35 grams of the trinitrophenyl derivative. H. M. D.

**Asymmetric Nitrogen. XXIX. Resolution of Phenylbenzylmethylbutylammonium Compounds.** EMANUEL FRÖHLICH and EDGAR WEDEKIND (*Ber.*, 1907, 40, 1646—1650. Compare this vol., i, 409, 410).—*Methylbutylaniline*, NMeBu<sup>o</sup>Ph, b. p. 240—244°, is best obtained by warming methylaniline with successive small quantities of butyl iodide, the basic mixture being separated after each addition of the iodide. The base and benzyl iodide yield crystals of *phenylbenzylmethylbutylammonium iodide*, m. p. 140—141° (decomp.). The corresponding *bromide* has m. p. 157—158° (decomp.). The *d-camphorsulphonate*, m. p. 159° (decomp.), is fractionated in chloroform solution by the addition of ether, the twenty-seventh fraction giving a constant value of  $[M]_D^{20} - 202.1^\circ$ , which leads to the value  $[M]_D^{20} - 253.8^\circ$  for the *l*-ammonium ion. *l*-Phenylbenzylmethylbutylammonium iodide has  $[M]_D^{20} - 319.6^\circ$  in alcohol and  $-346.1^\circ$  in chloroform ; the substance undergoes autoracemisation in the latter solvent, but at a much smaller velocity than in the case with the isomeric *isobutyl* compound. C. S.

**Diphenylcarbamyl Chloride as a Reagent for Phenols.** JOHANNES HERZOG (*Ber.*, 1907, 40, 1831—1834. Compare Abstr., 1905, i, 804 ; Erdmann and Huth, Abstr., 1896, i, 198 ; 1896, i, 35 ;

Erdmann, Abstr., 1902, i, 553).—All phenols and derivatives of phenols, excepting the carboxylic acids, react readily with diphenyl-carbamyl chloride in boiling pyridine solution, forming diphenyl-urethanes of the type  $\text{NPh}_2 \cdot \text{CO} \cdot \text{OPh}$  in 70—90% yields. The reaction of the esters of aromatic hydroxy-carboxylic acids is irregular and requires further investigation.

In the absence of a phenol, diphenylcarbamyl chloride reacts with pyridine, forming *diphenylcarbamylpyridine chloride*,



which crystallises in colourless needles, m. p.  $110^\circ$  (decomp.), becomes red on exposure to light, is decomposed by water, and reacts with phenols, forming urethanes.

The following urethanes, derived from the phenols mentioned, are described;  $\text{R} = \cdot \text{CO} \cdot \text{NPh}_2$ . Phenol,  $\text{R} \cdot \text{OPh}$ , m. p. 104—105; resorcinol,  $\text{C}_6\text{H}_4(\text{OR})_2$ , m. p. 129—130°; pyrogallol,  $\text{C}_6\text{H}_3(\text{OR})_3$ , m. p. 211·5—212·5°; *o*-cresol,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{OR}$ , m. p. 72—73°; *m*-cresol, m. p. 100—101·5°; *p*-cresol, m. p. 93—94°; *o*-nitrophenol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OR}$ , m. p. 113·5—114·5°; *o*-aminophenol,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OR}$ , becomes yellow at  $173^\circ$ , m. p.  $177^\circ$ ;  $\beta$ -naphthol,  $\text{C}_{10}\text{H}_7 \cdot \text{OR}$ , m. p. 140·5—141·5°; eugenole,  $\text{C}_{10}\text{H}_{11}\text{O} \cdot \text{OR}$ , m. p. 107—108°; salol,  $\text{C}_{13}\text{H}_9\text{O}_2 \cdot \text{OR}$ , m. p. 143—144·5°.

As these urethanes are readily hydrolysed by alcoholic potassium hydroxide at  $100^\circ$ , they may be employed in the purification as well as in the identification of phenols. G. Y.

**Constitution and Colour of Nitrophenols, and especially of Nitroquinol Dimethyl Ether.** ARTHUR HANTZSCH (*Ber.*, 1907, 40, 1556—1572. Compare Hantzsch, Abstr., 1906, i, 353, 833; Ley and Hantzsch, *ibid.*, 790).—A reply to Kauffmann (this vol., i, 127). The assumption that the formation of coloured ions from colourless substances is the result of a change in chemical structure is justified by the close resemblance of the yellow and red salts of the nitrophenols to the yellow and red salts of the dinitro-compounds (compare this vol., i, 500, 555). The relation between the affinity constants of nitrophenols and the hydrolysis of their salts follows from the data given by Praetorius (*Diss.*, 1902); *p*-nitrophenyl has the conductivity  $\mu_{50} = 0\cdot69$ , from which the affinity constant  $K = 735 \cdot 10^{-10}$ , and the degree of hydrolysis of the sodium salt, 0·23% with  $v = 32$ , are calculated; similarly, *o*-nitrophenol has the conductivity  $\mu_{165} = 1\cdot08$ , the affinity constant  $K = 557 \cdot 10^{-10}$ , and the degree of hydrolysis of the sodium salt, 0·26% with  $v = 32$ . The degree of hydrolysis of the sodium salt, as determined by Shield's methyl acetate method, with  $v = 32$ , is for *p*-nitrophenol, 0·28%, and for *o*-nitrophenol, 0·26%.

Molecular weight determinations of nitroquinol dimethyl ether show that, contrary to Kauffmann's assumption, both the solution in methyl alcohol, which is intensely yellow, and that in hexane, which is almost colourless, contain the unimolecular ether. The molecular weight increases with the concentration of the hexane, but not with that of the methyl-alcoholic solution, which points to the formation

of association products in the yellow solutions. In its yellow solutions, nitroquinol dimethyl ether behaves as a non-electrolyte.

Solutions of nitroquinol dimethyl ether in a number of solvents have been examined by means of Martens-Grünbaum's spectrophotometer, and are arranged according to the intensity of colour in the following order: sulphuric acid, water, methyl and ethyl alcohols, ethyl acetate, propyl butyrate, benzene, and hexane; the colour intensity of the solution in methyl alcohol is 20, in water 200, and in sulphuric acid almost 500 times that of the solution in hexane. The colour intensity is shown to increase with the dielectric constant of the solvent; this is still more marked, although more irregular, in the case of solutions in unsaturated (allyl alcohol and pentene) and halogen (chlorobenzene, chloroform, carbon tetrachloride, and bromoform) compounds. A similar relation between the dielectric constant of the solvent and the colour intensity of the solution is observed in the case of other aromatic nitro-compounds.

*p*-Nitroanisole, after repeated recrystallisations, forms solutions in methyl alcohol and ethyl acetate, which appear colourless and do not absorb blue, but absorb violet, rays when concentrated. Nitrobenzene absorbs rays in the extreme violet, and forms colourless solutions therefore only in solvents with small dielectric constants. It is unimportant, consequently, whether such nitro-compounds are termed coloured or colourless; of importance is that these true nitrophenol ethers are "practically colourless" in comparison with the intensely coloured *chromo*-salts and *chromo*-ethers.

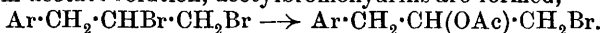
[With KURT MEISENBURG.]—In agreement with the results of the colorimetric investigation, it is found that the molecular refraction of aromatic nitro-compounds in various solvents agrees the more closely with the values calculated or determined with the undiluted, liquid substance the more indifferent the solvent. In the experiments described, the optical effects of the solvent have been eliminated by employing only solvents having similar refractive indices and dispersions: methyl alcohol, acetone, chloroform, *isobutyl* butyrate, and hexane; the molecular refractions in the first two, strongly dissociating, are compared with those in the three indifferent solvents. The molecular refractions have been determined for the following substances; the values given are the differences between the calculated molecular refractions and those found in the solvents named at 20°.

Anisole: chloroform, +0.14; acetone, +0.40; methyl alcohol, +0.48. Phenetole: chloroform, +0.39; acetone, +0.40; methyl alcohol, +0.71. Quinol dimethyl ether: chloroform, +0.35; methyl alcohol, +1.15. Nitrobenzene: chloroform, +0.13; acetone, +0.99; methyl alcohol, +0.74. *p*-Nitroanisole: chloroform, +2.68; acetone, +3.27; methyl alcohol, +3.60. *p*-Nitrophenetole: chloroform, +2.99; acetone, +3.61; methyl alcohol, +3.93. *p*-Nitrophenol: *isobutyl* butyrate, +2.79; acetone, +3.70; methyl alcohol, +3.84. *o*-Nitrophenol: chloroform, +1.89; acetone, +2.62; methyl alcohol, +2.69. Nitroquinol dimethyl ether: chloroform, +1.45; methyl alcohol, +2.42.

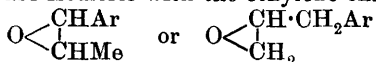
These results show that, contrary to Kauffmann's statement, the more

strongly dissociating the solvent the more the nature of the solute is changed on solution. G. Y.

**Dibromides of Allyl Phenolic Ethers. Formation of cyclo-Propanols.** MARC TIFFENEAU and DAUFRESNE (*Compt. rend.*, 1907, 144, 924—926).—In the dibromides of the allyl phenolic ethers, the bromine atom nearer the benzene nucleus is easily replaced (compare Pond, *Abstr.*, 1902, i, 449; 1903, i, 417; Hell, 1904, i, 385; Høring, 1904, i, 577; 1905, i, 592, 903). Thus, when heated with alcoholic potassium acetate solution, acetyl bromohydrins are formed,



The latter when heated with alcoholic potash are transformed into cyclopropanols,  $\text{Ar}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\text{Br} \rightarrow \text{CH}_2\begin{matrix} \text{CH}\cdot\text{Ar} \\ \text{CH}\cdot\text{OH} \end{matrix}$ , a ring-formation analogous to those observed by Henry (*Bull. Acad. roy. Belg.*, 1899, [iii], 37, 17) and Lipp (*Abstr.*, 1889, 843). The cyclopropanols so obtained are isomeric with the ethylene oxides,

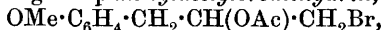


(Idzkowska and Wagner, *Abstr.*, 1899, i, 489), but are distinguished from them by their conversion into hydratropaldehydes,



whilst the oxides of the first formula are transformed into aryl acetones,  $\text{Ar}\cdot\text{CH}_2\cdot\text{COMe}$  (Hoering), and those of the second into hydrocinnamaldehydes,  $\text{Ar}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$  (Fourneau and Tiffeneau, *Abstr.*, 1905, i, 591).

*Estragole dibromide*, obtained by direct bromination, has b. p. 188—192°/18 mm. (decomp.),  $D^{27}$  1.639; when heated with alcoholic potassium acetate it gives *p-anisylacetyl bromohydrin*,



b. p. 160°/13 mm. (decomp.),  $D^0$  1.249, which on heating with alcoholic potash is transformed into *anisylcyclopropanol* in the form of slender needles, m. p. 79°. The latter is formed

$\text{CH}_2\begin{matrix} \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \text{CH}\cdot\text{OH} \end{matrix}$  directly from the dibromide by boiling with aqueous potassium carbonate solution. When

*anisylcyclopropanol* is boiled under ordinary pressure (b. p. 250—260°), it undergoes isomeric change into *p-methoxyhydratropaldehyde* already described. The propanol gives an *acetate*, b. p. 164—165°/13 mm.,  $D^0$  1.123. *Safrole dibromide* similarly gives an alcohol,  $\text{C}_{10}\text{H}_{10}\text{O}_3$ , b. p. 170—178°/15 mm.,  $D^0$  1.286, which must be 3:4-methylenedioxyphenylcyclopropanol, since it changes into the isomeric *methylenedioxyhydratropaldehyde*, which gives a

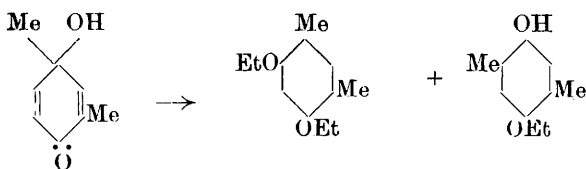
$\text{CH}_2\begin{matrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{matrix} \text{C}_6\text{H}_3\cdot\text{CH}\begin{matrix} \text{CH}\cdot\text{OH} \\ \text{CH}_2 \end{matrix}$  *semicarbazone*, m. p. 158°, and an *oxime*, m. p. 71°. This propanol gives

an *acetate* having  $D^0$  1.255.

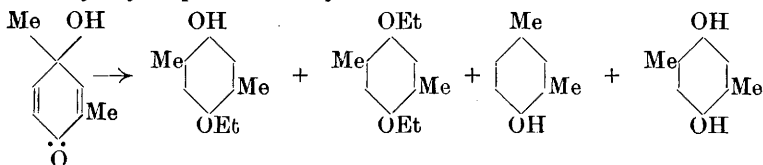
E. H.

**Iodo-derivatives of the Methyl Ethers of Catechol.** EUGÈNE TASSILLY and J. LEROIDE (*Compt. rend.*, 1907, 144, 757—759).—When guaiacyl acetate, prepared by the action of acetic anhydride on guaiacol,

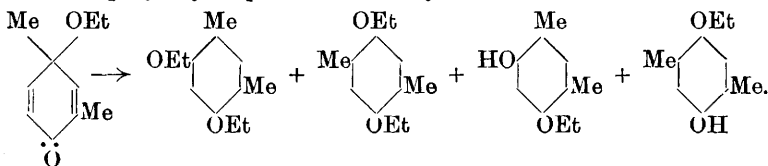




Xyloquinol is transformed by the action of a mixture of alcohol (2 vols.) and sulphuric acid (1 vol.) into a mixture of xylohydroquinone monoethyl ether, *as*-xylenol, and xylohydroquinone, together with a little xylohydroquinone diethyl ether :

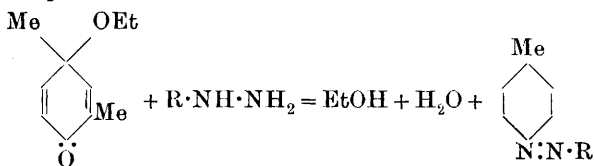


When xyloquinol ether is warmed with a mixture of concentrated sulphuric acid (1 vol.) and ethyl alcohol (30 vols.), the main product is *m*-xylorcinol diethyl ether; *p*-xylohydroquinone diethyl ether is also formed together with a little xylorcinol monoethyl ether and possibly traces of *p*-xylohydroquinone monoethyl ether :



The rest of the paper, which deals with the theoretical aspect of the subject, does not lend itself to adequate abstraction. A. MCK.

**Action of Ethyl- and Methyl-alcoholic Sulphuric Acid on *as*-*m*-Xylylhydroxylamine. I. Xyloquinol Ether.** EUGEN BAMBERGER (*Ber.*, 1907, 40, 1906—1917. Compare preceding abstract).—The main product of the action of a mixture of ethyl alcohol and sulphuric acid on *as*-*m*-xylylhydroxylamine is a neutral oil,  $C_{10}H_{14}O_2$ , which is shown to be the ethyl ether of 1 : 3-dimethylquinol, since it combines with *p*-nitrophenylhydrazine or with semicarbazide with the elimination of ethyl alcohol and the formation of an azo-compound :



The formation of a quinol ether is characteristic of para-alkylated

arylhydroxylamines; if the substitution of the alkyl group in the arylhydroxylamine takes place elsewhere than in the *para*-position, the action of alcoholic sulphuric acid on the resulting compound is to form phenetidine.

1:3-Xyloquinol ethyl ether (IV, preceding abstract) is an almost colourless oil, b. p.  $94-94.5^{\circ}/12$  mm. It is volatile with steam and has an odour reminiscent of that of menthol. It has D<sub>17</sub> 0.9957. When shaken with semicarbazide hydrochloride, it forms *p*-xylylazo-carboxylamide, orange-red needles, m. p.  $135-136^{\circ}$ , whilst with *p*-nitrophenylhydrazine hydrochloride, it forms *p*-nitrobenzene-azo-xylene, m. p.  $128.5-129.5^{\circ}$ .

*m*-Xylorcinol diethyl ether (see preceding abstract, V), obtained together with the preceding compound, has m. p.  $75^{\circ}$ . Azoxyxylene and azoxylene were also identified as products of the action.

*m*-Xylorcinol monoethyl ether (preceding abstract, VI) separates from light petroleum in glistening leaflets and, when reduced by hydriodic acid, is converted into *m*-xylorcinol. *as-m*-Xylenol was identified by the formation of a mononitro-derivative.

The following products were obtained from 100 grams of *as-m*-xylylhydroxylamine: (1) 30 grams of 1:3-dimethylquinol ethyl ether, (2) 7 grams of *m*-xylorcinol diethyl ether, (3) about 0.15 gram of *m*-xylorcinol monoethyl ether, (4) about 0.2 gram of *as-m*-xylenol, (5) about 5 grams of azoxyxylene, (6) about 0.1 gram of azo-xylene, (7) a very little *p*-xylohydroquinone, (8) 2.7 grams of bases, (9) much resin and ammonia, possibly also an appreciable amount of *p*-xylohydroquinone diethyl ether, and a little of the corresponding monoethyl ether.

*m*-Xylorcinol dimethyl ether,  $\text{OMe} \cdot \text{C} \begin{array}{c} \text{CMe} - \text{CH} \\ \text{CH} : \text{C}(\text{OMe}) \end{array} \text{CMe}$ , obtained by heating *as-m*-xylylhydroxylamine (5 grams) with a mixture of methyl alcohol (70 c.c.) and concentrated sulphuric acid (2.5 grams) for three to four hours at  $100^{\circ}$ , has m. p.  $76^{\circ}$ .

1:3-Xyloquinol ethyl ether may also be obtained from xyloquinol by ethylating it with ethyl iodide and sodium ethoxide.

A. McK.

**Action of Ethyl- and Methyl-alcoholic Sulphuric Acid on *as-m*-Xylylhydroxylamine.** II. **Imino-xyloquinol Ethers.** EUGEN BAMBERGER (*Ber.*, 1907, 40, 1918—1932. Compare preceding abstracts).—The formation of iminoxyloquinol ether as an intermediate product in the conversion of *as-m*-xylylhydroxylamine into 2:4-dimethylquinol ether occurs when a mixture of concentrated and fuming sulphuric acids is used and when the action is interrupted at the proper time. The following products are also obtained: (1) xyloquinol ether, (2) xyloquinol, (3) *p*-xylohydroquinone diethyl ether, (4) *as-m*-xylenol, (5) *as-m*-azoxyxylene, (6) *as-m*-dixylenol, (7) *p*-xyloquinone, (8) *as-m*-xylidine, (9) resin, ammonia, and another substance.

4-Imino-1:3-dimethylquinol 2-ethyl ether (III, p. 516) is an almost colourless oil, b. p.  $98-98.5^{\circ}/11$  mm., soluble in mineral acids, from the solutions in which it is precipitated by alkalis. It is readily



hydrolysed by water, slowly at the ordinary temperature and quickly at  $100^{\circ}$ , thus:  $\text{OEt}\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH} + \text{H}_2\text{O} = \text{OEt}\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{O} + \text{NH}_3$ , imino-xyloquinol ether being formed.

4-Chloroimino-1:3-dimethylquinol ethyl ether,  $\text{OEt}\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NCl}$ , obtained by the addition of the imino-ether to an aqueous solution of bleaching powder, forms glistening needles or prisms, m. p.  $31\cdot5^{\circ}$ , has an odour of bleaching powder, is volatile with steam, and liberates iodine from potassium iodide.

When the imino-ether is dissolved in dilute sulphuric acid and sodium nitrite added, a product is obtained which gives a marked Liebermann reaction.

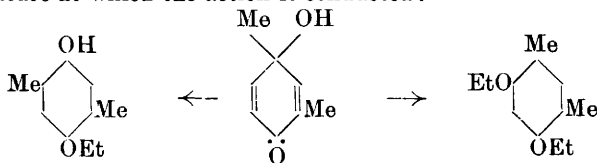
The presence of the imino-group in the imino-ether is also shown by the formation of a benzoyl derivative,  $\text{OEt}\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NBz}$ , which separates from alcohol or benzene in silky, colourless needles, m. p.  $79-80^{\circ}$ .

as-m-Dixylenol,  $\text{CH}\begin{smallmatrix} \text{CMe}\cdot\text{C(OH)} \\ \text{CMe}-\text{CH} \end{smallmatrix}\text{C}\equiv\text{C}\begin{smallmatrix} \text{C(OH)}\cdot\text{CMe} \\ \text{CH}-\text{CMe} \end{smallmatrix}\text{CH}$ , separates from dilute alcohol in needles, m. p.  $137\cdot5-138^{\circ}$  (compare Brun, *Inaug. Diss. Zürich*, 1902).

The action of methyl alcohol on as-m-xylylhydroxylamine in the presence of concentrated sulphuric acid is analogous to that of ethyl alcohol.

4-Imino-1:3-dimethylquinol 2-methyl ether,  $\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OMe}$ , is a yellow oil, b. p.  $94-95^{\circ}/13$  mm. The chloroimide forms glistening prisms, m. p.  $62\cdot5-63\cdot5^{\circ}$ . The imino-ether is readily hydrolysed by water with the formation of 1:3-dimethylquinol methyl ether (annexed formula), which forms colourless, glistening prisms, m. p.  $40-45^{\circ}$ . When its aqueous solution is shaken with p-nitrophenylhydrazine hydrochloride, p-nitrobenzeneazoxylene, m. p.  $128\cdot5-129\cdot5^{\circ}$ , is formed. A. McK.

**Action of Aliphatic Alcohols on 1:3-Dimethylquinol in the Presence of Concentrated Sulphuric Acid.** EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1907, 40, 1932-1949. Compare preceding abstracts).—When 1:3-dimethylquinol is acted on by ethyl alcohol in the presence of a little sulphuric acid, it is converted into a mixture of the acid ether of p-xylohydroquinone and the normal ether of m-xylorcinol, the proportions of which vary according to the temperature at which the action is conducted:



The constitution of these ethers was determined. The acid ether was hydrolysed by hydriodic acid to p-xylohydroquinone; it is also formed by ethylating the latter. The normal ether was hydrolysed to form m-xylorcinol; it is re-formed when the latter is ethylated.

The formation of these two ethers by the action of ethyl alcohol is a general one. Methyl, *n*-propyl, and *n*-butyl alcohols interact with xyloquinol in an analogous manner.

*p*-Xylohydroquinone monoethyl ether forms silky needles, m. p. 80.5—81.5°. Evidence for its constitution is also quoted in its formation from *p*-dimethyl-*p*-phenetidine, where the amino-group is replaced by the hydroxyl group in the usual manner.

*m*-Xylorcinol diethyl ether separates from alcohol in glistening needles, m. p. 75° and b. p. 132°/15 mm.

*m*-Xylorcinol dimethyl ether,  $C_{10}H_{14}O_2$ , forms colourless needles, glistening leaflets or plates, m. p. 76°. It is converted by hydriodic acid into methyl iodide and *m*-xylorcinol, and is re-formed by methylating the latter.

*p*-Xylohydroquinone monomethyl ether,  $C_9H_{12}O_2$ , separates from light petroleum in silky needles, m. p. 90°. Hydriodic acid converts it into *p*-xylohydroquinone. It may also be formed from dimethyl *p*-anisidine.

*m*-Xylorcinol dipropyl ether,  $C_{14}H_{22}O_2$ , separates from alcohol in silky needles, m. p. 33.5°. Hydriodic acid hydrolyses it to *m*-xylorcinol.

*p*-Xylohydroquinone monopropyl ether,  $C_{11}H_{16}O_2$ , separates from light petroleum in silky needles, m. p. 75°.

*p*-Xylohydroquinone mono-*n*-butyl ether has m. p. 40—45°. *m*-Xylorcinol di-*n*-butyl ether,  $C_{16}H_{26}O_2$ , separates from alcohol in leaflets, m. p. 42°. It is hydrolysed by hydriodic acid to *m*-xylorcinol.

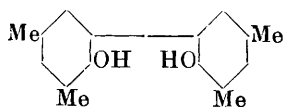
*m*-Xylorcinol monomethyl ether,  $OMe \cdot C \begin{smallmatrix} \diagup CH : C(OH) \\ \diagdown CMe - CH \end{smallmatrix} CMe$ , obtained by the action of sodium methoxide and methyl iodide on *m*-xylorcinol, separates from light petroleum in silky, felted needles, m. p. 78°.

A. McK.

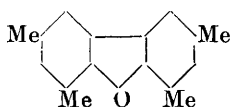
### Action of Alcoholic Sulphuric Acid on 1 : 3-Dimethylquinol.

EUGEN BAMBERGER and JOSEF BRUN (*Ber.*, 1907, 40, 1949—1955. Compare preceding abstracts).—Whilst 2 : 4-xyloquinol is converted by a little strong sulphuric acid at the ordinary temperature, mainly into *m*-xylorcinol diethyl ether, but in small amount into *p*-xylohydroquinone monoethylether together with traces of *p*-xylohydroquinone and *as*-*m*-xylenol, the action of more acid causes the formation of about the same amount of *p*-xylohydroquinone monoethyl ether, but no *m*-xylorcinol diethyl ether is obtained; the amount of *as*-*m*-xylenol and of *p*-xylohydrochinone formed increases, however, and other substances are obtained, namely, *p*-xylohydroquinone diethyl ether, an amorphous acid, probably  $C_{11}H_{12}O_2$ , and dixylenol (I).

That the two benzene nuclei are in the ortho-positions to the hydroxy-groups is shown by the behaviour of dixylenol when heated, when a substance,  $C_{16}H_{16}O$ , probably a tetramethylated dibenzofuran (II), is



(I.)



(II.)

obtained. *p*-Xylohydroquinone monoethyl ether has m. p. 80.5—81.5°.

Dixylenol separates from light

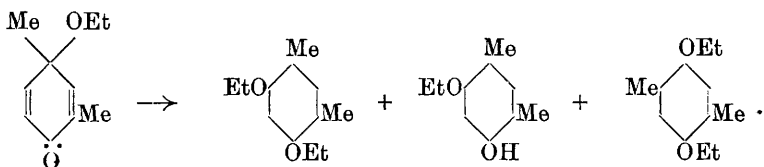
petroleum in rhombic plates or glistening needles, m. p. 137·5—138°. It gives an olive-green coloration with ferric chloride.

*Tetramethyldibenzofuran* separates from 90% alcohol in nacreous leaflets, m. p. 90—90·5°, and is insoluble in alkali.

*p*-Xylohydroquinone diethyl ether was identified by its odour of peppermint, its m. p. 106—107°, and by its conversion by hydriodic acid into *p*-xylohydroquinone.

A compound,  $C_{16}H_{16}O_4$ , of a quinone nature was also obtained, m. p. 297—298°. A. McK.

**Transformations of 2:4-Dimethylquinol Ethyl Ether.** EUGEN BAMBERGER (*Ber.*, 1907, 40, 1956—1958. Compare preceding abstracts).—2:4-Dimethylquinol ethyl ether, when left in contact with alcoholic sulphuric acid, is transformed into a mixture of *m*-xylorcinol diethyl ether, *m*-xylorcinol monoethyl ether, and *p*-xylohydroquinone diethyl ether, thus,



In this mixture, *m*-xylorcinol diethyl ether predominates.

A. McK.

**Unsaponifiable Matter in Chrysalidene Oil.** JULIUS LEWKOWITSCH (*Zeitsch. Nahr. Genussm.*, 1907, 13, 552).—Chrysalidene oil, the first fatty oil derived from insects (*ibid.*, 1906, 12, 659), was examined to see if, like all other fats and oils of animal origin, it contained cholesterol. The unsaponifiable matter from the oil, when heated with acetic anhydride, is separated into two constituents, cholesterol and a hydrocarbon, m. p. 54—62°

T. A. H.

**Phytosterol of the Soy Bean.** TIMOTHÉE KLOBB and ARMAND BLOCH (*Bull. Soc. chim.*, 1907, [iv], 1, 422—428).—The phytosterol obtained by Meissl and Böcker (*Abstr.*, 1883, 1024) has been prepared from yellow, black, and pale green varieties of Soy beans, *Glycine hispida*. It has the composition  $C_{26}H_{44}O, H_2O$ , m. p. 136°,  $[\alpha]_D - 32.03^\circ$  in chloroform, or  $-28.69^\circ$  in ether, and crystallises in warm alcohol in lamellæ. It gives the usual colour reactions of the phytosterols. The *benzoyl* derivative, m. p. 141—142°,  $[\alpha]_D - 13.77^\circ$  in chloroform, crystallises from boiling alcohol in rectangular lamellæ. The *acetate*, m. p. 130—131° when freshly prepared, or 125—126° on keeping, forms silky, hexagonal lamellæ from alcohol. Comparison of this phytosterol with the similar substances already known indicates that it is probably new, and the author proposes for it the name *sojasterol*.

T. A. H.

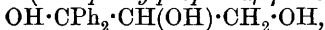
**Stereoisomeric  $\gamma$ -*p*-Methoxyphenyl- $\beta\gamma$ -propyleneglycols** [ $\gamma$ -*p*-Methoxyphenylpropane- $\beta\gamma$ -diols]. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 477—484).—The author has repeated the work of Varenne and Godefroy (*Abstr.*, 1905, i, 282) on the action of alcoholic potassium hydroxide on dibromoanethole, his results being quite different from those obtained by these authors. He has also succeeded in separating the two stereoisomeric glycols formed in the oxidation of anethole by mercuric acetate (*Abstr.*, 1902, i, 808), neither of these glycols being identical with the glycol described by Varenne and Godefroy (*loc. cit.*).

[With VINCENZO PAOLINI and G. DE CONNO.]—The action of alcoholic potassium hydroxide solutions of various concentrations on dibromoanethole, prepared according to Hell and Günther's directions (*Abstr.*, 1896, i, 20), does not yield  $\gamma$ -*p*-methoxyphenylpropane- $\beta\gamma$ -diol (Varenne and Godefroy, *loc. cit.*), but always gives anisyl ethyl ketone (Wallach and Pond, *Abstr.*, 1896, i, 94).

The  $\gamma$ -*p*-methoxyphenylpropane- $\beta\gamma$ -diol, m. p. 98°, obtained by the action of mercuric acetate on anethole (Balbiani, Paolini, and Nardacci, *Abstr.*, 1902 i, 808), consists of a mixture of two stereoisomerides: (1) the  $\beta$ -modification,  $C_{10}H_{14}O_3$ , which crystallises from 95% alcohol in aggregates of microscopic needles or from water in shining, superposed laminae, m. p. 114—115°, and (2) the  $\alpha$ -form, which crystallises from water with  $3H_2O$  in aggregates of shining laminae, m. p. 30—31° or, for the anhydrous compound, 62—63°; when heated, the  $\alpha$ -modification is partially transformed into the  $\beta$ -form. The  $\alpha$ -compound yields a diacetyl derivative,  $OMe \cdot C_6H_4 \cdot C_3H_5(OAc)_2$ , which is a viscous liquid, b. p. 203°/20 mm., dissolving in alcohol, and undergoing transformation into a mixture of the  $\alpha$ - and  $\beta$ -glycols on hydrolysis with sodium ethoxide. T. H. P.

***aa*-Diphenylglycerol.** CARL PAAL and KURT ZAHN (*Ber.*, 1907, 40, 1819—1821. Compare *Abstr.*, 1906, i, 400, 802).—The preparation of tri-, tetra-, and penta-hydric alcohols has been undertaken in extension of an investigation of diaryl substituted hexoses (*loc. cit.*), and that of *r-aa*-diphenylglycerol is described now.

*r-aa*-Diphenylglycerol (*aa*-diphenylpropan- $\alpha\beta\gamma$ -triol),

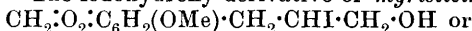


formed by the action of magnesium phenyl bromide on methyl *r*-glycerate, in a 42% yield, crystallises in colourless plates, m. p. 157—158°, and distils in small amounts almost unchanged. G. Y.

**Myristicin.** ENRICO RIMINI and F. OLIVARI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 663—665).—When myristicin and isomyristicin are treated in alcoholic solution with iodine and yellow mercuric oxide they yield the corresponding iodohydroxy-compounds. In the case of isomyristicin, however, the use of an excess of mercuric oxide determines the formation of a considerable quantity of an acetal, just as was found by Bougault with isosafrole (*Abstr.*, 1902, i, 452). These results confirm the conclusion previously arrived at (compare Rimini,

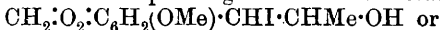
Abstr., 1905, i, 198) that myristicin contains an allyl and *isomyristicin* a propenyl side-chain.

The iodohydroxy-derivative of *myristicin*,

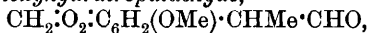


$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2(\text{OMe})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{I}$ , prepared by the action of iodine and yellow mercuric oxide on an alcoholic solution of myristicin, is a dense, colourless, highly refractive oil which decomposes on heating.

The corresponding derivative of *isomyristicin*,



$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{CHMeI}$ , prepared by the action of iodine (4 mols.) and yellow mercuric oxide (1 mol.) on *isomyristicin* (2 mols.), is obtained as an oily liquid. If the proportion of mercuric oxide used is doubled, this reaction yields *dioxymethylenemethoxyhydratropaldehyde*,



which is an oily liquid, b. p. 288—290°; its *semicarbazone*,  $\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}_3$ , crystallises from alcohol in white, mamillary masses, m. p. 140°; treatment of the aldehyde with benzenesulphhydroxyl-aminic acid gives a hydroxamic acid, which yields an intense reddish-violet coloration with ferric chloride and forms an insoluble bottle-green

*copper* compound,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2(\text{OMe})\cdot\text{CHMe}\cdot\text{C}\begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}\text{Cu}$ .

T. H. P.

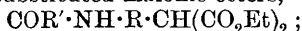
**Constitution of Myristicin and its Derivatives.** OSCAR RICHTER (*Ber. Deut. pharm. Ges.*, 1907, 17, 152—161).—An account is given of the views of Semmler (Abstr., 1890, 1150; 1892, 311) and of Thoms (Abstr., 1904, i, 47) as to the constitution of myristicin and its derivatives. The product obtained on reduction of *isomyristicin* by means of sodium and alcohol was considered by Thoms (*loc. cit.*) to be 5-methoxy-3-propylphenol, as the corresponding dimethoxypropylbenzene was found to be isomeric with dihydromethyleugenol. This is confirmed now by oxidation of the dimethoxypropylbenzene with potassium permanganate in alkaline solution, the product being identical with dimethyl-*a*-resorcylic acid (3:5-dimethoxybenzoic acid), m. p. 182° (175—176°: Tiemann and Streng, Abstr., 1882, 51), obtained by oxidation of orcinol dimethyl ether. A mixture of the oxidation product of the dimethoxypropylbenzene from *isomyristicin* with veratric acid, m. p. 181°, melted at 36°.

The action of bromine on 3:5-dimethoxypropylbenzene in glacial acetic acid at 0° leads to the formation of a *dibromo*-derivative, which on nitration yields a mixture of *bromonitro*- and *dinitro*-3-methoxy-5-propylbenzenes.

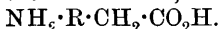
Dihydromyristicin forms a *dibromo*-derivative, from which the bromine can be removed by reduction with sodium and alcohol. Attempts to remove the bromine from the side-chain of dibromomyristicin dibromide led to results similar to those obtained by Höring with tribromo*isosa*frole dibromide (this vol., i, 411).

G. Y.

**Synthesis of Amino-Acids from Cyclic Imines.** JULIUS VON BRAUN (*Ber.*, 1907, 40, 1834—1846. Compare Abstr., 1906, i, 576; this vol., i, 151).—Cyclic imine bases are converted by Schotten's method (Abstr., 1883, 813; 1885, 176; 1886, 1104; Bunzel, Abstr., 1889, 904; Bamberger and Dieckmann, Abstr., 1893, i, 528) into amino-acids containing the same or a smaller number of carbon atoms in the nucleus. In this paper a method is described which leads to the formation of amino-acids having a number of carbon atoms in their molecules greater than is contained in the nuclei of the cyclic imine bases from which they are obtained. The new method consists in the conversion of the acylimines,  $R \cdot N \cdot COR'$ , by the action of phosphorus pentachloride into the chloro-amides,  $COR' \cdot NH \cdot R \cdot Cl$ , which are condensed with potassium cyanide or ethyl malonate, forming the nitriles,  $COR' \cdot NH \cdot R \cdot CN$ , or substituted malonic esters,



these on hydrolysis yield the amino-acids,  $NH_2 \cdot R \cdot CO_2H$  and



The series of reactions, which take place readily, leads to the formation of  $\epsilon$ - and  $\zeta$ -amino-acids from hexa-atomic, or of  $\delta$ - and  $\epsilon$ -amino-acids from penta-atomic, cyclic imines. The formation of  $\epsilon$ -leucine and  $\zeta$ -amino-*n*-heptic acid from piperidine and of *o*-aminophenylbutyric and *o*-aminophenylvaleric acids from tetrahydroquinoline is described.

Whilst on loss of water,  $\epsilon$ -leucine forms a small amount of the anhydride,  $CH_2 \cdot \left\langle \begin{smallmatrix} [CH_2]_4 \\ NH \end{smallmatrix} \right\rangle CO$ , together with much of the polymeric anhydride,  $(\cdot CO \cdot [CH_2]_5 \cdot NH \cdot)_x$ .  $\zeta$ -amino-*n*-heptic acid forms only the polymeric lactam,  $(\cdot NH \cdot [CH_2]_6 \cdot CO \cdot)_x$  (compare Gabriel and Maass, Abstr., 1889, i, 595; Manasse, Abstr., 1902, i, 351).

*o*-Aminophenylbutyric acid can be isolated only in the form of its salts with acids or bases, since on liberation it immediately loses water, yielding the lactam,  $C_6H_4 \cdot \left\langle \begin{smallmatrix} [CH_2]_3 \\ NH \end{smallmatrix} \right\rangle CO$ , termed *homohydrocarbostyryl*, which is hydrolysed by concentrated acids or alkalis (compare Fischer and Kuzel, Abstr., 1883, 1132). The conclusion is drawn that hepta-atomic rings are more capable of existence in the aromatic than in the aliphatic series.

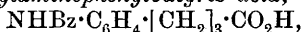
*Benzoyl- $\epsilon$ -amino-*n*-hexonitrile*,  $NHBz \cdot [CH_2]_5 \cdot CN$ , m. p.  $95^\circ$ , is hydrolysed by concentrated hydrochloric acid under pressure at  $160$ — $170^\circ$ . *Benzenesulphonyl- $\epsilon$ -leucine*,  $SO_2Ph \cdot NH \cdot [CH_2]_5 \cdot CO_2H$ , crystallises in long needles, sinters at  $120^\circ$ , m. p.  $122^\circ$ .

*Benzenesulphonyl- $\zeta$ -amino-*n*-heptic acid*,  $SO_2Ph \cdot NH \cdot [CH_2]_6 \cdot CO_2H$ , m. p.  $80^\circ$ , crystallises from hot water.

*Benzoyl- $o$ - $\gamma$ -iodo-*n*-propylanilide*,  $NHBz \cdot C_6H_4 \cdot C_3H_6I$ , formed by the action of sodium iodide on the chloro-compound in alcoholic solution, is obtained in white crystals, m. p.  $112$ — $113^\circ$ . *Benzoyl- $o$ -aminophenylvaleric acid*,  $NHBz \cdot C_6H_4 \cdot [CH_2]_4 \cdot CO_2H$ , forms white crystals, m. p.  $127^\circ$ .

*Benzoyl- $o$ -aminophenylbutyronitrile*,  $NHBz \cdot C_6H_4 \cdot [CH_2]_3 \cdot CN$ , crystallises in white needles, m. p.  $128^\circ$ , and is hydrolysed by fuming hydrochloric acid under pressure at  $125^\circ$ . *Homohydrocarbostyryl*, formed by heating the hydrochloride of  $\gamma$ -*o*-aminophenylbutyric acid

or on liberation of the butyric acid, crystallises in yellow needles, m. p. 139—140°. The *hydrochloride*, white needles, m. p. 201°, and *platinichloride*, m. p. 208°, of  $\gamma$ -*o*-aminophenylbutyric acid are described.  $\gamma$ -*o*-Benzoylamino-phenylbutyric acid,



forms white crystals, m. p. 156°. *Ethyl*  $\gamma$ -*o*-aminophenylbutyric acid,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_6 \cdot \text{CO}_2\text{Et}$ , is obtained as a colourless, viscid oil, b. p. 191°/10 mm., and forms a syrupy *hydrochloride*, a readily soluble *platinichloride*, and a *benzoyl* derivative,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_6 \cdot \text{CO}_2\text{Et}$ , crystallising in white leaflets, m. p. 97°. G. Y.

**Arylthioglycollic [Arylthiolacetic] Acids.** PAUL FRIEDLÄNDER and A. CHWALA [and, in part, Z. SLUBEK] (*Monatsh*, 1907, 28, 247—280. Compare Friedländer and Mauthner, *Abstr.*, 1905, i, 102; Friedländer, *Abstr.*, 1906, i, 378; this vol., i, 334).—Thiolacetic acid (Holmberg, *Abstr.*, 1905, i, 323; Klason and Carlson, *Abstr.*, 1906, i, 232) is obtained in almost quantitative yields by adding a concentrated solution of sodium chloroacetate to a hot concentrated solution of sodium disulphide prepared by addition of flowers of sulphur to fused commercial sodium sulphide, and reduction of the resulting dithioglycollic acid with zinc dust and dilute sulphuric acid. In aqueous solution, thiolacetic acid reacts quantitatively with diazo-salts, forming stable arylazothiolic acids,  $\text{N}_2\text{R} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which detonate feebly when heated in the dry state, and when heated with water or indifferent solvents lose nitrogen and form arylthiolacetic acids,  $\text{SR} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , the yields being almost quantitative, especially if the aryl nucleus contains negative groups such as hydroxyl or carboxyl. Nitro- and dinitro-phenylthiolacetic acids are formed by the action of *o*- and *p*-chloronitrobenzene and *l*-chloro-2 : 4-dinitrobenzene on thiolacetic acid in presence of potassium hydroxide; on reduction with tin and hydrochloric acid the *o*-nitro-phenylthiolacetic acids yield 3-keto-3 : 4-dihydro-1 : 4-benzothiazines,  $\text{C}_6\text{H}_3\text{R}' \begin{smallmatrix} < \text{NH} \cdot \text{CO} \\ \text{S} - \text{CH}_2 \end{smallmatrix}$  (compare Hofmann, *Abstr.*, 1880, 389).

Diazobenzene chloride reacts with thioacetic acid in aqueous solution forming *diazobenzene thioacetate*, which is obtained as an unstable, colourless oil. Thioacetates of substituted diazobenzenes are mostly crystalline; the diazo-thioacetates derived from *p*-nitro- and *p*-bromo-aniline, which are slightly more stable, are described.

*p*-Nitrodiazobenzene thioacetate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{S} \cdot \text{COMe}$ , crystallises from a mixture of chloroform and light petroleum in yellow needles, detonates when heated, decomposes slowly at the ordinary temperature, more quickly in solution, and does not couple with  $\beta$ -naphthol in alkaline solution. When heated in alcoholic solution, it yields nitrobenzene, sulphur, and gives an odour of aldehyde; the action of iodine in alcoholic solution leads to the formation of nitro- and *p*-iodonitrobenzene. When heated with anhydrous thioacetic acid, the nitrodiazothioacetate yields *as-diacetyl-p-nitrophenylhydrazide* and small amounts of *p*-nitroacetanilide; if the thioacetic acid is evaporated, triacetyl-*p*-nitrophenylhydrazide, or if moisture is present, *s*-acetyl-*p*-nitrophenylhydrazide, is formed.

*as-Diacetyl-p-nitrophenylhydrazide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NAc}_2$ , crystallises

in yellow needles, m. p.  $181.5^{\circ}$ , is soluble in aqueous sodium hydroxide or carbonate, less so in ammonia, is reprecipitated unchanged by acids, yields *p*-phenylenediamine on reduction with tin and hydrochloric acid, and when boiled with concentrated hydrochloric acid forms *p*-nitrophenylhydrazine hydrochloride.

*p*-Bromodiazobenzene thioacetate,  $C_6H_4Br \cdot N_2 \cdot S \cdot COMe$ , crystallises in yellow needles, closely resembles the *p*-nitro-compound, and yields *p*-bromiodobenzene when treated with alcoholic iodine or *s*-acetyl-*p*-bromophenylhydrazine with thioacetic acid.

*p*-Tolylazothioliacetic acid,  $C_6H_4Me \cdot N_2 \cdot S \cdot CH_2 \cdot CO_2H$ , crystallises in long, yellow needles, is decomposed by acids, and forms a stable sodium salt.

*p*-Nitrophenylazothioliacetic acid,  $C_6H_4O_4NS$ , crystallises in small, yellow needles; the sodium salt forms brownish-yellow leaflets.

*p*-Carboxybenzeneazothioliacetic acid, from *p*-aminobenzoic acid, crystallises in yellow needles, m. p.  $153^{\circ}$  (decomp.).

The azothioliacetic acid derived from  $\beta$ -naphthylamine forms a sparingly soluble sodium salt; the acid derived from  $\alpha$ -aminoanthraquinone crystallises in colourless needles.

The following arylthioliacetic acids,  $SR \cdot CH_2 \cdot CO_2H$ , are described; the temperatures are melting points.

$R = C_6H_4Me(o)$ : flat needles,  $108-109^{\circ}$ , on oxidation with potassium permanganate in neutral solution yields *o*-toluenesulphoneacetic acid,  $C_7H_7 \cdot SO_2 \cdot CH_2 \cdot CO_2H$ , colourless crystals,  $107^{\circ}$ ; silver salt,  $C_9H_9O_4Ag$ , stable, colourless needles.  $R = C_6H_4Me(p)$ : colourless leaflets,  $95^{\circ}$ , when fused with sodium hydroxide yields *p*-thiocresol.  $R = C_6H_4 \cdot NO_2(o)$ : light yellow needles,  $162-164^{\circ}$ , yields benzothiazole when heated with aqueous sodium hydroxide.  $R = C_6H_4 \cdot OH(o)$ : brown oil, soluble in water, forms crystalline salts; the barium salt was analysed.  $R = C_6H_4Cl(o)$ : formed from *o*-aminophenylthioliacetic acid by Sandmeyer's reaction, colourless needles,  $112^{\circ}$ .  $R = C_6H_4Cl(m)$ : colourless needles,  $81-82^{\circ}$ .  $R = C_6H_4Cl(p)$ : colourless needles,  $105^{\circ}$ .  $R = C_6H_4Br(p)$ : yellow leaflets,  $107^{\circ}$ .  $R = C_6H_4 \cdot NO_2(p)$ : from the corresponding azothioliacetic acid, or together with *pp'*-dichloroazoxybenzene from *p*-chloronitrobenzene, yellow needles,  $156-158^{\circ}$ ; the methyl ester crystallises in stout yellow plates,  $50-51^{\circ}$ ; the ethyl ester, yellow needles,  $46-47^{\circ}$ .  $R = C_6H_4 \cdot NH_2(p)$ : by reduction of the *p*-nitro-acid, colourless needles,  $196-197^{\circ}$  (decomp.).  $R = C_6H_3(NO_2)_2(op)$ : yellow needles,  $167-168^{\circ}$ ; the methyl ester, compact needles,  $93-94^{\circ}$ .  $R = C_6H_4 \cdot CO_2H(p)$ :  $267-269^{\circ}$  (decomp.), forms soluble alkali salts; the dimethyl ester,  $C_{11}H_{12}O_4S$ , colourless needles,  $63-64^{\circ}$ ; the diethyl ester, white needles,  $98^{\circ}$ .

The following 3-keto-3:4-dihydro-1:4-benzothiazines are described.

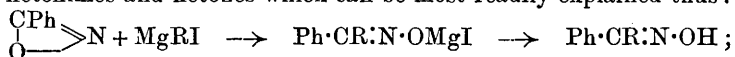
$R' = 6$ -amino-: formed by reduction of 2:4-dinitrophenylthioliacetic acid, colourless needles, m. p.  $222-224^{\circ}$ , becomes brown when moist, forms soluble salts, and reduces platinum chloride in hydrochloric acid solution; the acetyl derivative, long needles, m. p.  $257^{\circ}$ .  $R' = 6$ -chloro-: formed from the 6-amino-compound by Sandmeyer's reaction, colourless needles, m. p.  $205^{\circ}$ , is converted by concentrated aqueous sodium hydroxide into 4-chloro-2-aminophenylthioliacetic acid. G. Y.



**Nitrile Oxides.** HEINRICH WIELAND (*Ber.*, 1907, **40**, 1667—1676).—Benzonitrile oxide, prepared according to Werner's method from benzhydroxamic chloride and sodium hydroxide (*Abstr.*, 1894, **i**, 585), is a solid, m. p. 15°. Its polymerisation into glyoxime peroxide takes place in one hour at the ordinary temperature; the change is hastened by alkali. This change has also been traced in an aqueous solution by determining the molecular weight at intervals by the freezing point method. The velocity of the reaction is dependent on the concentration and also on the nature of the solvent employed.

Of the two possible formulæ for this compound,  $\text{Ph}\cdot\text{C}:\text{N}:\text{O}$  and  $\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{N} \\ \diagup \\ \text{O} \end{smallmatrix}$ , the second is considered to be the more probable, for the following reasons. No additive compounds of the nature of amidoximes,  $\cdot\text{C}:(\text{NOH})\cdot\text{NHR}$ ,

could be obtained, as ammonia, aniline, or phenylhydrazine are without action; the system  $\text{C}:\text{N}:\text{O}$  would be expected to be unsaturated. Bromine, iodine, hydrogen chloride, or phosphorus pentachloride do not react with the compound in the cold. It is quantitatively reduced by zinc dust to benzonitrile, and magnesium alkyl compounds give rise to ketoximes and ketones which can be most readily explained thus:



magnesium methyl iodide gave acetophenone and acetophenoneoxime, magnesium ethyl iodide gave propiophenone and propiophenoneoxime and magnesium phenyl bromide, benzophenoneoxime, and an alkali soluble substance.

[With HUGO BAUER.]—Benzhydroxamic chloride decomposes spontaneously in a closed tube at 25—30° in the course of fourteen days into hydrogen chloride and dibenzenyloxoazoxime (Wieland and Bauer, *Abstr.*, 1906, **i**, 412); no trace of glyoxime peroxide could be detected. This forms a good method for the preparation of the oxoazoxime. In contradistinction to the peroxide, it is basic, uniting with hydrogen chloride in the absence of water to form a *dihydrochloride*,  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\cdot 2\text{HCl}$ , m. p. 161° (decomp.); the hydrogen chloride is not lost in a vacuum. An oxonium salt is also obtained from hydroferriicyanic acid. The interaction of phosphorus pentachloride and dibenzenyloxoazoxime, forming dibenzenyl-azoxime (*loc. cit.*), serves to show that the compound does not contain the six-membered ring,  $\text{C}\begin{smallmatrix} \text{N}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{N} \end{smallmatrix} \text{C}$ , but possesses the

complex  $\text{O}\begin{smallmatrix} \text{N}-\text{C} \\ | \quad \diagup \\ \text{C}\cdot\text{O} \end{smallmatrix} \text{N}$ . Fission of the ring readily occurs with alkali in the cold, the products are benzoic acid and benzonitrile, the latter probably from benzhydroxyamidoxime.

The author has not been successful in isolating other nitrile oxides. Ethyl chloro-oximino-acetate gave a quantitative yield of ethyl glyoxime peroxide dicarboxylate; an odour of nitrile oxide was, however, observed. Acethydroxamic chloride (this vol., **i**, 492) yielded a closely related acid, probably the compound,  $\text{OH}\cdot\text{CMe}:\text{NO}\cdot\text{CMe}:\text{NOH}$ .

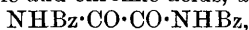
W. R.

**Termolecular Benzoyl Cyanide.** OTTO DIELS and HUGO STEIN (*Ber.*, 1907, 40, 1655—1667. Compare Nef, *Abstr.*, 1896, i, 71).—Termolecular benzoyl cyanide,  $(\text{BzCN})_3$ , cannot be regarded as a cyanuric acid derivative (compare Nef, *loc. cit.*) for the following reasons. Only one carboxyl group has a ketonic function, since only a *monophenylhydrazone*, m. p.  $226^\circ$ , crystallising in colourless needles, can be obtained. Sodium methoxide eliminates one benzoyl group, giving a *substance* having the composition  $(\text{COPh}\cdot\text{CN})_2\cdot\text{HCN}$  (I), which sinters at  $350^\circ$ , has m. p.  $365^\circ$  (decomp.), cannot be acylated or etherified, is not attacked by nitrous acid, and forms a colourless *sodium salt*,  $\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_3\text{Na}$ . Phosphoric acid at  $180^\circ$  converts (I) into a *substance*,  $\text{COPh}\cdot\text{CN}\cdot 2\text{HCN}\cdot\text{H}_2\text{O}$ , (II), which crystallises in colourless leaflets, darkens at  $220^\circ$ , decomposes at  $265^\circ$ , and possesses both acid and basic properties, the latter being the more pronounced.

The yellow termolecular benzoyl cyanide, by solution in boiling glacial acetic acid or by the addition of concentrated hydrochloric acid to its solution in methyl ethyl ketone, is converted into a colourless *hydrate*,  $3\text{BzCN}\cdot\text{H}_2\text{O}$ , (III), m. p.  $185$ — $186^\circ$ , which does not react with phenylhydrazine, phenylcarbimide, or acetic anhydride, and which forms a yellow *ammonium salt*,  $\text{C}_{24}\text{H}_{20}\text{O}_4\text{N}_4$ . By heating termolecular benzoyl cyanide with acetic anhydride and zinc chloride for thirty minutes, the *compound*,  $\text{BzCN}\cdot 2\text{HCN}\cdot\text{MeCO}_2\text{H}$ , (IV), is obtained in colourless needles, m. p.  $226^\circ$  (decomp.), sintering at  $215^\circ$ . By shorter heating with the same reagents, termolecular benzoyl cyanide yields the *substance*,  $\text{BzCN}\cdot 2\text{AcCN}\cdot\text{MeCO}_2\text{H}$ , (V), m. p.  $153^\circ$ , sintering at  $148^\circ$ .

When (III) is treated with sodium methoxide, the *compound*,  $2\text{BzCN}\cdot\text{HCN}\cdot\text{H}_2\text{O}$ , (VI), m. p.  $208$ — $210^\circ$ , is obtained, which forms a *sodium salt*,  $2\text{BzCN}\cdot\text{HCN}\cdot\text{NaOH}$ , (VII), and is converted by boiling dilute sodium hydroxide into (I). Acetic anhydride and zinc chloride change (VI) into (IV); hence the two benzoyl groups in (III), which are eliminated by acetylation, are not similarly situated, since only one is displaced by the action of sodium methoxide.

When (VI) is treated in glacial acetic acid with nitrous fumes, or is oxidised by boiling acetic and chromic acids, *dibenzoyloxamide*,

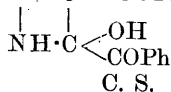


m. p.  $214$ — $215^\circ$ , is obtained, identical with the substance prepared from ethyl oxalate and sodium benzamide. This reaction shows that in termolecular benzoyl cyanide two benzoyl groups attached to nitrogen are separated by the group C·C. The third carboxyl group of ketonic character is attached to carbon. The authors propose the

formula (VIII) 
$$\begin{array}{c} \text{COPh}\cdot\text{N}:\text{C}:\text{C}:\text{N}\cdot\text{COPh} \\ \text{N}:\text{C}\cdot\text{COPh} \end{array}$$
 for termolecular benzoyl cyanide.

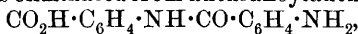
The absence of colour in the hydrate (III) is due to the saturation of 
$$\text{COPh}\cdot\text{N}:\text{C}:\text{C}:\text{N}\cdot\text{COPh}$$

the double linking in the ring; formula (IX),

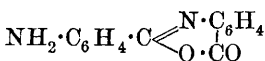


**Bimolecular Anhydrides of Anthranilic Acid.** GEORG SCHROETER (*Ber.*, 1907, 40, 1610—1621).—The author has already shown (*Abstr.*, 1906, i, 415) that benzenesulphonylsulphanilic acid and benzenesulphonylnaphthionic acid respectively couple with diazotised *p*-nitroaniline to form azo-dyes, whilst diazo-salts are formed from other aromatic amines. This result led the author to test the behaviour of benzenesulphonylaminobenzoic acids in the same direction. Benzenesulphonylanthranilic acid was accordingly prepared by the action of benzenesulphonyl chloride on an alkaline solution of anthranilic acid; as a by-product, a substance was obtained which was insoluble in alkali and which investigation showed to be a bimolecular anhydride of benzenesulphonylanthranilic acid with the formula  $C_6H_4 \begin{smallmatrix} \swarrow N(SO_2Ph) \cdot CO \\ \searrow CO \cdot N(SO_2Ph) \end{smallmatrix} C_6H_4$ .

The compound is analogous to Anschütz's tetrasalicylide. The fundamental type of the bimolecular anhydride described is the hitherto unknown bimolecular anhydride,  $C_6H_4 \begin{smallmatrix} \swarrow NH \cdot CO \\ \searrow CO \cdot NH \end{smallmatrix} C_6H_4$ , which the author designates as dianthranilide. Attempts to prepare this are described. Water was eliminated from anthranoylanthranilic acid,



when a yellow anhydride was obtained, which is either the desired anhydride or anthranoylanthranil,  $NH_2 \cdot C_6H_4 \cdot CO \cdot N \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow CO \end{smallmatrix}$  or



*Benzenesulphonylanthranilic acid* separates from 70% alcohol in needles, m. p. 223°.

*p*-Benzenesulphonylaminobenzoic acid, obtained by the action of benzenesulphonyl chloride on *p*-aminobenzoic acid, separates from 60% alcohol in silvery leaflets, m. p. 212°.

*Dibenzesulphonyldianthranilide* separates from glacial acetic acid in needles, m. p. 264°. Determinations of its molecular weight by the cryoscopic method in phenol solution gave values agreeing with the formula  $C_{26}H_{18}O_6N_2S_2$ . When boiled with strong aqueous sodium hydroxide, it dissolves, and on acidification, benzenesulphonylanthranilic acid is precipitated. Derivatives of this acid are already described by Ullmann, Franke, and others.

*Benzenesulphonylanthranilic chloride*,  $C_6H_4 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot COCl$ , obtained by the action of phosphorus pentachloride on the acid, separates from benzene in crystals, which seem to be stable on exposure to air and which have m. p. 155°. The corresponding *amide* has m. p. 166—167°, and the *ethyl* ester has m. p. 92—93°. When the chloride is dissolved in pyridine, dibenzesulphonyldianthranilide separates.

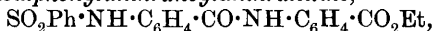
*Ethyl o-nitrobenzoylanthranilate*,  $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO_2Et$ , obtained from *o*-nitrobenzoyl chloride and ethyl anthranilate in benzene solution, separates from alcohol in glistening, yellow prisms, m. p. 132°. When reduced by stannous chloride, it forms *ethyl anthranoylanthranilate*,  $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO_2Et$ , which separ-

ates from alcohol in yellow prisms, m. p. 105—106°. The analogous methyl ester has m. p. 115° (H. Meyer gives 118—119°), and its *hydrochloride* has m. p. 175—180°. When warmed with aqueous sodium hydroxide it forms *anthranoylanthranilic acid*, m. p. 203°.

When the latter acid is moistened with benzene and thionyl chloride added, *anthranoylanthranilic anhydride hydrochloride*,  $C_{14}H_{11}O_2N_2Cl$ , is formed, which, by the action of water or sodium hydroxide, is converted into the *compound*,  $C_{14}H_{10}O_2N_2$ ; the latter forms canary-yellow needles, and has m. p. 162°.

*Benzenesulphonylanthranoylanthranilic anhydride*, obtained by the action of benzenesulphonyl chloride on the yellow anhydride, separates from alcohol or benzene in white needles, m. p. 214—215°.

*Ethyl benzenesulphonylanthranoylanthranilate*,



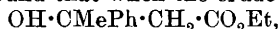
obtained from ethyl anthranilate and benzenesulphonylanthranilic chloride, separates from alcohol in needles, m. p. 132°. The corresponding *acid* has m. p. 222°, and when acted on by thionyl chloride, forms benzenesulphonylanthranoylanthranilic anhydride.

A. MCK.

**$\beta$ -Alkylcinnamic Acids. II.** GEORG SCHROETER [and, in part, HANS KESSELER, CARL OTTO LEVERKUS, and FRIEDRICH WÜLFING] (*Ber.*, 1907, 40, 1589—1604. Compare *Abstr.*, 1904, i, 415).—The method, previously used by the author for forming  $\beta$ -methylcinnamic acid from acetophenone and ethyl iodoacetate, is now found to be a general one for the preparation of  $\beta$ -alkylcinnamic acids. *p*-Methylacetophenone, propiophenone, butyrophenone, *isovalerophenone*, and phenyl amyl ketone respectively interact with ethyl iodoacetate and magnesium in benzene solution according to the equation:  $Ar \cdot CO \cdot R + MgI \cdot CH_2 \cdot CO_2Et \rightarrow Ar \cdot CR \cdot (OMgI) \cdot CH_2 \cdot CO_2Et$ . The  $\beta$ -arylalkylhydracrylic acids,  $Ar \cdot CR(OH) \cdot CH_2 \cdot CO_2H$ , obtained by decomposing the magnesium compound with water and then saponifying the ester, lose water with varying ease to form  $\beta$ -alkylcinnamic acids,



It was sometimes found that when the crude ester,



was distilled, the elimination of water was not complete and an *acid*,  $C_{20}H_{22}O_5$ , was obtained, which separated from light petroleum in crystals, m. p. 62°; since this acid decolorised bromine and permanganate, it may be a molecular compound of  $\beta$ -phenylmethylhydracrylic acid and  $\beta$ -methylcinnamic acid. Generally, however, the elimination of water from  $\beta$ -phenylmethylhydracrylic acid proceeds in the normal manner with the formation of  $\beta$ -methylcinnamic acid, whilst  $\beta$ -methylstyrene and acetophenone are formed as by-products.

*Methyl  $\beta$ -methylcinnamate* has m. p. 28° and b. p. 152°/26 mm.; the *ethyl ester* has b. p. 162—163°/27 mm.

*$\beta$ -Methylcinnamic acid dibromide*,  $CMePhBr \cdot CHBr \cdot CO_2H$ , obtained by the action of bromine on  $\beta$ -methylcinnamic acid, has m. p. 128° (decomp.). The *methyl ester dibromide*,  $CMePhBr \cdot CHBr \cdot CO_2Me$ , separates from light petroleum in prisms, m. p. 78—79°.

*p*-Nitro- $\beta$ -methylcinnamic acid,  $NO_2 \cdot C_6H_4 \cdot CMe : CH \cdot CO_2H$ , obtained

by nitrating  $\beta$ -methylcinnamic acid; forms yellow needles, m. p. 168—169°. When heated with dilute nitric acid in a sealed tube at 160°, it forms *p*-nitrobenzoic acid.

*Ethyl p-nitro- $\beta$ -methylcinnamate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ , obtained by the nitration of ethyl  $\beta$ -methylcinnamate, has m. p. 74°. *Methyl p-nitro- $\beta$ -methylcinnamate* has m. p. 121—122°. When *p*-nitro- $\beta$ -methylcinnamic acid is reduced by ammonium sulphide it forms *p-amino- $\beta$ -methylcinnamic acid*,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ , m. p. 124—125° (decomp.).

$\beta$ -Phenylbutyric acid,  $\text{CHMePh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is obtained in a 98% yield by reducing  $\beta$ -methylcinnamic acid in aqueous alcoholic solution with 3% sodium amalgam; it has b. p. 168—169°/14 mm. and m. p. 39—40° (Kohler gives 47°). Its *methyl ester* has b. p. 133—134°/22 mm.

*p-Nitro- $\beta$ -phenylbutyric acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained by nitrating the preceding acid, has m. p. 164°, and forms *p*-nitrobenzoic acid when oxidised by dilute nitric acid. Its *methyl ester* has m. p. 63—64°. *p-Amino- $\beta$ -phenylbutyric acid*, obtained by reducing the nitro-acid with ammonium sulphide, has m. p. 176°.

*o-p-Dinitro- $\beta$ -phenylbutyric acid*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained by nitrating the mononitro-acid with fuming nitric acid, forms glistening, yellow crystals, m. p. 139—140°. Its *methyl ester* has m. p. 61°. When the dinitro-acid is reduced by ammonium sulphide, a compound,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ , m. p. 177°, is formed.

*p- $\beta$ -Dimethylcinnamic acid*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , obtained from *p*-tolyl methyl ketone, ethyl iodoacetate, magnesium, and benzene, separates from carbon disulphide or light petroleum in rhombic prisms, m. p. 135° (Tiffeneau gives 136°). Its *methyl ester* has m. p. 46°.

*$\beta$ -Phenyl- $\beta$ -ethylhydracrylic acid*,  $\text{OH} \cdot \text{CEtPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained from propiophenone, separates from benzene in needles, m. p. 122—123°. When acted on by concentrated sulphuric acid, it forms  $\beta$ -ethylcinnamic acid,  $\text{CEtPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , which separates from light petroleum in glistening, rhombic plates, m. p. 95° and b. p. 172°/15 mm. Its *sodium salt* separates from acetone in glistening leaflets. Its *methyl ester* has b. p. 148°/22 mm. Its *dibromide* has m. p. 124—125° (decomp.). Its *mononitro-derivative*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CEt} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ ,

separates from benzene in leaflets, m. p. 155°.

*$\beta$ -n-Propylcinnamic acid*,  $\text{OH} \cdot \text{CPr}^a \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , obtained from butyrophenone, has b. p. 183—184°/14 mm. and separates from light petroleum in transparent prisms, m. p. 94°.

*$\beta$ -Phenyl- $\beta$ -isobutylhydracrylic acid*,

$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CPh}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained from isovalerophenone, has m. p. 128—129° and contains  $1\text{H}_2\text{O}$ .  *$\beta$ -isoButylcinnamic acid*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , separates from aqueous alcohol in white crystals, m. p. 86°.

*$\beta$ -n-Amylcinnamic acid*,  $\text{C}_5\text{H}_{11} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ ,  $\text{H}_2\text{O}$ , obtained from phenyl amyl ketone, separates from light petroleum, carbon disulphide, or dilute alcohol in long needles, m. p. 79—80·5°.

*Phenyl amyl ketone*,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_5\text{H}_{11}$ , obtained from hexoyl chloride, benzene, and aluminium chloride, has b. p. 132—134°/14 mm. and m. p. 27°. Its *semicarbazone* has m. p. 132°. A. McK.

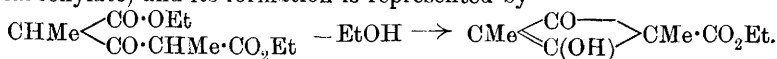
**Abietic Acid.** FRANZ KORITSCHONER (*Zeitsch. angew. Chem.*, 1907, 20, 641—645. Compare Fahrion, this vol., i, 329).—This investigation was carried out in order to decide whether abietic acid should be represented by the formula  $C_{20}H_{30}O_2$  or  $C_{19}H_{28}O_2$ , and, further, whether the acid contains one carboxyl group or two hydroxyl groups. The electrical conductivity of an aqueous solution of the acid was determined, very small quantities of  $N/10$  sodium hydroxide were then added successively, and the conductivity measured after each addition of the alkali. By plotting these conductivity values against the quantities of alkali added, a curve is obtained which shows a decided break. Since weak carboxylic acids, such as benzoic acid, give exactly similar curves, whereas phenols such as resorcinol give rounded curves without any break, it is evident that abietic acid is a carboxylic acid. That  $C_{20}H_{30}O_2$  and not  $C_{19}H_{28}O_2$  is the formula for this acid follows from the fact that the break in the abietic acid curve occurs at that point when the quantity of alkali added should be sufficient to completely neutralise the acid present, assuming the acid to possess the formula  $C_{20}H_{30}O_2$ . W. H. G.

**Hydroxybenzoates.** WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1907, 144, 756—757).—With the object of determining whether *p*-hydroxybenzoic acid could be transformed into salicylic acid, the author has studied the action of heat on barium *p*-hydroxybenzoate. The latter is not changed by prolonged heating at any temperature below  $280^\circ$ . Barium *p*-hydroxybenzoate, when heated at  $280$ — $281^\circ$ , evolves carbon dioxide, probably owing to interaction with its water of crystallisation, thus:  $(OH \cdot C_6H_4 \cdot CO_2)_2Ba + 2H_2O = BaCO_3 + 2C_6H_5 \cdot OH + CO_2 + H_2O$ . The residue consists of a brown mass with a phenolic odour. It dissolves partially in cold water to a clear rose, in hot water to a hyacinth-red, in ammonia or potash to a clear red, in hydrochloric or acetic acid to a deep yellow, in dilute nitric acid to a brown, and in sulphuric acid to a clear red, solution. Neither benzoquinone nor diphenylene oxide are formed. If dry barium *p*-hydroxybenzoate is heated, the basic salt,  $C_6H_4 \begin{smallmatrix} O \\ \diagup \diagdown \\ CO_2 \end{smallmatrix} Ba$ , and phenol are formed with evolution of carbon dioxide. If by  $\alpha$  is signified the amount of hydroxybenzoate dissolved by 10 c.c. of a solvent in one hour, then for barium *p*-hydroxybenzoate in water,  $\alpha_{18^\circ} = 1.4$  gram; in methyl alcohol,  $\alpha_{16.2^\circ} = 0.37$  gram; in ethyl alcohol (95%),  $\alpha_{19.5^\circ} = 0.27$  gram.

Under similar conditions, calcium *p*-hydroxybenzoate commences to evolve carbon dioxide at  $245$ — $246^\circ$ . For this salt in water,  $\alpha_{20^\circ} = 1.09$  gram; in ethyl alcohol (95%),  $\alpha_{18^\circ} = 1.13$  gram. It combines with methyl alcohol at the ordinary temperature. Barium salicylate begins to evolve carbon dioxide at  $250$ — $251^\circ$ ; in water,  $\alpha_{18^\circ} = 0.28$  gram; in methyl alcohol,  $\alpha_{18^\circ} = 0.18$  gram; in ethyl alcohol,  $\alpha_{16.5^\circ} = 0.1333$  gram. Sodium salicylate first evolves carbon dioxide at  $260$ — $261^\circ$ . E. H.

**Formation of a Tetramethylene Ring by Condensation of *s*-Ethyl Dimethylacetonedicarboxylate.** GEORG SCHROETER and C. STASSEN (*Ber.*, 1907, 40, 1604—1610).—The authors find that *s*-ethyl dimethylacetonedicarboxylate, when dissolved in concentrated

sulphuric acid, forms, after twenty hours at the ordinary temperature, the acid,  $C_9H_{12}O_4$ . The latter is probably ethyl 1:3-dimethylcyclobutene-4-ol-2-one-1-carboxylate (ethyl *aci*-dimethyldiketocyclobutane-carboxylate) and its formation is represented by



It separates from dilute alcohol in colourless needles, m. p. 133—135°. It is a monobasic acid, and may be titrated sharply with sodium hydroxide, using phenolphthalein as indicator. Determinations of the molecular weight by the cryoscopic method in phenol and glacial acetic acid solutions respectively gave values corresponding with the formula  $C_9H_{12}O_4$ . Its sodium salt is a colourless powder. The acid itself is somewhat unstable, and after a time is transformed into an oil. The acid decolorises alkaline permanganate at once and also decolorises a solution of bromine in chloroform. It combines, although not with ease, with phenylhydrazine, hydroxylamine, and semicarbazide respectively. When boiled with aqueous barium hydroxide, it loses carbon dioxide, and is converted into 1:3-dimethylcyclobutene-4-ol-2-one (*aci*-2:4-diketo-1:3-dimethylcyclobutane), thus:

$$CMe \begin{array}{c} \text{CO} \\ \text{C(OH)} \end{array} CMe \cdot CO_2Et \rightarrow CMe \begin{array}{c} \text{CO} \\ \text{C(OH)} \end{array} CHMe, \text{ which separates from benzene in crystals, m. p. } 135^\circ, \text{ and is a monobasic acid.}$$

When the sodium salt of the acid,  $C_9H_{12}O_4$ , is boiled with an ethyl-alcoholic solution of methyl iodide for three hours, it is converted into ethyl trimethylacetonedicarboxylate,  $CO_2Et \cdot CHMe \cdot CO \cdot CMe_2 \cdot CO_2Et$ , which boils at 132—133°/12 mm. It does not give a violet coloration with ferric chloride, and is not condensed by concentrated sulphuric acid. A. McK.

**4-Hydroxydeoxybenzoin-3-carboxylic Acid.** FRITZ GLASSNER (*Monatsh.*, 1907, 28, 281—295. Compare Weisl, *Abstr.*, 1905, i, 904).—Attempts to condense phenylacetic acid with the three hydroxybenzoic acids or phenylacetyl chloride with *o*- and *m*-hydroxybenzoic acids in presence of aluminium chloride were unsuccessful. The action of phenylacetyl chloride on salicylic acid in nitrobenzene solution at 70° leads to the formation of an *acyl* compound which will be described later, but in presence of aluminium chloride to the formation of 4-hydroxydeoxybenzoin-3-carboxylic acid,  $CH_2Ph \cdot CO \cdot C_6H_3(OH) \cdot CO_2H$ . This crystallises from dilute alcohol in colourless, rectangular plates, m. p. 224°, gives a cherry-red coloration with alcoholic ferric chloride, and yields carbon dioxide and *p*-hydroxydeoxybenzoin when heated with water at 180—200°, or toluene and 4-hydroxyisophthalic acid when heated with 70% potassium hydroxide at 170—200°. The sodium ( $\frac{1}{2}H_2O$ ) and silver salts of the keto-acid are described; the acetyl derivative,  $C_{17}H_{14}O_5$ , crystallises in needles, m. p. 140°, and is hydrolysed by boiling water; the oxime,  $C_{15}H_{13}O_4N$ , m. p. 170°, gives a dark blue coloration with alcoholic ferric chloride, and is partially hydrolysed by boiling water, forming the keto-acid. The action of 7·5 atoms of bromine on 1 mol. of the keto-acid in glacial acetic acid solution leads to the formation of dibromo-4-hydroxydeoxybenzoin,

$$CH_2Ph \cdot CO \cdot C_6H_2Br_2 \cdot OH, H_2O,$$

which crystallises in monoclinic prisms [ $a : b : c = 1.6772 : 1 : 1.3627$ ;  $\beta = 97^\circ 24'$ ], m. p.  $138-142^\circ$ , and does not give a coloration with ferric chloride. The *ammonium*, *sodium*, *potassium*, *silver*, and *barium* derivatives of the dibromo-compound are described.

The action of iodine on the keto-acid in alkaline solutions leads to the formation of a small amount of a *product* crystallising in needles, m. p.  $139-147^\circ$ , whilst in ammoniacal solution two *products* are formed; one of these forms a sparingly soluble *ammonium* salt, crystallising in needles, m. p.  $48^\circ$ , and decomposing gradually at the ordinary temperature. The second product crystallises when precipitated by hydrochloric acid from its solution in alcoholic potassium hydroxide, decomposes at  $279^\circ$ , and contains nitrogen. G. Y.

**Nitrated Phenylglutaric Acids. III.** HANS MEERWEIN and GEORG SCHROETER (*Ber.*, 1907, 40, 1586—1589. Compare Abstr., 1902, i, 544; 1903, i, 831).—It was stated formerly by the authors that *o*-nitro- $\beta$ -phenylglutaric acid is converted into an isomeric *iso-o*-nitro- $\beta$ -phenylglutaric acid by means of ammonium sulphide. This observation is now found to have been incorrect, since the *o*-nitro- $\beta$ -phenylglutaric acid formerly used contained from 15% to 20% of the meta-isomeride; the latter was reduced by the ammonium sulphide, whilst the former was not.

*m*-Aminophenylglutaric acid,  $C_{11}H_{13}O_4N$ , obtained from the mother liquors of the reduction of crude *o*-nitrophenylglutaric acid by stannous chloride, separates from water in needles, m. p.  $214.5^\circ$  (decomp.); its *dimethyl* ester separates from a mixture of benzene and light petroleum in transparent octahedra, m. p.  $46^\circ$ . That the acid in question is the meta-isomeride is shown by its identity with the product of the reduction of *m*-nitro- $\beta$ -phenylglutaric acid, obtained by the condensation of *m*-nitrobenzaldehyde and ethyl acetoacetate.

Crude *o*-nitrophenylglutaric acid may be purified either by means of ammonium sulphide or by fractionation of its methyl ester, or by oxidation with permanganate. The latter reagent attacks the meta-acid more readily than it does the ortho-acid.

The solubility in water of the crude *o*-nitrophenylglutaric acid (m. p.  $176^\circ$ ) was also determined and compared with that of the pure ortho-acid (m. p.  $205^\circ$ ) and of the pure meta-acid (m. p.  $204^\circ$ ), and of a mechanical mixture of the two. The latter mixture (70% ortho-acid and 30% meta-acid) had the same melting point ( $177^\circ$ ) as that of the crude ortho-acid.

When  $\beta$ -phenylglutaric acid is nitrated under the conditions formerly quoted (*loc. cit.*), about 50% of *p*-nitrophenylglutaric acid, about 38% of *o*-nitrophenylglutaric acid, and about 12% of *m*-nitrophenylglutaric acid are produced. The para-acid may easily be separated, as it is sparingly soluble in water. The meta- and ortho-acids, however, are not readily separated by fractional crystallisation. The ortho-acid may be obtained (1) from the dimethyl esters (resulting from the mixture of ortho- and meta-acids) by means of a mixture of ether and petroleum, (2) by oxidation of the mixture with permanganate, or (3) by ammonium sulphide, the latter method being the most convenient of the three. A. McK.



**Preparation of Aromatic Hydroxy-aldehydes.** PHILIPPE CHUIT (*Bull. Soc. ind. Mulhouse*, 1907, 72—73) and JULES DEMANT (*ibid.*, 73—74).—In Reimer's synthesis of hydroxy-aldehydes, by heating phenols with chloroform in aqueous or aqueous-alcoholic solution, the greater part of the product is resinified by the hot alkali; thus in the preparation of vanillin from guaiacol in aqueous-alcoholic solution, although the reaction takes place almost completely, the yield of hydroxy-aldehyde is not more than 10% of the phenol, and much resin is formed. Chuit proposes to avoid this disadvantage by carrying out the reaction in cold aqueous alkaline solution, the liquids being mixed by energetic stirring. In this manner he obtains vanillin in a yield of 20% of the guaiacol, accompanied by small amounts of *m*-methoxysalicylaldehyde and by only very little resin. The unchanged guaiacol and chloroform are recovered readily.

Following Tiemann and Koppe's instructions (*Abstr.*, 1882, 54), Demant has obtained vanillin in a 33·7% yield and regained 47·5% of the guaiacol, whilst under Chuit's conditions he obtains only 22·5% of vanillin and 50% of regained guaiacol. G. Y.

**Behaviour of Organo-magnesium Compounds towards Oximes and their *O*-Ethers.** MAX BUSCH and RICHARD HOBEIN (*Ber.*, 1907, 40, 2096—2099).—The action of alkyl magnesium bromides on oximes leads, in the first place, to the substitution of the hydroxyl group by alkyl, and subsequent formation of an additive compound,  $\text{CHRR}'\cdot\text{NR}'\cdot\text{MgBr}$ . Similarly, *C*-alkoxyl groups are also replaced by alkyl, since *O*-ethers of the oximes yield the same secondary bases. From  $\alpha$ -benzaldoxime and magnesium phenyl bromide, the hydrochloride of anilindiphenylmethane,  $\text{CHPh}_2\cdot\text{NHPh}$ , is obtained (compare Busch and Rinck, *Abstr.*, 1905, i, 519).  $\alpha$ -Benzaldoxime and magnesium  $\alpha$ -naphthyl bromide give rise only to the intermediate substitution product, benzylidene- $\alpha$ -naphthylamine. The methyl and benzyl ethers of  $\alpha$ -benzaldoxime yield the same products as the oxime. These reactions are in no case simple, a very considerable proportion of by-product being formed. E. F. A.

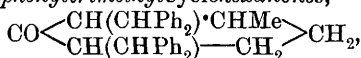
**Reaction between Unsaturated Compounds and Organic Magnesium Compounds. XI. Cyclic Ketones.** ELMER P. KOHLER (*Amer. Chem. J.*, 1907, 37, 369—392).—Experiments have been carried out with three types of unsaturated cyclic ketones, namely, those containing unsaturated side-chains, those having an unsaturated nucleus, and those with two ethylene linkings, one in the nucleus and the other in the side-chain.

By the addition of pulegone, a ketone of the first type, to magnesium methyl iodide, Grignard (*Abstr.*, 1901, i, 681) obtained a hydrocarbon, evidently formed by loss of water from an intermediate alcohol. Since, however, ketones of this type generally behave like the corresponding open-chain compounds, it seemed probable that the result was due to the presence of the two methyl groups attached to one of the unsaturated carbon atoms, and this view has been confirmed by examining the behaviour of dibenzylidenemethylcyclohexanone which has been found to react in the same way as dibenzylideneacetone.

The reaction with ketones of the second type has been studied by

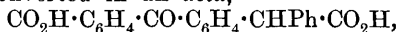
Bamberger and Blangley (Abstr., 1903, i, 557), and by Auwers and Keil (Abstr., 1903, i, 620). In both cases, 1:2-additive compounds were obtained. It is evident that 1:4-compounds are not obtained with the simplest ketones of this type, and an attempt was therefore made to ascertain whether a different result would be obtained with ketones in which the reactivity of the carboxyl group is diminished by substituents in the  $\alpha$ -position. Carvone was chosen for this purpose, but just as the work on this substance was completed, the papers of Rupe and Liechtenhan (Abstr., 1906, i, 374), and Klages and Sommer (*ibid.*, 1906, i, 566) appeared. The author's results confirm those of Rupe and Liechtenhan, but their assumption that the reaction takes place by 1:2-addition is incorrect, compounds obtained by the action of Grignard's reagent on such ketones being formed by 1:4-addition. This is proved conclusively by experiments with diphenylcyclohexanone, which behaves towards Grignard's reagent in the same way as unsaturated open-chain compounds.

By the action of magnesium phenyl bromide on dibenzylidenemethylcyclohexanone, two isomeric ketones,  $C_{27}H_{26}O$ , m. p.  $192^\circ$  and  $132^\circ$ , crystallising in needles, are produced together with a third compound, m. p.  $154-156^\circ$ , which was not obtained in sufficient quantity for analysis. The isomeric ketones give orange-coloured solutions in strong sulphuric acid, decolorise bromine solution, and reduce potassium permanganate. When oxygen is passed through the ethereal solution, obtained from the decomposition of the magnesium derivative from dibenzylidenemethylcyclohexanone with cold hydrochloric acid, isomeric peroxides,  $C_{27}H_{26}O_3$ , m. p.  $176^\circ$  and  $142^\circ$ , are obtained, which crystallise in colourless needles. Each of the isomeric ketones reacts with magnesium phenyl bromide with formation of two stereoisomeric tetraphenyltrimethylcyclohexanones,



m. p.  $282^\circ$  and  $190^\circ$ , which crystallise in needles.

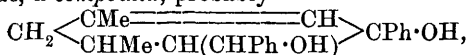
Diketobenzylidenehydrindene reacts with magnesium phenyl bromide in an unexpected manner with formation of  $C_6H_4 \cdot C \cdot C_6H_4$  a ketone, m. p.  $162^\circ$ , which separates from alcohol in yellow plates and, on oxidation with potassium permanganate, is converted in an acid,



m. p.  $131-133^\circ$ , which crystallises in flat, colourless needles. The name "bindene" is suggested for the hydrocarbon from which the ketone is derived, the ketone itself being "6-phenylbindene-8-one."

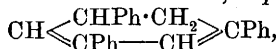
Phenyldimethylcyclohexanol,  $CH_2 < \begin{array}{c} CMe = CH \\ CHMe \cdot CH_2 \end{array} > CPh \cdot OH$ , m. p.

$111^\circ$ , obtained by the action of magnesium phenyl bromide on dimethylcyclohexanone, separates from ether in large, colourless plates. When benzylidenedimethylcyclohexanone is treated with magnesium phenyl bromide, a compound, probably



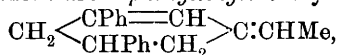
m. p.  $106^\circ$ , is produced, which forms large, lustrous tables, and on oxidation with permanganate yields benzoic acid.

[With MARY VIOLET DOVER.]—In preparing diphenylcyclohexanone by the action of ethyl acetoacetate on benzylideneacetophenone as described by Knoevenagel and Schmidt (*Annalen*, 1894, 281, 59), it was found that the additive compound obtained when sodium ethoxide is used as the condensing agent is not identical, but isomeric, with that obtained when diethylamine is employed; the former has m. p. 168°, and the latter, m. p. 121°. Diphenylcyclohexanone has m. p. 83° (not 70—72° as stated by Knoevenagel and Schmidt, *loc. cit.*). The *oxime*, m. p. 163—164°, crystallises in needles. By the action of magnesium phenyl bromide on the ketone, triphenylcyclohexadiene,

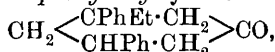


m. p. 111°, is produced, which on oxidation with potassium permanganate is converted into 1 : 3 : 5-triphenylbenzene.

The products of the action of a large excess of magnesium ethyl bromide on diphenylcyclohexanone are diphenylethylidenecyclohexene,



b. p. 152°/22 mm., and diphenylethylcyclohexanone,



b. p. 170°/24 mm. When diphenylethylidenecyclohexene is oxidised with potassium permanganate, it is converted into  $\gamma$ -benzoyl- $\beta$ -phenylbutyric acid, the *methyl* ester of which has m. p. 94°. It has been proved that the diphenylethylcyclohexanone is formed by 1 : 4-addition by treating it with magnesium ethyl bromide, when  $\text{O} \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHPh}$  diphenylethylcyclohexanol peroxide, m. p. 269—270°, is produced, which forms small,  $\text{O} \cdot \text{CH} \cdot \text{CPhEt} \cdot \text{CH}_2$  hard prisms. If diphenylcyclohexanone is treated with an equivalent quantity, instead of excess, of magnesium ethyl bromide, the same hydrocarbon is produced, but instead of the ketone a compound,  $\text{C}_{38}\text{H}_{38}\text{O}_2$ , m. p. 256°, is obtained, which is similar to the substances formed from unsaturated, open-chain ketones. E. G.

**1-Chloroacetyl-2 : 4-dichlorobenzene.** FRANZ KUNCKELL (*Ber.*, 1907, 40, 1702—1703).—The interaction of *m*-dichlorobenzene, chloroacetyl chloride, and aluminium chloride in carbon disulphide on the water-bath, results in the formation of 1-chloroacetyl-2 : 4-dichlorobenzene,  $\text{C}_8\text{H}_5\text{OCl}_3$ , crystallising in long, pale yellow prisms, m. p. 57°. The position of the chloroacetyl residue was determined by oxidation with potassium permanganate to the corresponding dichlorobenzoic acid.

*p*-Dichlorobenzene does not react with chloroacetyl chloride under the above conditions. W. R.

**Reduction of Ketones by Alcoholic Stannous Chloride and Hydrochloric Acid.** Correction. HERMANN APITZSCH (*Ber.*, 1907, 40, 1803—1804. Compare Apitzsch and Metzger, *Abstr.*, 1904, i, 510; Klages, *Abstr.*, 1906, i, 674.).—Benzoin is not reduced by alcoholic stannous chloride and hydrochloric acid; benzil is, however, reduced to benzoin, and the same product is formed when benzoin-anilide or ethylbenzoin is heated with the reducing agents at

150—170°. Cuminoin and benzylideneacetophenone are not reduced. Anisoin and anisil both yield deoxyanisoin and not *isohydroanisoin*.

J. J. S.

**The Benzil Reaction.** ARTHUR HANTZSCH and WALTER H. GLOVER (*Ber.*, 1907, 40, 1519—1523. Compare Liebermann and Homeyer, *Abstr.*, 1880, 259; Bamberger, *Abstr.*, 1885, 807; Bamberger and Scholl, *Abstr.*, 1899, i, 701).—This work was undertaken with the object of throwing light on the constitution of the violet products formed by the action of potassium ethoxide on benzil and on a mixture of benzil and benzoin. Bamberger and Scholl's assumption that the products are identical (*loc. cit.*) cannot be correct, since whilst 4:4'-dichlorobenzil gives no coloration with cold alcoholic-aqueous potassium hydroxide, but a purple-red on boiling, 4:4'-dichlorobenzoin, colourless needles, m. p. 88°, gives at the ordinary temperature a greenish-blue coloration becoming blue gradually on boiling, and mixtures of 4:4'-dichlorobenzoin with benzil and with 4:4'-dichlorobenzil give a deep-blue coloration with either the cold or the hot alkali. Moreover, the coloration obtained on adding potassium hydroxide to an alcoholic solution of benzil and benzoin disappears on shaking, whereas that formed by boiling benzil with alcoholic potassium hydroxide is stable.

When treated with a concentrated ethereal solution of potassium ethoxide, benzil yields a small amount of benzilic acid and a blue solution, which on evaporation in a vacuum deposits an indigo-blue mass, decolorised by air. It is shown that this potassium compound is not decomposed by water and therefore cannot be analogous to Beckmann and Paul's blue sodium salt formed by the action of sodium on benzil in ethereal solution. By treating the concentrated, deep-red, aqueous solution of the potassium compound with carbon dioxide, a small amount of a *product*,  $C_{28}H_{20}O_4$ , is obtained as a yellow powder, m. p. 65—67°; this is considered to be the *aldol* of benzil,  $COPh \cdot CPh(OH) \cdot C_6H_4 \cdot CO \cdot COPh$ . In concentrated aqueous solution, its potassium derivative is intense blue by reflected, deep-red by transmitted, light. An indigo-blue, acid *barium* salt is described.

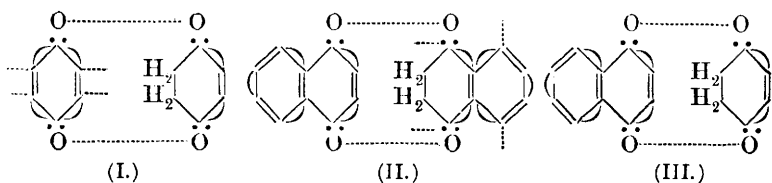
The aldol does not appear to be an intermediate product in the conversion of benzil into benzilic acid (compare Montagne, *Abstr.*, 1902, i, 473).

G. Y.

**Decahydro-*a*-naphthyl Ketone and Decahydro-*a*-naphthylamine.** HENRI LEROUX (*Compt. rend.*, 1907, 144, 981—983. Compare *Abstr.*, 1905, i, 601; 1906, i, 16).—*Decahydro-*a*-naphthyl ketone*, m. p. 32°, obtained by oxidising decahydro-*a*-naphthol with chromic acid, crystallises from light petroleum in bulky, prismatic tablets, has an odour like that of menthol, and yields a crystalline *additive product* with sodium hydrogen sulphite. The *semicarbazone*, m. p. 230° (approx.), forms colourless needles; the *phenylhydrazone* is amorphous; the *oxime*, m. p. 165°, crystallises from alcohol, sublimes at 100°, forming long, colourless needles, and on reduction with sodium in alcohol yields *decahydro-*a*-naphthylamine*, b. p. 96—97°/14 mm. This is a colourless, unpleasant-smelling liquid, which absorbs carbon

dioxide on exposure to air. The *hydrochloride*, m. p. 190° (decomp.), *platinichloride*, and *picrate*, m. p. 210° (decomp.), are crystalline. The *acetyl* derivative, m. p. 182°, forms slender needles from alcohol and sublimes at 125°. The *benzoyl* derivative, m. p. 195°, crystallises in slender needles from alcohol and sublimes at 150°. T. A. H.

**Mixed Quinhydrones.** GUSTAV URBAN (*Monatsh.*, 1907, 28, 299—318).—It was shown by Biltris (Abstr., 1897, i, 199) that the action of benzoquinone on thymoquinol leads to the immediate formation of quinol and thymoquinone together with small amounts of the mixed quinhydrone. It follows that thymoquinol is oxidised to thymoquinone more easily than quinol to benzoquinone. The present work was undertaken to compare in this manner the relative ease with which  $\alpha$ -naphthaquinol and quinol are oxidised to  $\alpha$ -naphthaquinone and benzoquinone respectively, and at the same time to compare the mixed quinhydrones formed, on the one hand, from  $\alpha$ -naphthaquinol and benzoquinone and, on the other, from quinol and  $\alpha$ -naphthaquinone. It is found that whilst a mixed quinhydrone is formed directly from  $\alpha$ -naphthaquinone and quinol in molecular proportions in ethereal light petroleum solution, the same compound is obtained from  $\alpha$ -naphthaquinol and benzoquinone; its formation in this case being preceded by that of  $\alpha$ -naphthaquinone and quinol. The constitution of the quinhydrones is discussed in the light of Thiele's theory of partial valencies, and the following tautomeric structural formulæ are ascribed to ordinary quinhydrone (I), to  $\alpha$ -naphthaquinhydrone (II), and to the mixed quinhydrone from  $\alpha$ -naphthaquinone and quinol (III).



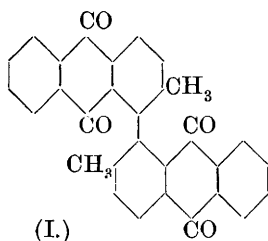
The mixed *quinhydron*,  $C_{16}H_{12}O_4$ , crystallises from a mixture of ether and light petroleum in negatively doubly refracting, rhombic leaflets or needles [ $a : b : c = 0.4590 : 1 : 0.2929$ ]; m. p.  $123^\circ$ , is a dark green by reflected, red by transmitted, light, and is decomposed into  $\alpha$ -naphthaquinone and quinol on solution in alcohol, ether, or light petroleum, but can be recrystallised unchanged from glacial acetic acid.

The action of 2 mols. of benzoquinone on 1 mol. of  $\alpha$ -naphthaquinol in warm glacial acetic acid solution leads to the formation of ordinary quinhydrone which crystallises out,  $\alpha$ -naphthaquinone remaining in solution. On mixing 1 mol. of benzoquinone with 2 mols. of  $\alpha$ -naphthaquinol in warm glacial acetic acid solution,  $\alpha$ -naphthaquinhydrone crystallises out and quinol remains in the mother liquor.

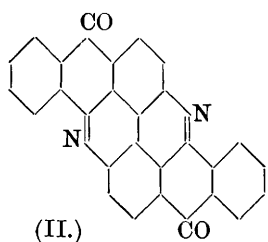
**Dianthraquinonyl and its Derivatives.** BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 180157).—It is well known that metallic

copper is a useful condensing agent for the halogenated derivatives of benzene and naphthalene and this reaction has now been applied in the production of quinones in the anthracene series. 2:2'-Dimethyl-1:1'-dianthraquinonyl is thus prepared by heating an intimate mixture of 1-iodo-2-methylanthraquinone and copper powder at 210°. The product crystallises from xylene in yellowish-brown prisms which are soluble in aniline or nitrobenzene. G. T. M.

**Constitution and Synthesis of Flavanthrene.** ROLAND SCHOLL (*Ber.*, 1907, 40, 1691—1702).—*Flavanthrene* is obtained from 2-aminoanthraquinone by heating with molten potassium hydroxide at 350° (D.R.-P. 136015), with aluminium chloride (138119), heating with antimony pentachloride in boiling nitrobenzene (139633), or by acid oxidising materials such as chromic acid (141355); in the latter case it is accompanied by indanthrene. It is a yellow dye, which gives a dark blue bath on reduction with alkaline hyposulphite. Unmordanted vegetable fibres are coloured deep blue in this bath, and on exposure to the air for a few minutes they become yellow (D.R.-P. 139835, 140573, 142963, 139633). Flavanthrene is a weak base, very sparingly soluble in solvents of high boiling point, and towards heat it is very stable.

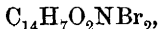


[With KARL HOLDERMANN, JOHANNES MANSFELD, and MAX. A. KUNZ.]—The constitution of flavanthrene has been determined by its synthesis from 1-amino-2-methylanthraquinone (Abstr., 1883, 70). The first step was the preparation of 1-iodo-2-methylanthraquinone,  $C_{15}H_9O_2I$ , from the amino-compound by the diazo reaction, it crystallises in brown leaflets, m. p. 169—169.5°. This was converted into 2:2'-dimethyl-1:1'-dianthraquinonyl (I) by Ullmann's copper method (Abstr., 1904, i, 725), the temperature employed being 270°. The mass obtained is first treated with benzene to remove dark coloured impurities, then reduced with alkaline hyposulphite, and filtered to remove copper and copper iodide, the dimethyldianthraquinonyl being precipitated by blowing air through the filtrate, and finally crystallised from xylene; it forms yellowish-brown needles, m. p. 366—367° (corr.).



It was also obtained by Knoevenagel's method from the diazonium sulphate of the methylanthraquinone by means of copper powder and acetic anhydride (Abstr., 1895, i, 669). On oxidation with chromic acid and glacial acetic acid, 1:1'-dianthraquinonyl-2:2'-dicarboxylic acid,  $C_{30}H_{14}O_8$ , is obtained, crystallising in yellowish-brown crystals, m. p. 334—337° (decomp.). The amide,  $C_{30}H_{16}O_6N_2$ , was next obtained in pale yellow crystals, and converted into flavanthrene by means of potassium hydroxide and bromine. The dye must therefore have the annexed constitution (II), and in obtaining it from 2-aminoanthraquinone, 2 molecules must unite with loss of 2 molecules of water and 2 atoms of hydrogen.

[With CARL STOLL.]—1 : 3-Dibromo-2-aminoanthraquinone,



obtained by shaking the aminoanthraquinone with bromine and water for nine hours, crystallises from glacial acetic acid in yellowish-brown prisms, m. p. 239°. Its diacetate,  $\text{C}_{18}\text{H}_{11}\text{O}_4\text{NBr}_2$ , m. p. 202°, forms greenish-yellow crystals, and when heated with copper powder at 200° gives 2-diacetylaminanthraquinone, m. p. 258°, instead of the 3 : 3'-dibromo-2 : 2'-diamino-1 : 1'-dianthraquinyl expected. W. R.

### Crystallographic Constants of Some Organic Compounds.

ARRIEN JOHNSON (*Jahrb. Min.*, 1907, i, 89—106).—Crystals of the following are described. Pyrazole methiodide; furylhydrophenanthraquinone; optically active camphorylhydroxylamine; optically active camphorylhydroxylamine and its ethyl ester; *i*-bromomalic acid; *i*-isobromomalic acid; *i*-chloromalic acid; oxycitraconic acid; *i*- $\alpha$ - and  $\beta$ -bromocitramalic acids; *i*-chlorocitramalic acid; platodiethylamine chloride, bromide and nitrate; active benzoylcamphorylhydroxylamine; potassium *o*-chlorophenol-*p*-sulphonate; bromostychnine; succinylhydroxylamine; *i*- $\alpha$ - and  $\beta$ -methylmalic acids; methyl tetraphenylenesuccinate; isobromometacrylic acid; chloral hydrosulphide; magnesium *d*-tartrate, and hydrous magnesium *d*-tartrate. L. J. S.

**Terpenes and Ethereal Oils. LXXXIII.** OTTO WALLACH and HEINRICH WIENHAUS (*Annalen*, 1907, 353, 209—227).—I. *Observations in the Fenchone Series*.—Fenchone semicarbazone, obtained by Rimini (Abstr., 1900, i, 554) from isopernitrosofenchone, is formed by the action of semicarbazide hydrochloride and sodium acetate on *d*- or *l*-fenchone in aqueous-alcoholic solution at the ordinary temperature in about two weeks; it crystallises from dilute alcohol in long, stout, rhombic prisms, m. p. 182—183° (186—187°: Rimini, *loc. cit.*). *d*-Fenchone semicarbazone,  $[\alpha]_D + 47.04^\circ$ ; *l*-fenchone semicarbazone,  $[\alpha]_D - 46.88^\circ$ ; *r*-fenchone semicarbazone, m. p. 172—173°, crystallises with difficulty. It is found that *l*-fenchone, prepared from thuja oil (Abstr., 1893, i, 105; 1898, i, 486), contains *l*-camphor and yields a mixture of *l*-camphor semicarbazone, m. p. 238°,  $[\alpha]_D - 39.9^\circ$ , and *l*-fenchone semicarbazone. The *l*-camphor is not present in the thuja oil, as the fractions, b. p. 200—220°, yield  $\alpha$ -thujone semicarbazone, but not camphor semicarbazone until after hydrolysis and oxidation (compare Abstr., 1905, i, 147). The source of the *l*-camphor, therefore, is considered to be *l*-borneol esters present in the thuja oil.

Commercial *d*-fenchone contains *d*-camphor, as it yields *d*-camphor semicarbazone, m. p. 238° (Tiemann, Abstr., 1895, i, 675); a small amount of substance, m. p. 245°, obtained on recrystallisation, is not the pure semicarbazone (compare Rimini, *loc. cit.*).

The camphor cannot be removed from *d*- or *l*-fenchone by energetic treatment with nitric acid, but the pure fenchones may be obtained by acting on the mixtures with semicarbazide for two days and distilling the fenchone with steam; the camphor remains in the distillation residue as the semicarbazone.

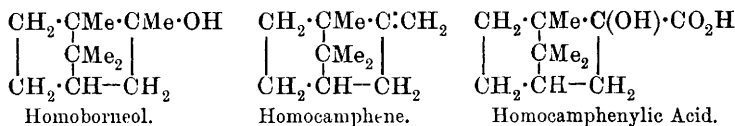
It has been found previously that several isomeric fenchones are

obtained from fenchyl alcohol, whilst analogous observations have been made in the camphene series by Moycho and Zienkowski (Abstr., 1905, i, 710). Hence it seemed desirable to investigate the behaviour in this respect of a homologue of fenchyl alcohol. Homofenchyl alcohol

( $\alpha$ -methylfenchol),  $C_7H_{12}$   $\begin{matrix} \text{CHMe} \\ \diagup \\ \text{CMe-OH} \end{matrix}$  (Zelinsky, Abstr., 1901, i, 660),

m. p.  $61^\circ$ , b. p.  $215-216^\circ$ ,  $[\alpha]_D + 1.12 - + 2.2^\circ$ , when heated with potassium hydrogen sulphate at  $160^\circ$ , yields *homofenchene*,  $C_{11}H_{18}$ , m. p.  $32-37^\circ$ , b. p.  $170-172^\circ$ ,  $D_{20} 0.8520$ ,  $n_D^{20} 1.4557$ ,  $[\alpha]_D + 23.06^\circ$ , which contains an ethylene linking and closely resembles camphene. On oxidation with potassium permanganate, a crude homofenchene, obtained from fenchone containing camphor, yielded small amounts of *homocamphenylic acid*, derived from camphene, and of a hydroxy-lactone (?),  $C_{11}H_{16}O_3$ , m. p.  $157^\circ$ . This oxidation is to be repeated with a homofenchene derived from pure fenchone.

II. *Homocamphene and Homocamphenylic (a-Borneolcarboxylic) Acid*.—*Homocamphene*, m. p.  $28^\circ$ , b. p.  $166-168^\circ$ , obtained by heating the product of the action of magnesium methyl iodide on camphor with potassium hydrogen sulphate, resembles camphene. On oxidation with potassium permanganate it yields *homocamphenylic (a-borneolcarboxylic) acid*,  $OH \cdot C_{10}H_{16} \cdot CO_2H$ , which crystallises in stout needles, m. p.  $179^\circ$ ,  $[\alpha]_D - 30.72 - - 34.8^\circ$ , and forms a sparingly soluble *sodium salt*; the *silver salt* was analysed. As homocamphenylic acid yields camphor when heated with lead dioxide and dilute sulphuric acid, the following formulæ are suggested :



(compare Bredt and Burkheiser, Abstr., 1906, i, 680). G. Y.

**Constitution of the Terpenes.** GUSTAV WENDT (*Pharm. Zeit.*, 1907, 52, 331—332).—A number of new formulæ for various terpenes are proposed without, however, adducing any experimental evidence in support of them. The main feature of the formulæ is that they all

Me  
 contain the grouping  $\text{C} - \text{C} - \text{C}$  in which the central or so-called "pure"  
 Me  
 carbon atom is surrounded by four others.

P. H.

**The Terpene Oils of Manila Elemi.** ALPHONSO M. CLOVER (*Philippine J. Sci.*, 1907, 2, 1—40).—The resins obtained from twenty-one specimens of *Canarium luzonicum* have been investigated. The resin from each tree was worked up separately, as a preliminary examination indicated that the terpenes obtained from the resins of different trees varied considerably. The resin was heated in a flask placed in an oil-bath at  $125-150^\circ$ , and the terpenes distilled under a pressure of 10—15 mm. A second distillate was collected when the



temperature was raised to 200°, and heavy oils were collected from 200—230° or 200—250°. No changes appear to occur at these temperatures. Of the twenty-one samples, ten gave pure *d*-limonene, and nine contained more or less phellandrene. Several of the latter also contained *l*-limonene and probably another terpene of the limonene series. Pinene does not appear to be present.

The remaining two samples of resin gave terpenes which were practically inactive, and these proved to be terpinene and terpinolene. The terpinolene extracted from the fresh resin is practically pure, but when kept for some time, or when heated, it gradually undergoes a change, yielding dipentene, a small amount of *d*-phellandrene, and an unknown levorotatory terpene. This is the only case in which terpinolene has been found in a natural product.

The specific gravities, rotatory powers, refractive indices, and solubilities in 55% alcohol of some of the higher fractions have been determined. In most cases these fractions were inactive or slightly levorotatory. In one case only was a strongly dextrorotatory fraction,  $\alpha_D^{30} + 71.6^\circ$ , obtained. This fraction gave analytical results agreeing with the formula  $C_{15}H_{26}O$ , and when rubbed with a glass-rod, solidified. It is probably a sesquiterpene alcohol. Factors which affect the composition of the oils obtained from the resins are: (1) age of the resin; (2) temperature of distillation, and (3) time occupied in distilling. The two latter factors affect the yields of higher oil more than of the terpenes proper.

The optical activity of both *d*-limonene and of phellandrene decreases when the terpenes are kept, probably owing to oxidation. If dipentene is formed from *d*-limonene at high temperatures (compare Wallach, Abstr., 1885, 550), the change is extremely slow, and even at 380° it would take many hours for the formation of an amount sufficient for detection. Limonene is almost completely polymerised when heated on the water-bath with a little dilute sulphuric acid dissolved in glacial acetic acid. Boiling with a mixture of absolute alcohol and a little dilute sulphuric acid converts the terpene into a mixture of inactive terpenes with relatively high boiling points, 184—200°, whereas boiling with sulphuric acid in dilute alcohol produces hydration. The addition of hydrochloric acid to limonene and its subsequent removal by means of aniline transforms a considerable proportion of the limonene into dipentene. Limonene hydrochloride has b. p. 89—91°/12 mm. The phellandrene obtained from the different resins was Wallach's  $\alpha$ -phellandrene. The nitrite after solution in ethyl acetate at 30° and crystallising at the temperature of a freezing mixture has m. p. 120—121°, but if crystallised from hot ethyl acetate it has the lower m. p. given by Wallach. The solution of the nitrite in chloroform gradually diminishes in activity, and after some four hours is inactive, but after a longer period may become dextrorotatory.

The hydrocarbon is not racemised when heated at 200° for ten hours in a sealed tube, but at 225—250° the phellandrene is decomposed. It forms a hydrochloride which decomposes when distilled under reduced pressure. The dibromide is a mobile oil. When kept for some time, phellandrene is oxidised by the atmospheric oxygen, yielding

a crystalline compound,  $C_{10}H_{18}O_2$ , *dihydroxyphellandrene*, which separates from hot ethyl acetate in colourless needles, m. p.  $164\cdot5$ — $165\cdot5^\circ$ .  
J. J. S.

**Volatile Oil of Juniperus Phœnicea.** J. RODÉ (*Bull. Soc. chim.*, 1907, [iv], 1, 492—497. Compare Abstr., 1906, i, 971. Bennett and Umney, *Pharm. J.*, 75, 827).—The portion of this oil boiling above  $180^\circ$  contains a minute quantity of an aldehyde and 25·17% of alcohols calculated as  $C_{10}H_{18}O$ , of which 5·03% occurs in the form of esters. The *aldehyde*, isolated by means of its crystalline compound with sodium hydrogen sulphite, furnishes a liquid *oxime* and a corresponding *naphthacinchonic acid*, which is crystalline and decomposes at  $275$ — $276^\circ$ . On oxidation with alkaline permanganate the aldehyde appears to be completely decomposed. It does not seem to be identical with any of the aldehydes known to occur in volatile oils.

The more volatile portion of the mixture of acids obtained by saponifying the esters contained in the non-terpenic portion of the oil include acetic and hexoic acids, and in addition probably a minute quantity of a second acid soluble in water. Two other acid fractions were obtained, the one boiling at  $210$ — $255^\circ$  and the other at  $255$ — $265^\circ$ ; the latter is near the boiling point of decoic acid, but the material differs from this in specific gravity, and may be a mixture of a fatty with a hydroxy-acid, or is possibly identical with the acid which Fromm (Abstr., 1900, i, 402) obtained from German savin. T. A. H.

**Resin-balsam of Pinus halepensis.** ALEXANDER TSCHIRCH and H. SCHULZ (*Arch. Pharm.*, 1907, 245, 156—163).—This resin is used in Greece for preserving and flavouring wine; the sample examined had approximately acid number 130 and saponification number 150. From a solution of it in ether, 1% aqueous ammonium carbonate extracts *halepopinic acid*,  $C_{21}H_{32}O_3$ ; this is amorphous, with m. p.  $72^\circ$ , acid number 171 (corresponding with monobasicity), and saponification number 217; its lead salt is soluble in alcohol.

From the remaining ethereal solution, 1% aqueous sodium carbonate solution extracted a crude acid, which yielded lead salts respectively insoluble and soluble in alcohol. The acid of which the lead salt is insoluble in alcohol, *halepopinolic acid*,  $C_{17}H_{26}O_2$ , is crystalline, has m. p.  $148$ — $149^\circ$ , acid number 187 (corresponding with monobasicity), and saponification number 246; its *silver* salt was analysed. This acid can be isolated from the balsam in several different ways. The acid of which the lead salt is soluble in alcohol, *halepopinitolic acid*,  $C_{16}H_{26}O_2$ , is amorphous, and has m. p.  $78$ — $80^\circ$ , acid number 188 (corresponding with monobasicity), and saponification number 247.

From the remaining ethereal solution the ether was distilled off, and the residue was distilled with steam. An *essential oil* passed over, with b. p.  $150$ — $152^\circ$ , and D  $0\cdot897$ , whilst a small quantity of a *resen* remained behind.

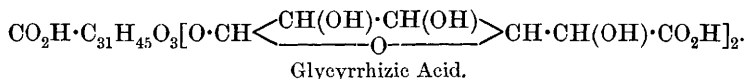
The balsam also contains a *bitter principle* in small amount.

In one hundred parts of the resin there are contained approximately: halepopinic acid, 5; halepopinolic and halepopinitolic acids, 59;

essential oil, 21—26; resen, 0.6; the residue consists of impurities mechanically mixed with the balsam. C. F. B.

**Glycyrrhizin.** ALEXANDER TSCHIRCH and H. CEDERBERG (*Arch. Pharm.*, 1907, 245, 97—111).—Glycyrrhizin consists of the potassium and calcium salts of glycyrrhizic acid and was isolated from liquorice.

*Glycyrrhizic acid*,  $C_{44}H_{64}O_{19}$ , m. p. 205°, does not contain nitrogen, has a sweet taste, and is optically inactive. Its acid number corresponds with tribasicity; the mono-potassium and mono-ammonium salts, obtained by crystallisation from acetic acid, were analysed. The acid forms a *hexa-acetyl* derivative, with m. p. 210°. It does not reduce ammoniacal silver solution or Fehling's solution. When fused with potassium hydroxide, it yields acetic and oxalic acids, but no protocatechuic or *p*-hydroxybenzoic acid. When it is boiled for five hours with 3% sulphuric acid, air being excluded, *glycyrrhetic acid*,  $C_{32}H_{48}O_7$  (molecular weight determined ebullioscopically), m. p. 210° (hitherto known as "glycyrrhetin"), is precipitated, and can be crystallised from acetic acid; this has an acid number corresponding with monobasicity, and forms a *diacetyl* derivative with m. p. 219°. The solution from which this acid has separated contains glycuronic acid, which has not been obtained hitherto from a vegetable source. The behaviour of glycyrrhizic acid is thus in harmony with the formula



The drug contains about 3% of glycyrrhizic acid, also 0.2% of a fatty substance with a bitter taste, and dextrose. Mannitol is present in the liquid from which the crude glycyrrhizic acid has been precipitated with sulphuric acid, but it is not present in the original drug. C. F. B.

**Jafferabad and Uganda Aloes.** EUGÈNE LÉGER (*J. Pharm. Chim.*, 1907, 25, [vi], 476—483. Compare Abstr., 1900, i, 512; 1902, i, 549, 685, ii, 484; 1903, i, 356; 1904, i, 907).—Jafferabad aloes, derived from *Aloe abyssinica*, contains barbaloin, identical with that present in Barbadoes aloes (compare Shenstone, *Pharm. J.*, 13, 461, and Tschirch and Hoffbauer, Abstr., 1905, i, 913). Uganda aloes, probably derived like Cape aloes from *Aloe ferox*, also contains barbaloin (compare Naylor and Bryant, *Pharm. J.*, 1899, 296, and Tschirch and Klaveness, Abstr., 1901, i, 602). It is pointed out that as the melting points of the aloins are indefinite they are untrustworthy as means of identification. T. A. H.

**Rottlerin.** HERMANN THOMS (*Arch. Pharm.*, 1907, 245, 154—155).—A reply to Telle (this vol., i, 435). C. F. B.

**Action of Magnesium Phenyl Bromide on Caffeine, and some of its Derivatives.** HEINRICH SCHULZE (*Ber.*, 1907, 40, 1744—1754).—By the interaction of magnesium phenyl bromide and caffeine or bromocaffeine in benzene solution a compound,  $C_{20}H_{20}ON_4$ , is formed along with diphenyl and triphenyl carbinol. This separates in

colourless, short, many-faced crystals, m. p. 249—250°, and is a mono-acid base; the *hydrochloride* crystallises in long, colourless, silky needles, m. p. 250°; the *aurichloride* forms yellowish-red needles, m. p. 200—202° (decomp.); the *platinichloride*, brownish-yellow, glistening plates, decomposing about 183°.

8-Methylcaffeine gives a *compound*,  $C_{21}H_{22}ON_4$ , m. p. 224—225°, crystallising in long, glistening needles; the *hydrochloride* forms colourless needles decomposing at 262—263°, and the *platinichloride*, brownish-yellow, glistening plates, m. p. 234° (decomp.). A considerable quantity of bases soluble in water is also produced during the above reactions.

Ethoxycaffeine yields a faintly basic *compound*,  $C_{26}H_{24}ON_4$ , m. p. 235°, crystallising in colourless, right-angled plates which dissolves in sulphuric acid with a red coloration; the *aurichloride* forms orange-red, glistening plates, m. p. 215°, whilst the corresponding *platinichloride* forms orange plates, which darkens at 250°, m. p. 271—272°. This compound is also produced from methoxycaffeine; it is probably an homologue of the compounds  $C_{20}H_{20}ON_4$  and  $C_{21}H_{22}ON_4$ , in which the alkoxy-group has been replaced by phenyl.

In addition, a strongly basic *compound*,  $C_{20}H_{22}N_4$ , m. p. 152—153°, crystallising in bright, yellow, long needles is formed either from ethoxy- or methoxy-caffeine. The *hydrochloride* crystallises in yellow needles, which become fiery red on heating, m. p. 224° (decomp.); it dissolves in water with a reddish-yellow coloration.

Ethoxycaffeine yields a third faintly basic substance, sparingly soluble in water, crystallising in long, colourless, silky needles, which darkens about 200°, m. p. 255° (decomp.). Methoxycaffeine does not yield a similar product.

E. F. A.

**Derivatives of Cincholeupone.** I. PAUL RABE [and ERNST ACKERMANN] (*Ber.*, 1907, 40, 2013—2015. Compare Rabe, this vol., i, 78; Königs, Bernhart, and Ibele, this vol., i, 345).—*iso*Nitroso-methylcinchotoxine (Rohde and Schwab, *Abstr.*, 1905, i, 228) when treated with phosphorus pentachloride and then poured into ice-cold water, yields cinchonic acid and the *nitrile* of methylcincholeupone,

$CN \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CHEt} \cdot CH_2 \\ \text{CH}_2 - CH_2 \end{smallmatrix} NMe$ . The latter is a clear liquid with an odour of piperidine and is moderately soluble in water; b. p. 186—187°/90—95 mm.,  $D_4^{20}$  0.9366,  $n_D^{20}$  1.4707. The *methiodide*,  $C_{11}H_{21}N_2I$ , form prismatic needles, decomposing at about 270°. The *picrate*,  $C_{16}H_{22}O_7N_5$ , crystallises in lemon-yellow plates, m. p. 142°, and the *picrolonate*,  $C_{20}H_{26}O_5N_6$ , in rhombic, pale orange-coloured plates, m. p. 208°.

J. J. S.

**Action of Nitric Acid on Cinchonine.** PAUL RABE and ERNST ACKERMANN (*Ber.*, 1907, 40, 2016—2017. Compare Weidel, *Annalen*, 1874, 173, 76).—A diacid *base*,  $C_{19}H_{20}O_6N_4$ , has been obtained by heating cinchonine with nitric acid (D 1.3) in an oil-bath at 100—110° for some forty-eight hours. It is isolated by pouring into ice-cold water and adding a slight excess of ammonia. It crystallises from alcohol in slender needles, m. p. 238° (decomp.), is insoluble in ether or light petroleum and only sparingly soluble in benzene, chloro-

form, or alcohol. The *hydrochloride*,  $C_{19}H_{20}O_6N_4 \cdot 2HCl$ , decomposes at  $238^\circ$ . The base is stable towards permanganate, but is oxidised by chromic acid to cinchonic acid.

J. J. S.

**Constitution of Morphine and of Hydroxymethylmorphimethine.** ROBERT PSCHORR and HANS EINBECK (*Ber.*, 1907, 40, 1980—1983).—A reply to Knorr and Hörlein (*Abstr.*, 1906, i, 877). Hydroxymethylmorphimethine (Knorr and Schneider, *Abstr.*, 1906, i, 449) reacts not only as an alcohol, but also as a ketone. The *semicarbazone*,  $C_{20}H_{26}O_4N_4$ , m. p.  $155^\circ$ , crystallises from ethyl acetate in glistening plates containing the solvent. The *oxime* is not crystalline; its *hydrochloride*,  $C_{19}H_{25}O_4N_2Cl$ , decomp.  $279^\circ$  (corr.). Neither hydroxycodine (Ach and Knorr, *Abstr.*, 1903, i, 849) nor  $\alpha$ - or  $\beta$ -methylmorphimethine give semicarbazones or oximes and the conclusion is drawn that the bridge of the phenanthrene nucleus is dihydrogenised in hydroxycodine, but unsaturated in hydroxymethylmorphimethine, and (in opposition to Knorr) that there is attached to it the nitrogen and not the carbon side-ring in hydroxycodine and in the morphine alkaloids, thus providing a further support for Pschorr's pyridine formula for morphine.

W. R.

**Morphine. IX. isoCodeinone and the Isomerism of Codeine, isoCodeine, and  $\psi$ -Codeine.** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, 40, 2032—2039. Compare this vol., i, 151; Schryver and Lees, *Trans.*, 1901, 79, 576).—Codeine and  $\psi$ -codeine when oxidised carefully with chromic acid yield the same ketone, *isocodeinone*, isomeric with codeinone. When decomposed, this ketone yields a phenanthrene derivative isomeric with that obtained from codeinone. The conclusion drawn from these facts is that *iso*- and  $\psi$ -codeine are structurally identical and only stereoisomeric, whereas codeine and *isocodeine* are structurally isomeric. All three compounds yield the same deoxycodine (this vol., i, 235), and the isomerism is probably due to the different positions occupied by the hydroxyl group in the compounds, and the conversion of codeine into the isomeric bases is then accompanied by a wandering of the hydroxyl radicle.

*isocodeinone*,  $C_{18}H_{19}O_3N$ , may be isolated as its sparingly soluble chromate. It crystallises from alcohol in long, compact prisms, m. p.  $174$ — $175^\circ$ , decomposes at  $240^\circ$ ,  $[\alpha]_D^{25} - 25^\circ$  in 99% alcohol. It does not give a characteristic reaction with sulphuric acid, and, unlike codeinone, is comparatively stable towards dilute hydrochloric acid. With concentrated hydrochloric acid, it yields phenolic bases. With acetic anhydride, it is decomposed, yielding methylethanamine, but the main product is triacetylthebenine (Freund and Michaels, *Abstr.*, 1897, i, 495).

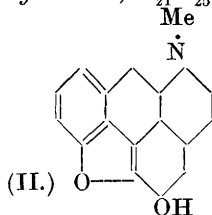
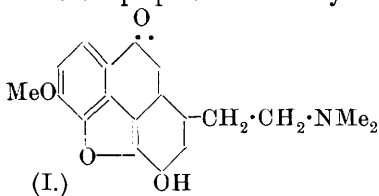
*isocodeinone-oxime*,  $C_{18}H_{20}O_3N_2$ , has been obtained in an amorphous condition only; the *semicarbazone*,  $C_{19}H_{22}O_3N_4$ , forms slender needles, m. p.  $180^\circ$  (decomp.), the corresponding *codeinone semicarbazone* has m. p.  $185^\circ$  (decomp.), and then solidifies and begins to decompose at about  $250^\circ$ . *isocodeinone methiodide*,  $C_{18}H_{19}O_3N \cdot MeI$ , crystallises in flat needles, which decompose at about  $220^\circ$ ,  $[\alpha]_D^{25} - 12^\circ$  in aqueous solution. It is more stable than codeinone methiodide and may be crystallised from water, but is decomposed by sodium hydroxide,

yielding a *phenolic base*,  $C_{19}H_{21}O_3N$ , which decomposes at about  $235^\circ$ . When heated with alcohol at  $160$ — $170^\circ$ , the methiodide yields a diacetoxymethoxyphenanthrene, m. p.  $155$ — $156^\circ$ , which is isomeric with the product obtained from codeinone methiodide (Knorr, Abstr., 1904, i, 916) and dimethylaminoethyl ether, J. J. S.

**Morphine. X. 9-Amino-3:4-dimethoxyphenanthrene and 3:4-Dimethoxyphenanthrene-9-carboxylic Acid.** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, 40, 2040—2042).—The *ethyl ester* of dimethylmorphole-9-carboxylic acid,  $C_{19}H_{18}O_4$  (Pschorr and Sumuleanu, Abstr., 1900, i, 487) form compact crystals, m. p.  $80^\circ$ . With hydrazine hydrate in absolute alcoholic solution, it yields the *hydrazide*,  $C_{17}H_{16}O_3N_2$ , m. p.  $207$ — $208^\circ$ . The corresponding *azide*,  $C_{17}H_{13}O_3N_3$ , crystallises in pale yellow plates, decomposes at about  $85^\circ$ , and when heated with ethyl alcohol yields the *urethane* of 9-aminodimethylmorphole,  $C_{19}H_{19}O_4N$ , m. p.  $145^\circ$ . When hydrolysed with alcoholic potassium hydroxide, the urethane yields 9-aminodimethylmorphole as an oil. The *hydrochloride* and *sulphate* are both sparingly soluble.

J. J. S.

**Morphine. XI. Hydroxymethylmorphimethine (Ketodihydromethylmorphimethine).** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, 40, 2042—2048).—The degradation of hydroxycodine (Knorr and Schneider, Abstr., 1906, i, 449) is analogous to the toxin decomposition of quinine alkaloids or to the conversion of narcotine into narceine, and the compound described as hydroxymethylmorphimethine (*loc. cit.*) is now shown to be *ketodihydromethylmorphimethine* (I). With acetic anhydride it yields a mono- and not a diacetyl derivative. The following derivatives of the acetyl derivative have been prepared and analysed: *hydriodide*,  $C_{21}H_{25}O_5N, HI$ ,

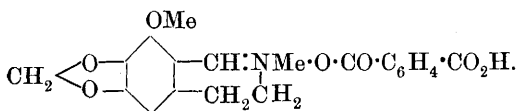


m. p.  $270^\circ$  (decomp.); *hydrobromide*, quadratic plates, decomposing at  $280$ — $285^\circ$ ; *methiodide* (*loc. cit.*). Hydroxycodine yields a diacetyl derivative (Ach and Knorr, Abstr., 1903, i, 849). It would thus appear that the oxygen atom introduced into the molecule of codeine in its oxidation to hydroxycodine is present in this latter as a hydroxy-group, but is no longer present in this form in ketodihydromethylmorphimethine, but appears again as phenolic hydroxyl when the base is decomposed with acetic anhydride, yielding a phenanthrene derivative. The ketonic nature of ketodihydromethylmorphimethine has been proved by conversion into an oxime and semicarbazone. The *oxime* yields a crystalline *methiodide*,  $C_{19}H_{24}O_4N_2, MeI$ , which changes colour at  $250^\circ$  and decomposes rapidly at  $270^\circ$ .

The annexed formula (II) is suggested for morphine.

J. J. S.

**Preparation of Acid and Normal Cotarine Phthalates.** KNOLL and Co. (D.R.-P. 180395).—*Cotarnine hydrogen phthalate*



is prepared by shaking or stirring together in absolute ether an intimate mixture of cotarnine and phthalic anhydride until the

product is completely soluble in water. The reagents are employed in molecular proportion and when the amount of cotarnine is doubled the normal *cotarnine phthalate* is produced. G. T. M.

**Application to Pyridine of the Direct Method of Hydrogenation by Means of Nickel.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, 144, 784—786).—When pyridine vapour mixed with excess of hydrogen is passed over a column of reduced nickel kept at 160—180°, the product is found to contain a small quantity of an amine which is not piperidine, but is probably normal amylamine, it resembles *isoamylamine* in properties. If the nickel is heated at 220°, the amylamine formed breaks down into pentane and ammonia (compare Hoffmann Abstr., 1883, 813), at 350° the destruction of the pyridine is much more rapid. This rupture of the pyridine nucleus on attempted hydrogenation in presence of nickel has already been observed by Padoa and Carughi (Abstr., 1906, i, 765) in the case of quinoline, methyl-*o*-toluidine here being the final product. The fact that the benzene nucleus is readily hydrogenated by this method, whilst the pyridine ring is not, is evidence against the Körner formula for the latter substance. On passing piperidine vapour alone over reduced nickel heated at 250°, it is completely decomposed into pyridine and hydrogen. E. H.

**Derivatives of Quinquevalent Chromium. III.** RUDOLF F. WEINLAND and MAX FIEDERER (*Ber.*, 1907, 40, 2090—2093. Compare this vol., ii, 31, and Weinland and Friedrich, Abstr., 1906, i, 37).—The pyridinium tetrachlorohydroxychromanate,  $C_5NH_5 \cdot CrCl_4 \cdot OH$ , previously described, is most conveniently prepared by saturating glacial acetic acid with hydrogen chloride, dissolving chromic acid in this, and after an interval adding pyridine dissolved in acetic acid. The salt crystallises without water in brownish-red, doubly refractive, right-angled plates. The quinolinium salt can be prepared in a similar manner; it also crystallises without water. The method is also available for preparing the alkali salts of the type  $CrOCl_3 \cdot 2KCl$ . E. F. A.

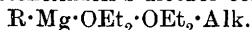
**New Method of Introducing Alkyl or Aryl Groups into Pyridine or Quinoline Bases. Constitution of Mixed Organo-magnesium Compounds.** BERNARDO ODDO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 538—545).—The author has continued the study of the compounds obtained by the action of mixed organo-magnesium compounds on the pyridine and quinoline bases (Abstr., 1904, i, 920; see also Sachs and Sachs, Abstr., 1904, i, 925; Tschelinzeff, Abstr.,

1905, i, 40). The results obtained render it possible to determine the constitution of all the organo-magnesium compounds yet prepared, starting from the known constitutions of Grignard's compounds.

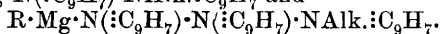
It is found that when magnesium, an alkyl or aromatic halogen compound, and traces of pyridine or quinoline are brought into contact in toluene, benzene, or light petroleum, a reaction begins, in some cases in the cold, but soon ceases and leaves most of the magnesium unchanged, even though a small quantity of iodine is added and the mixture heated for a long time in a reflux apparatus. Hence, pyridine and quinoline do not act catalytically as does dimethylaniline, the reaction only proceeding as far as the formation of substituted ammonium iodide. If, however, 1 mol. of the pyridine or quinoline is added per mol. of the halogen compound, all the magnesium disappears and the reaction is complete in a few minutes. With aliphatic halogen compounds, the reaction proceeds in presence of either toluene or benzene or light petroleum, but with halogen derivatives of the aromatic series it is necessary for the solvent to have a b. p. of at least about 80°. The organo-magnesium compounds thus formed are obtained as a fine powder or crystalline magma, and alter far more rapidly than those described previously (Abstr., 1904, i, 920). The latter, when treated with water, yield the hydrocarbon corresponding with the alkyl radicle and the free base, but the compounds now described give, under the action of water, the base with an alkyl radicle in the nucleus. Thus, from bromobenzene, quinoline, and magnesium in toluene solution, 2-phenylquinoline is obtained.

Similar results are obtained on attempting to prepare the mixed compound of pyridine and quinoline with magnesium phenyl bromide by adding 1 mol. of each base to 1 mol. of the organo-metallic compound prepared by Grignard's method.

These compounds possess the structure  $R \cdot Q \cdot Mg \cdot Alk$  (where  $Q$  = quinoline or other base), whilst those previously described are represented by  $R \cdot Mg \cdot Q \cdot Alk$ ; these constitutions are indicated by the behaviour of the compounds towards water, a reaction which the author employs generally for determining the structure of mixed organo-magnesium compounds. In this way it is found that the constitutions of all the organo-magnesium compounds known are as follow. I. Oxonium type: (a) Grignard's mono-ether compounds,  $R \cdot Mg \cdot OEt_2 \cdot Alk$ ; (b) Tschelinzeff's diether compound,



(*loc. cit.*). II. Ammonium type, corresponding with the preceding in formula and in chemical behaviour: (a) Tschelinzeff's monodimethylaniline compound,  $R \cdot Mg \cdot Q \cdot Alk$ ; (b) monoquinoline compound of Sachs and Sachs (*loc. cit.*),  $R \cdot Mg \cdot Q \cdot Alk$ ; (c) polyquinoleic compounds of Oddo,  $R \cdot Mg \cdot N(C_9H_7) \cdot NAlk \cdot C_9H_7$  and



III. Mixed oxonium-ammonium type: pyridine-ether compounds of Oddo,  $R \cdot Mg \cdot N(C_5H_5) \cdot N(C_5H_5) \cdot OEt_2 \cdot Alk$ , or with the ether molecule interchanged with one or other of the  $N:C_5H_5$  groups. All the above compounds, when treated with water, yield the hydrocarbons corresponding with the alkyl radicle of the haloid compound employed.

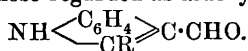
IV. Ammonium type, isomeric with those of class II: (a) Oddo's



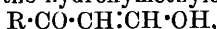
compounds (Abstr., 1904, i, 920),  $R \cdot Q \cdot Mg \cdot Alk.$ ; (b) compound obtained by Oddo by the simultaneous action of pyridine and quinoline on Grignard's compounds,  $R \cdot N(:C_9H_7) \cdot Mg \cdot NAlk.:C_5H_5$ . The action of water on these compounds yields the alkylated bases. T. H. P.

**Indoles.** ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 381—384. Compare this vol., i, 436).—The action of nitrous acid on indole yields a compound,  $N \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C:N \cdot OH$ , which is probably identical with the so-called nitrosoindole prepared by Zatti and Ferratini (Abstr., 1890, 1293; 1891, 67) by the action of sodium nitrite on an acetic acid solution of indole.

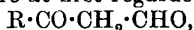
The action of formic acid on indoles, which should give rise to compounds of the form  $N \leq \begin{smallmatrix} C_6H_4 \\ CR \end{smallmatrix} > C:CH \cdot OH$ , yields, instead, compounds identical with those regarded as aldehydes,



On the other hand, ethyl formate generally yields hydroxymethylene derivatives. This explains why pyrrole-2-aldehyde (Bamberger and Djigerdjan, Abstr., 1900, i, 309), which exhibits behaviour only slightly resembling that of ordinary aldehydes, does not react with dihydroxyammonia (Abstr., 1905, ii, 385) to form the corresponding hydroxamic acid. Also the hydroxymethylene compounds,

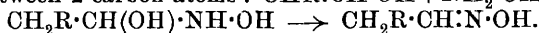


which are formed by the action of ethyl formate on the ketones,  $R \cdot CO \cdot CH_3$ , and which were at first regarded as aldehydes,



do not react with dihydroxyammonia, although they yield oximes, hydrazones, &c. The reaction with dihydroxyammonia is not given by 2-methylindole-3-aldehyde (Plancher and Ponti, this vol., i, 341), which, however, reacts readily with hydrazines and condenses with pyruvic acid and naphthylamines.

The authors term "true aldehydes,"  $R \cdot CHO$ , and "nitroso-derivatives,"  $R \cdot NO$ , the compounds which react with dihydroxyammonia, to distinguish them from hydroxymethylene compounds,  $CHR:CH \cdot OH$ , and oximes,  $CHR:N \cdot OH$ . In the case of true aldehydes, the formation of oximes and hydrazones takes place by addition of hydroxylamine or hydrazine to the double linking between carbon and oxygen:  $R \cdot CH:O + NH_2 \cdot OH = R \cdot CH(OH) \cdot NH \cdot OH \rightarrow R \cdot CH:N \cdot OH$ , whilst, with hydroxymethylene compounds, the addition as to the double linking between 2 carbon atoms:  $CHR:CH \cdot OH + NH_2 \cdot OH =$



T. H. P.

**Action of Bromoacetophenone on Thiocarbimides and Thiourethanes.** REINHOLD VON WALTHER and H. GREIFENHAGEN (*J. pr. Chem.*, 1907, [ii], 75, 201—211. Compare this vol., i, 349; Völtzkow, Abstr., 1881, 43).—The stability of the condensation products of *s*-diphenyl- and *s*-ditolyl-thiocarbamides with bromoacetophenone

towards hydrochloric acid rendered attempts to prepare oxythiazolines,  $\text{CO} \begin{smallmatrix} \text{NR} \cdot \text{CPh} \\ \diagdown \quad | \\ \text{S} \quad \text{CH} \end{smallmatrix}$ , by hydrolysis of the arylimino-group, unsuccessful.

It is found now that such oxythiazolines are formed when phenyl- or *p*-tolyl-thiocarbimide is heated with bromoacetophenone in alcoholic, but not in benzene, solution under pressure at  $110^\circ$ . The condensation takes place in three stages: the thiourethane,  $\text{NHR} \cdot \text{CS} \cdot \text{OEt}$ , formed in the first stage, reacts with the bromoacetophenone, forming ethyl bromide and the intermediate product,  $\text{NHR} \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2\text{Bz}$ , which undergoes ring condensation with loss of water. Oxythiazolines cannot be obtained from *o*- or *m*-tolylthiocarbimide, but are formed by the action of bromoacetophenone on phenyl-, *o*-*m*-, or *p*-tolyl-thiourethane in boiling alcoholic solution, the ring condensation being completed on prolonged boiling with glacial acetic acid. The intermediate substance,  $\text{NHR} \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2\text{Bz}$ , can be isolated only from the product of the action of bromoacetophenone on *o*-tolylthiourethane.

*2-Oxy-3:4-diphenyl-2:3-thiazoline* crystallises in small prisms, m. p.  $124^\circ$ , and has feeble basic properties.

Tolylthiocarbimides are formed in 80% yields by boiling *s*-ditolyl-thiocarbamides with acetic anhydride.

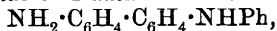
*2-Oxy-4-phenyl-3-p-tolyl-2:3-thiazoline*,  $\text{R} = \text{C}_7\text{H}_7$ , crystallises from alcohol in needles, m. p.  $130.5^\circ$ .

*2-Oxy-4-phenyl-3-m-tolyl-2:3-thiazoline* crystallises in needles, m. p.  $123^\circ$ , dissolves in concentrated acids, and is reprecipitated by dilution with water.

The compound,  $\text{o-C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COPh}$ , crystallises from alcohol in slender needles, m. p.  $138^\circ$ , dissolves in aqueous sodium hydroxide, forming a yellow solution, which has an odour of acetophenone, and yields a flocculent precipitate and an odour of hydrogen sulphide on addition of dilute sulphuric acid, and is converted slowly by cold concentrated sulphuric acid into *2-oxy-4-phenyl-3-o-tolyl-2:3-thiazoline*. This separates from glacial acetic acid in stout crystals, m. p.  $109^\circ$ , dissolves in concentrated acids, and when heated with concentrated sulphuric acid yields *o*-toluidine sulphate.

G. Y.

**Triphenylhydrazine.** MAX BUSCH and RICHARD HOBEIN (*Ber.*, 1907, 40, 2099—2102).—*Triphenylhydrazine*,  $\text{NPh}_2 \cdot \text{NHPh}$ , prepared by the interaction of magnesium phenyl bromide with phenylhydroxylamine, crystallises in colourless needles which turn brown at  $139^\circ$ , m. p.  $142^\circ$ . It shows no basic properties and dissolves in anhydrous sulphuric or acetic acids with a yellow coloration which changes to violet. The *nitrosoamine*,  $\text{NPh}_2 \cdot \text{NHPh} \cdot \text{NO}$ , forms reddish-brown needles, m. p.  $115^\circ$ . When cautiously treated with ethereal hydrogen chloride, a more or less green, crystalline, rearrangement product is formed, the *hydrochloride of 4-amino-4'-anilinodiphenyl*,



m. p.  $136\text{--}137^\circ$ . This dissolves in concentrated sulphuric acid with a violet-red coloration, and is coloured intensely violet-red by a trace of nitrate or nitrite.

*p*-Chlorophenylhydroxylamine and magnesium phenyl bromide under

similar conditions yield *p*:*p'*-dichloroazobenzene,  $C_6H_4Cl \cdot N:N \cdot C_6H_4Cl$ , m. p.  $184^\circ$ , crystallising in silky, glistening, yellow needles.

E. F. A.

**Additive Products of Trinitrobenzene Derivatives with Certain Aromatic Nitrogen Compounds.** III. ROBERTO CRUSA and C. AGOSTINELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 409—412. Compare Abstr., 1906, i, 891, 962).—The authors describe further additive products, including several formed from picryl chloride and phenylhydrazones of aromatic aldehydes. These compounds are sparingly soluble in ordinary solvents and, like the corresponding trinitrobenzene, trinitrotoluene, and trinitrophenol derivatives, exhibit variations in colour and solubility related to the different radicles present in the benzene nuclei of the original aldehydes. That these radicles influence also the stability of the additive products is seen from the facts that the phenylhydrazones of benzaldehyde, *m*-nitrobenzaldehyde, and anisaldehyde yield compounds with *m*-dinitrobenzene which exist in solution, but could not be isolated, whilst piperonaldehyde-phenylhydrazone gives a well crystallised, additive compound with *m*-dinitrobenzene. These results are related to the observation that *isosafrole* and *isoapiole*, which contain the dioxymethylene group, give more stable picrates than *isomethyleugenol* and *asarone*, which contain only methoxy-groups.

The conclusion is drawn that the phenylhydrazones exhibit behaviour analogous to that of the secondary amines. If derived from aliphatic aldehydes or ketones, they have a marked basic character and yield yellow picrates, whilst those derived from aromatic aldehydes exhibit no basic character and give intensely-coloured picrates, and trinitrobenzene and trinitrotoluene derivatives. Similarly, aliphatic secondary amines yield yellow picrates, whilst diphenylamine, the indoles and carbazole give intensely-coloured, additive products with aromatic polynitrohydrocarbon derivatives.

Benzaldehydephenylhydrazone and picryl chloride give the *compound*,  $C_{13}H_{12}N_2 \cdot 2C_6H_2O_6N_3Cl$ , which crystallises from alcohol in dark maroon, shining needles, m. p.  $90-91^\circ$ .

Piperonaldehydephenylhydrazone and picryl chloride give the *compound*,  $C_{14}H_{12}O_2N_2 \cdot 2C_6H_2O_6N_3Cl$ , crystallising from alcohol in almost black, shining needles, m. p.  $123^\circ$ .

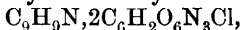
Piperonaldehydephenylhydrazone and *m*-dinitrobenzene yields the *compound*,  $C_{14}H_{12}O_2N_2 \cdot C_6H_4(NO_2)_2$ , which forms dark red, rhombic prisms, m. p.  $73-74^\circ$ .

Anisaldehydephenylhydrazone and picryl chloride give the *compound*,  $C_{14}H_{14}ON_2 \cdot 2C_6H_2O_6N_3Cl$ , crystallising in shining, black, flattened needles, m. p.  $92^\circ$ .

*m*-Nitrobenzaldehydephenylhydrazone and picryl chloride yield the *compound*,  $C_{13}H_{11}O_2N_3 \cdot 2C_6H_2O_6N_3Cl$ , which forms shining, brick-red needles, m. p.  $105^\circ$ .

Cinnamaldehydephenylhydrazone and picryl chloride give the *compound*,  $C_{15}H_{14}N_2 \cdot 2C_6H_2O_6N_3Cl$ , which separates in minute, brick-red needles, m. p.  $112-113^\circ$ , sparingly soluble in alcohol.

2-Methylindole and picryl chloride yield the *compound*,



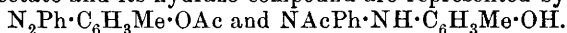
crystallising from alcohol in long, dark red needles, m. p. 115—116°.

3-Methylindole and picryl chloride give the *compound*,



which forms long, dark red needles, m. p. 112—113°. T. H. P.

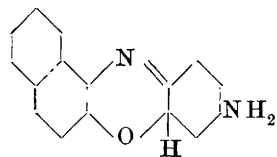
**Conversion of Quinonephenylhydrazones into Hydroxyazo-compounds.** KARL AUWERS (*Ber.*, 1907, 40, 2154—2159).—In a preliminary notice the author states briefly his reasons for regarding the acyl derivatives of hydroxyazo-compounds, excluding McPherson's quinonoid isomerides of the para series, as *O*-esters. Benzeneazo-*p*-cresol acetate and its hydrazo-compound are represented by



The latter should yield by careful oxidation the quinonoid *N*-acetate,  $\text{NAcPh}\cdot\text{N}:\text{C}_6\text{H}_3\text{Me}:\text{O}$ , but in all cases the ordinary, yellow *O*-ester is obtained.

The benzylation of  $\beta$ -benzeneazo- $\alpha$ -naphthol in pyridine produces a dark red benzoate, which is apparently different from McPherson's yellow benzoate obtained from  $\beta$ -naphthaquinone and  $\alpha$ -benzoylphenylhydrazine, but the two substances are shown to be identical by the method of mixed melting point, by their chemical transpositions, and by their crystallographic properties; the benzoate must be an *O*-ester, since it yields a hydrazo-compound by reduction. Similar results are recorded in the case of  $\beta$ -benzeneazo- $\alpha$ -naphthol acetate. In connexion with the wandering of the acetyl group which must take place during the change of the quinonoid structure into the benzene nucleus, the author quotes his experiments on *p*-alkylidenedihydrobenzenes (this vol., i, 399). C. S.

**Azoxonium Compounds. V. Azoxonium Compounds derived from  $\beta$ -Naphthaquinone.** FRIEDRICH KEHRMANN, H. DE GOTTRAU, and G. LEEMANN (*Ber.*, 1907, 40, 2071—2089).—The Nietzki-Otto dye (Abstr., 1888, 949) produced by condensation of quinonedichloroimide with  $\beta$ -naphthol contains an amide group, since in acid solution, on heating, the azo-group is removed and salts of naphthaphenazoxonium are formed. These are immediately further oxidised in the naphthalene nucleus, forming 3-aminophenonaphthazoxone. Similarly, the Nietzki-Otto compound, when ground with aniline, left exposed to the air for twenty-four hours, and treated with alcohol, gives rise to a metallic green powder and a violet filtrate; the former is 3-amino-6-anilinonaphthaphenazoxonium, whilst the violet dye contains the anilino-group substituted in the benzene nucleus; the



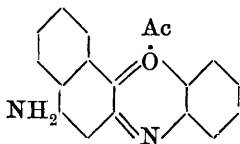
*leuco*-compound (annexed formula) crystallises as *hydrochloride* in bright yellow needles and forms an *acetyl* derivative of which the brownish-yellow crystals decompose at 210° and give a yellow, fluorescent solution. On oxidation with ferric chloride a reddish-violet coloration is produced which changes to purple-red and gives a dark red precipitate with sodium chloride

solution which slowly decolorises in water. The salts at first formed are unstable and oxidise to acetaminophenonaphthazoxone.

4-Amino-1 : 2-naphthaquinone and *o*-aminophenol condense in acid solution to a compound,  $C_{16}H_{12}ON_2$ , isomeric with the Nietzki dye, which is citron-yellow coloured and a pronounced base. Condensation in acetic acid solution leads to the production of the *acetate*. The *nitrate* forms dark brown, metallic, glistening needles; the *platini-chloride* is a brownish-red, crystalline powder, and the *dichromate* a bright red. The *base* gives an *anhydride* crystallising in straw-yellow, glistening needles, m. p.  $215^\circ$ . Nitrous acid is quite without action on the base. The *acetate* crystallises in orange-yellow, glistening needles, m. p.  $193-194^\circ$ , and forms magenta-red salts of undoubtable azoxonium constitution, whereas the base itself and its orange-red salts are true *p*-quinoneimide derivatives. *o*-Amino-*m*-cresol yields a similar red dye, forming a red *platini-chloride* and orange-yellow *acetate*, decomposing at  $170-180^\circ$ .

4-Acetylamino- $\beta$ -naphthaquinone condense to a *pseudo-base*,  $C_{18}H_{14}O_3N_2$ , decomposing at  $160-170^\circ$ , of which the greenish-yellow crystals give a reddish-violet coloration in concentrated sulphuric acid. The *chloride* is red and can also be prepared by direct condensation with *o*-aminophenol hydrochloride.

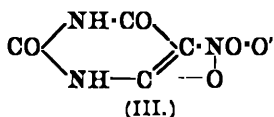
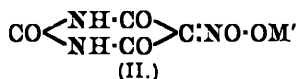
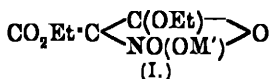
9-Aminoisonaphthaphenazoxonium salts :—the *methylate* of the *pseudo-base*,  $C_{17}H_{14}O_2N_2$ , forms sulphur-yellow needles, m. p.  $170^\circ$  (decomp.), which dissolve in sulphuric acid with a magenta-red coloration; the *chloride* forms blackish-violet crystals and the *platini-chloride* glistening, violet needles. The *chloride* gives a blood-red solution in warm water, which, on evaporation, yields violet and yellow crystals, the former corresponding with the oxonium and the latter with the quinoneimide formula. The *pseudo-base*,  $C_{19}H_{16}O_3N_2$ , obtained in a similar manner from *o*-amino-*m*-cresol and acetylamino-naphthaquinone, decomposes at  $170-180^\circ$ , dissolves in sulphuric acid with a bluish-violet coloration, and forms orange-red oxonium salts. The *pseudo-base* of 9-amino-2-methylisonaphthaphenazoxonium decomposes at  $160^\circ$  and behaves similarly to the lower homologue. E. F. A.



Colourless, Yellow, and Red Salts of Nitro-ketones. ARTHUR HANTZSCH [and, in part, A. SALWAY] (*Ber.*, 1907, 40, 1523—1532; compare this vol., i, 500, 513).—The salt-forming nitro-ketones containing the group  $\cdot CO \cdot CH(NO_2) \cdot$  are closely related to the *o*-nitrophenols, the grouping  $\cdot C(OH) \cdot C(NO_2) \cdot$ , formed in the case of the former by enolisation, being present in both classes. In agreement with this is the formation by nitro-ketones of red and yellow salts; more important, however, is the formation of colourless salts, unknown in the case of the nitrophenols, which shows that, contrary to Kauffmann's view, a metallic atom or the group  $\cdot OM'$  has no auxochromic properties.

Of the substances containing the grouping  $\cdot CO \cdot CH(NO_2) \cdot$  which have been investigated, nitromalonamide, having the affinity constant

$K = 0.058$ , forms with colourless metallic ions, colourless salts yielding colourless solutions. Ethyl nitromalonate,  $K = 0.073$ , forms colourless salts,  $\text{OM}'\cdot\text{NO}\cdot\text{C}(\text{CO}_2\text{Et})_2$ , which are yellow in aqueous solution when the structure of the ion may correspond to the salt (I). The mono-metallic salts of nitrobarbituric acid are colourless when solid, but yellow in aqueous solution; the solid salts are considered to have the structure (II), but the yellow ion the structure (III).



The di- and tri-metallic salts of nitrobarbituric acid, which are yellow, must be derived from the coloured ion.

Contrary to statements in the literature, nitrodimethylbarbituric acid, when free from dimethylvioluric acid, yields only two series of salts: colourless salts,  $\text{CO}\begin{array}{c} \text{NMe}\cdot\text{CO} \\ \text{NMe}\cdot\text{CO} \end{array}\text{C}\cdot\text{NO}\cdot\text{OM}'$  ( $\text{M}' = \text{NH}_4$  or  $\text{Ag}$ ),

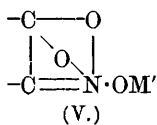
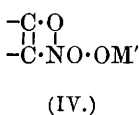
and yellow salts,  $\text{CO}\begin{array}{c} \text{NMe}\cdot\text{C} \\ \text{NMe}\cdot\text{CO} \end{array}\text{C}\cdot\text{NO}\cdot\text{OM}'$  ( $\text{M}' = \text{Li}, \text{Na}, \text{K}, \text{Rb},$

$\text{Cs}$ , or  $\text{NPhMe}_3$ ); the aqueous solutions are yellow, whilst the *aci*-ether,  $\text{CO}\begin{array}{c} \text{NMe}\cdot\text{CO} \\ \text{NMe}\cdot\text{CO} \end{array}\text{C}\cdot\text{NO}\cdot\text{OMe}$ , is colourless.

4-Nitro-1-phenyl-3-methylpyrazolone forms yellow *lithium*, *ammonium*, and *trimethylammonium* salts which crystallise with 1 mol. of water of crystallisation; the yellow sodium salt ( $\text{H}_2\text{O}$ ) is formed in aqueous solution, or anhydrous by the action of sodium ethoxide on the nitropyrazolone in benzene solution; when boiled with toluene it is converted into a red, anhydrous salt. The *potassium* salt ( $\text{H}_2\text{O}$ ) is yellow, loses  $\text{H}_2\text{O}$  at  $135^\circ$  without change of colour, but at  $150^\circ$  is converted into the red, anhydrous salt. The anhydrous *silver* and *mercurous* salts are colourless.

In the discussion of these experimental results, it is noted that the formation of yellow solutions from colourless salts is at variance with the view previously put forward that colour does not appear on simple ionisation. The formation of coloured salts cannot depend on the extent of the isomerisation of the enolic nitro-ketone, since the nitropyrazolone, which is only a feeble acid, behaves similarly to the strongly acid nitrodimethylbarbituric acid, neither can the colour be connected with the presence or absence of water of crystallisation. The nature of the "colourless" metallic ion has a certain influence, since the strongly positive alkali metals have more tendency to the formation of coloured salts than the more feebly positive ammonium, silver, or mercury; on the other hand, the tendency to the formation of the red salt of the nitropyrazolone is more pronounced with sodium than with the more positive of the alkali metals.

It is argued that the colourless (*leuco*-) salts and ethers are derivatives of the *aci*-nitro-ketones containing the group  $\text{-CO}\cdot\text{C}(\text{NO}\cdot\text{OH})\text{-}$ , whilst the coloured (*chromo*-) salts contain the grouping (IV); the yellow and red salts are possibly *syn*- and *anti*-stereoisomerides, but may be structural isomerides, one containing the preceding grouping, the other the grouping (V).



G. Y

[Carbalkyloxy-5:5-dialkylbarbituric Acids.] WILHELM TRAUBE (D.R.-P. 180424).—In the condensation of dialkylmalonyl chlorides with urethanes the main product is a dialkylmalonylurethane, but a further decomposition occurs to some extent, leading to the formation of a carbalkyloxydialkylbarbituric acid. Thus diethylmalonyl chloride and urethane when heated for some time in boiling zylene yield principally diethylmalonyldiurethane, but carbethoxydiethylmalonide and *carbethoxydiethylbarbituric acid*, m. p. 60–65°,  $\text{CO}\langle\text{CEt}_2\cdot\text{CO}\rangle\text{N}\cdot\text{CO}_2\text{Et}$ , are also produced.

The latter which is isolated by distillation under reduced pressure is converted into diethylbarbituric acid by the action of either fuming sulphuric acid or alkaline agents such as sodium ethoxide.

*Carbethoxydipropylbarbituric acid* is similarly prepared, but has not been obtained crystalline; it is readily converted into dipropylbarbituric acid.

G. T. M.

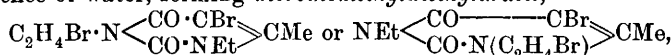
**Alkyl Derivatives of Methyluracil.** OTTO HOEBEL (*Annalen*, 1907, 353, 242–266. Compare Behrend and Dietrich, *Abstr.*, 1900, i, 120; Behrend and Thurm, *Abstr.*, 1902, i, 832).—It was shown by Behrend and Fricke (*Abstr.*, 1903, i, 739) that hydroxy-1:4-dimethyluracil is obtained on oxidation of trimethyluracil by means of potassium permanganate, and by Behrend and Hufschmidt (*Abstr.*, 1906, i, 310) that whilst on oxidation 1:4-dimethyluracil yields hydroxy-1:4-dimethyluracil, 3:4-dimethyluracil is oxidised to hydroxy-4-methyluracil. This difference in the stability towards oxidising agents of alkyl groups in positions 1 and 3 in uracil has been studied now in the case of ethyl and benzyl derivatives of 4-methyluracil. It is found that whilst 4-methyl-1-ethyluracil,  $\text{NEt}\langle\text{CO}\cdot\text{CH}\rangle\text{CMe}$ , on oxidation in acetic acid solution with potassium permanganate, equivalent to two atoms of oxygen, yields hydroxy-4-methyl-1-ethyluracil,  $\text{NEt}\langle\text{CO}\cdot\text{C}(\text{OH})\rangle\text{CMe}$ , under the same conditions 4-methyl-3-ethyluracil,  $\text{NH}\langle\text{CO}\cdot\text{CH}\rangle\text{CMe}$ , yields acetaldehyde, hydroxy-4-methyluracil,  $\text{NH}\langle\text{CO}\cdot\text{C}(\text{OH})\rangle\text{CMe}$ , and oxaluric acid. Ethyloxaluric acid,  $\text{NH}_2\cdot\text{CO}\cdot\text{NEt}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (?), is formed from both methylethyluracils on oxidation with potassium permanganate equivalent to three atoms of

oxygen in alkaline solution, but together with acetylmethyluracil,  $\text{NHEt}\cdot\text{CO}\cdot\text{NHAc}$ , from 4-methyl-1-ethyluracil only.

The benzyl groups of 1-benzyl- and 3-benzyl-4-methyluracils undergo oxidation more easily than the ethyl groups of the above methylethyluracils, since both benzyl compounds yield considerable amounts of benzaldehyde and benzoic acid. The 1-benzyl compound is more stable than its isomeride, since it yields hydroxybenzylmethyluracil,  $\text{CH}_2\text{Ph}\cdot\text{N}\langle\begin{smallmatrix} \text{CO}\cdot\text{C}(\text{OH}) \\ \text{CO}\text{---NH} \end{smallmatrix}\rangle\text{CMe}$  (?), together with traces of oxaluric acid, whilst much oxaluric acid, but no hydroxybenzylmethyluracil, is obtained on oxidation of the 3-benzyl compound. Both benzyl compounds yield also the same benzyloxaluric acid, but no acetylbenzylcarbamide.

The action of ethyl bromide on potassium 4-methyluracil in alcoholic solution on the water-bath leads to the formation of two isomeric ethyl derivatives (compare Hoffmann, Abstr., 1890, 31). 4-Methyl-3-ethyluracil crystallises from absolute alcohol in needles, m. p.  $195^\circ$ , and on methylation yields 1:4-dimethyl-3-ethyluracil, m. p.  $110^\circ$  (Behrend and Thurm, *loc. cit.*). 4-Methyl-1-ethyluracil crystallises from water in microscopic needles, m. p.  $195^\circ$ , is soluble in alcohol, and on methylation yields 3:4-dimethyl-1-ethyluracil, m. p.  $111.5\text{---}113.5^\circ$  (Behrend and Thurm, *loc. cit.*). A mixture of the two methylethyluracils has m. p.  $160\text{---}165^\circ$ .

4-Methyl-1:3-diethyluracil (Hoffmann, *loc. cit.*), which is formed together with the monoethyl compounds, reacts with bromine in presence of water, forming *dibromomethyldiethyluracil*,



which crystallises in octahedra, m. p.  $121\text{---}122^\circ$ , and on treatment with an excess of bromine yields *tribromohydroxymethyldiethyluracil*,  $\text{C}_2\text{H}_4\text{Br}\cdot\text{N}\langle\begin{smallmatrix} \text{CO}\cdot\text{CBr}_2 \\ \text{CO}\cdot\text{NEt} \end{smallmatrix}\rangle\text{CMe}\cdot\text{OH}$  or  $\text{NEt}\langle\begin{smallmatrix} \text{CO}\text{---}\text{CBr}_2 \\ \text{CO}\cdot\text{N}(\text{C}_2\text{H}_4\text{Br}) \end{smallmatrix}\rangle\text{CMe}\cdot\text{OH}$ , m. p.  $94\text{---}97^\circ$ ; this is reconverted into the dibromo-compound on prolonged boiling with absolute alcohol.

The action of benzyl chloride on potassium methyluracil in alcoholic solution on the water-bath leads to the formation of a mixture of benzylmethyluracils, of which the more sparingly soluble in alcohol is *3-benzyl-4-methyluracil*, crystallising in microscopic, hexagonal leaflets, m. p.  $232\text{---}233^\circ$ . On methylation this yields *3-benzyl-1:4-dimethyluracil*, crystallising in hexagonal leaflets, m. p.  $82^\circ$ .

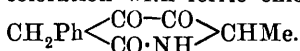
1-Benzyl-4-methyluracil crystallises from alcohol in microscopic, rectangular leaflets, m. p.  $174\text{---}177^\circ$ , and on methylation yields 1-benzyl-3:4-dimethyluracil, long needles, m. p.  $159\text{---}161^\circ$ , which is formed also by benzylation of 3:4-dimethyluracil.

*Hydroxy-4-methyl-1-ethyluracil* decomposes at  $230^\circ$ , gives a blue coloration with ferric chloride, and forms an *acetyl* derivative,  $\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$ , which crystallises in needles, m. p.  $189^\circ$ .

*Ethylloxaluric acid*,  $\text{C}_5\text{H}_8\text{O}_4\text{N}_2$ , crystallises in glistening leaflets, decomposes at  $167\text{---}169^\circ$ , and gives the characteristic reaction for oxaluric acids with ammonia and calcium chloride (compare Behrend and Grünwald, Abstr., 1902, i, 834).



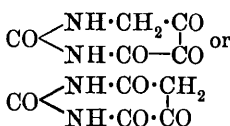
*Hydroxy-1-benzyl-4-methyluracil* crystallises from methyl alcohol in leaflets and commences to decompose at  $220^{\circ}$ ; as it does not give a blue coloration with ferric chloride, it may have the ketonic constitution



*Benzylloxaluric acid* crystallises from alcoholic hydrochloric acid in needles, m. p.  $157\text{--}159^{\circ}$  (decomp.), and gives the oxaluric acid reaction with ammonia and calcium chloride; it was obtained only in small amount, has not been analysed, and might be possibly benzoyloxaluric acid.

*5:5-Dibromohydroxy-1-benzyl-4-methyluracil*, prepared by the action of bromine on 1-benzyl-4-methyluracil, is obtained as a white powder, decomposes at  $98\text{--}105^{\circ}$ , evolves benzaldehyde at  $110^{\circ}$ , and when boiled with absolute alcohol yields *5-bromo-1-benzyl-4-methyluracil*, which crystallises in small needles, and decomposes at  $238^{\circ}$ . G. Y.

**Pyrimidines: Synthesis of Uracil-5-carboxylic Acid.** HENRY L. WHEELER, TREAT B. JOHNSON, and CARL O. JOHNS (*Amer. Chem. J.*, 1907, 37, 392—405).—Biscaro and Belloni (*Abstr.*, 1905, i, 672) have



isolated a substance from milk which they have termed "orotic acid" and which they regard as having the annexed structure. It is pointed out that the properties of this compound and the fact that it yields carbamide on oxidation, rendered it probable that it might be a pyrimidine and

possibly either uracil-4-carboxylic acid,  $\text{NH} \begin{array}{c} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH} \end{array} \text{C} \cdot \text{CO}_2\text{H}$ , or

uracil-5-carboxylic acid,  $\text{NH} \begin{array}{c} \diagup \text{CO} \text{---} \text{NH} \\ \diagdown \text{CO} \cdot \text{C}(\text{CO}_2\text{H}) \end{array} \text{CH}$ . Both these com-

pounds have now been prepared; the latter is described in the present paper and an account of the former will be given later. Uracil-5-carboxylic acid is not identical with orotic acid, although it resembles it in many respects.

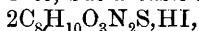
When an alkaline, aqueous solution of ethyl- $\psi$ -thiocarbamide hydrobromide is treated with ethyl ethoxymethylenemalonate, *ethyl 2-ethylthiol-6-oxypyrimidine-5-carboxylate*,  $\text{NH} \begin{array}{c} \diagup \text{C}(\text{SEt}) \text{---} \text{N} \\ \diagdown \text{CO} \cdot \text{C}(\text{CO}_2\text{Et}) \end{array} \text{CH}$ , m. p.  $131^{\circ}$ , is obtained, which forms long, colourless prisms or needles, is soluble in hot alcohol, and has both acid and basic properties.

*Ethyl uramidomethylenemalonate*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH} \cdot \text{C}(\text{CO}_2\text{Et})_2$ , m. p.  $206^{\circ}$  (decomp.), which is also produced in this reaction, crystallises in colourless prisms and has acid properties. *2-Ethylthiol-6-oxypyrimidine-5-carboxylic acid*, m. p.  $167^{\circ}$ , forms colourless plates, dissolves readily in hot alcohol, and when warmed with hydrochloric acid yields mercaptan and uracil-5-carboxylic acid.

*Uracil-5-carboxylic acid*, m. p.  $278^{\circ}$  (decomp.), forms minute, colourless pyramids containing  $1\text{H}_2\text{O}$ , and is sparingly soluble in water. When this substance is heated alone above its m. p., uracil is produced. Uracil is also formed when the acid is heated with sulphuric acid in a sealed tube at  $160\text{--}169^{\circ}$  or boiled with concentrated hydrochloric acid. The *ethyl* ester, m. p.  $236\text{--}237^{\circ}$ ; the *methyl* ester, m. p.

225—233° (decomp.), and the *ammonium*, *potassium*, *barium*, and *silver* salts are described. The *dimethyl* derivative, m. p. 254—256°, obtained by the action of methyl iodide on the di-silver salt, crystallises in small prisms; the corresponding *diethyl* derivative, m. p. 162—163°, forms clusters of blunt prisms.

When ethyl ethoxymethylenemalonate is treated with methyl- $\psi$ -thiocarbamide hydriodide, ethyl 2-methylthiol-6-oxypyrimidine-5-carboxylate does not separate, but a basic *hydriodide*,



is produced, which crystallises in needles. When this salt is warmed with potassium hydroxide, 2-methylthiol-6-oxypyrimidine-5-carboxylic acid,  $N \begin{array}{c} \diagup C(SMe) = N \\ \diagdown CO \cdot C(CO_2H) \end{array} CH$ , m. p. 235°, is obtained, which separates from hot water in colourless prisms. E. G.

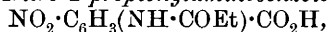
**Condensations with Carbamide; Carbamide as a Source of Ammonia.** OTTO KYM (*J. pr. Chem.*, 1907, [ii], 75, 323—327).—2-Hydroxy- and 2-mercapto-benziminazoles are prepared best by heating *o*-phenylenediamine with carbamide at 130—140° and with thiocarbamide at 170—180° respectively.

When heated with carbamide at 200—210° for eight hours, 2:4-dinitrophenol is converted to the extent of 75% into 2:4-dinitroaniline; dinitro- $\alpha$ -naphthol to the extent of 77% into dinitro- $\alpha$ -naphthylamine, and 3:5-dinitro-*o*-cresol to the extent of 47% into 3:5-dinitro-*o*-toluidine. G. Y.

**Quinazolines. XVIII. 2:3-Dialkyl-4-quinazolones [4-Keto-2:3-dialkyldihydroquinazolines] and the Products obtained by Alkylating 2-Alkyl-4-quinazolones (4-Hydroxy-2-alkyl-quinazolines).** MARSTON T. BOGERT and HARVEY A. SEIL (*J. Amer. Chem. Soc.*, 1907, 29, 517—536).—The existence of two series of derivatives in the quinazoline group, namely, oxygen derivatives,  $\cdot C(OR):N\cdot$ , and nitrogen derivatives,  $\cdot CO \cdot NR\cdot$ , has long been recognised and the present work was undertaken with the object of ascertaining the relative extent to which these derivatives are produced in the alkylation of 4-hydroxyquinazolines (4-quinazolones) and the factors which determine their formation. A *résumé* is given of the results already obtained in this direction by various workers with  $\alpha$ -hydroxypyridines ( $\alpha$ -pyridones), carbostyrils ( $\alpha$ -quinolones), isocarbostyrils ( $\alpha$ -isoquinolones), 6-hydroxypyrimidines (6-pyrimidones), and 4-hydroxyquinazolines (4-quinazolones), and the following general conclusions are drawn. When alkylation is effected by methyl iodide or methyl sulphate in presence of alcohol and alkali hydroxide, the *N*-methyl derivative is always produced and, in some cases, small quantities of the *O*-ether also are formed. When an ethyl halide is used, the likelihood of obtaining the *O*-ether is considerably greater. On treating the silver salt with methyl iodide, both *O*- and *N*-derivatives are produced, but with ethyl iodide it frequently happens that the pure *O*-ether is obtained. Oxygen ethers are best prepared by the action of the alkyloxy on the chloro-derivatives. The *O*-ethers have higher m. p.'s and b. p.'s, are more likely to have an odour, are more readily

hydrolysed by mineral acids, and are more stable towards oxidising agents than the corresponding *N*-derivatives. Many *O*-ethers have been converted into the corresponding *N*-isomerides by the action of heat or by other means, but the reverse transformation does not appear to have ever been effected.

The preparation of the alkylidihydroquinazolines which are described was effected by the condensation of acylantranils with ammonia and primary amines. 6-Nitro-2-propionylaminobenzoic acid,



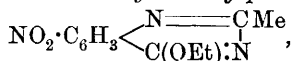
m. p. 218° (corr.), forms hard, transparent crystals and is converted by acetic anhydride into the corresponding *anthranil*. 4-Keto-2:3-dimethyldihydroquinazoline (4-hydroxy-2:3-dimethylquinazoline),

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{CO} \cdot \text{NH} \end{array} \rightleftharpoons \text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{C}(\text{OH}) \cdot \text{N} \end{array},$$

from acetylanthranil and methylamine, is identical with the compound obtained by Weddige (Abstr., 1887, 1044) by the methylation of 4-hydroxy-2-methylquinazoline. 7-Nitro-4-keto-2-methyl-3-ethylidihydroquinazoline,

$\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{CO} \cdot \text{NEt} \end{array}$ , has m. p. 175° (corr.), and the corresponding 2-methyl-3-isoamyl compound has m. p. 117—118°. Bromo-5-nitro-3-diacylamino-4-keto-2-methyldihydroquinazoline has m. p. 170°. 5-Nitro-4-keto-2-ethylidihydroquinazoline (5-nitro-4-hydroxy-2-ethylquinazoline) has m. p. 240° (corr.), and crystallises well from dilute alcohol. 5-Nitro-4-keto-3-methyl-2-ethylidihydroquinazoline and the corresponding 2:3-diethyl compound have m. p. 197—198° (corr.) and 181° (corr.) respectively.

On methylating 5-nitro-4-keto-2-methyldihydroquinazoline (Bogert and Chambers, Abstr., 1905, i, 615), 5-nitro-4-keto-2-ethylidihydroquinazoline, and 7-nitro-4-keto-2-methyldihydroquinazoline (Bogert and Steiner, Abstr., 1905, i, 946), the *N*-derivative only was obtained in each case, whether the reaction was carried out at the ordinary pressure or in a sealed tube. On ethylation, however, only the *O*-ethers were usually produced. 5-Nitro-4-ethoxy-2-methylquinazoline,



m. p. 161° (corr.), can be repeatedly crystallised from alcohol without being converted into its *N*-isomeride. When the ethylation of 5-nitro-4-keto-2-ethylidihydroquinazoline takes place under the ordinary pressure, the pure *O*-ether is obtained, but if the reaction is carried out in a sealed tube a mixture of the *O*- and *N*-isomerides is produced. 5-Nitro-4-ethoxy-2-ethylquinazoline, m. p. 148—149°, is completely transformed into the corresponding *N*-derivative by recrystallisation from alcohol. 7-Nitro-4-ethoxy-2-methylquinazoline, m. p. 105—106° (corr.), is not changed on recrystallisation. 7-Nitro-4-isoamyloxy-2-methylquinazoline, m. p. 104° (corr.), forms large, flat plates, and does not show any tendency to undergo rearrangement.

E. G.

**New Dyes obtained from Triphenylmethane.** MAURICE PRUD'HOMME (*Bull. Soc. ind. Mulhouse*, 1907, 79—81).—If reduced with zinc dust and hydrochloric acid in cooled aqueous or aqueous-

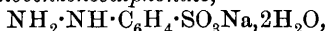
alcoholic solution, *o*-nitrophenyl- and *m*-nitrophenyl-tetramethyldiaminodiphenylmethanes yield the corresponding *hydroxylamino*-derivatives,  $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{OH}$ , which when heated with hydrochloric acid undergo transformation into 2-amino-5-hydroxyphenyl- and 5-amino-2-hydroxyphenyl-tetramethyldiaminodiphenylmethane,  $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{OH}$ , yielding a bluish-green and a greenish-yellow dye respectively on oxidation with lead dioxide and acetic acid. It is considered that the amino-groups are protected from the action of the oxidising agent by the *p*-hydroxyl groups. No advantage is gained by sulphonation of these aminohydroxy-dyes, as is the case in the formation of patent-blue.

The 2-amino-5-hydroxy-compound dissolves partially in ammonia, forming a blue solution, which is decolorised only slowly; the dye obtained on acidification of this solution has a purer shade than the crude dye. On diazotisation in presence of the theoretical amount of hydrochloric acid cooled by ice, the 2-amino-5-hydroxy-dye yields a blue solution, and when boiled is converted into 2:5-dihydroxyphenyl-tetramethyldiaminodiphenylmethane,  $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$ . The product, obtained on oxidation of this with lead dioxide and acetic acid, dyes unmordanted wool, or silk, black or grey, and cotton, mordanted with tannin and tartar emetic, grey. The same dihydroxy-compound must be obtained from the 5-amino-2-hydroxy-dye.

G. Y.

**Some Semicarbazide Derivatives of *iso*Propionic Acid, Benzoic Acid, and Benzenesulphonic Acid.** SALOMON F. ACREE (*Amer. Chem. J.*, 1907, 37, 361—369).—In connexion with the physico-chemical study of semicarbazides and urazoles, it became necessary to obtain substances of greater solubility in water than that possessed by most of the phenyl derivatives of these compounds. Some such substances, containing an acid side-chain, have already been prepared by Bailey and Acree (*Abstr.*, 1900, i, 528), and others are now described.

*Sodium p-hydrazinobenzenesulphonate*,



is white. By the action of potassium cyanate on *p*-hydrazinobenzenesulphonic acid, *α*-semicarbazino-*p*-benzenesulphonic acid,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ , m. p. 243°, is obtained, which is very soluble in water; the *potassium* salt is white, crystalline, and anhydrous, and rapidly reduces potassium permanganate.

*α*-Carbethoxysemicarbazino-*α*-isopropionitrile,



m. p. 173°, prepared by boiling *α*-semicarbazinoisopropionitrile (Bailey and Acree, *loc. cit.*) with ethyl chlorocarbonate, crystallises from alcohol, is very soluble in acetone and fairly so in water or alcohol, and on hydrolysis yields *urazole-α*-isopropionic acid.

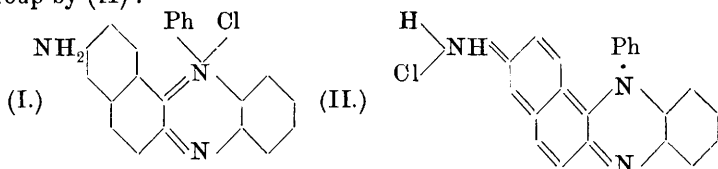
The *hydrobromide* of *o*-hydrazinobenzoic acid (Fischer, *Abstr.*, 1880, 647), m. p. 207—210°, crystallises in needles.

*α*-*o*-Semicarbazinobenzoic acid,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 225°, obtained by the action of potassium cyanate on *o*-hydrazinobenzoic acid, is very soluble in alcohol and fairly so in water, and

yields a white *silver* salt which rapidly darkens. Potassium permanganate solution is instantly decolorised by the acid, and on adding sulphuric acid a red precipitate is formed which is probably the azocarbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ .

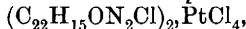
When *potassium*  $\delta$ -phenyl- $\alpha$ -o-thiosemicarbazinobenzoate,  $\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ , obtained by the interaction of potassium o-hydrazinobenzoate and phenylthiocarbimide, is treated with dilute sulphuric acid, the corresponding *anhydride*,  $\text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{CO} - \text{S} \end{smallmatrix} \cdot \text{C} \cdot \text{NHPh}$ , m. p.  $238^\circ$ , is produced, which is insoluble in alkali hydroxides. E. G.

**A New Type of Quinonoid Grouping in Onium Compounds.** FRIEDRICH KEHRMANN [and in part C. SABO and WERNER-GRESLEY] (*Ber.*, 1907, 40, 1960—1966. Compare Willstätter and Parnas, this vol., i, 425).—The azonium dye of the constitution (I) differs in its physical and chemical properties from those of its isomerides which do not contain the amino-group in the *p*-position to any of the azine nitrogen atoms. The author represents a *bicyclo-p*-quinonoid group by (II):



which is an alternative formula for the azonium one.

6-Hydroxy-1:2-naphthaquinone is prepared as follows. 2:6-Dihydroxynaphthalene is dissolved in an ice-cold aqueous solution of sodium hydroxide and converted into the corresponding azo-dye by coupling with diazobenzene chloride. When the dye is reduced by stannous chloride, 1-amino-2:6-dihydroxynaphthalene hydrochloride is formed, which, when oxidised by ferric chloride, is converted into the above quinone, which separates from acetone in brick-red leaflets, decomposing at about  $165^\circ$ . The solution of the quinone in cold water is golden-yellow. When added to a solution of o-aminodiphenylamine hydrochloride in alcohol, containing a little sulphuric acid, the quinone is readily dissolved, and from the solution, 7-hydroxyphenylisonaphthaphenazonium chloride was obtained in glistening, reddish-brown needles. The *platinichloride*,



was analysed.

The condensation of 6-acetylamino- $\beta$ -naphthaquinone with o-aminophenol is also described in this preliminary communication.

A. MCK.

**apoSafranin and its Homologues.** PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1907, [iv], 1, 468—474. Compare Abstr., 1906, i, 51, 989; 1907, i, 160).—Since commercial pheno-safranin has been shown to consist of about 85% of the *as*-compound

with 15% of the *s*-isomeride (*loc. cit.*), the *aposafranine* prepared from it by diazotisation and subsequent boiling of the diazo-compound with alcohol may have the constitution  $C_6H_3:NH \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} > C_6H_4$  or

$C_6H_4 \begin{smallmatrix} \text{N} \\ \text{NCl}(C_6H_4 \cdot NH_2) \end{smallmatrix} > C_6H_4$ , although possibly the latter may be unstable and only the first form will be produced in the reaction.

*apoSafranine* may be prepared by heating *p*-aminoazobenzene hydrochloride with aniline hydrochloride dissolved in water saturated with aniline in a closed vessel at 160–170°. The *hydrochloride* forms small copper-coloured crystals, and the *platinichloride* is a crystalline powder. The dye gives a magenta-red solution in water; the alcoholic solution is strongly dichroic, and that with sulphuric acid is violet, but becomes red on dilution. The dye can be diazotised and then coupled with naphthol-sulphonic acids, yielding colouring matters which may have commercial applications. In addition to *aposafranine* there is formed a small quantity of Caro's "soluble induline." The formation of *aposafranine* is regarded as taking place according to the following equations:

(1)  $NPh:N \cdot C_6H_4 \cdot NH_2 = NPh \cdot C_6H_3 \begin{smallmatrix} NH \\ NH \end{smallmatrix}$ , (2)  $NPh \cdot C_6H_3 \begin{smallmatrix} NH \\ NH \end{smallmatrix} + NH_2Ph = NH:C_6H_3 \begin{smallmatrix} N \\ NPh \end{smallmatrix} > C_6H_4 + NH_3 + H_2$ , whilst Caro's "soluble

induline," which is represented as  $C_6H_4 \begin{smallmatrix} N \\ NPh \end{smallmatrix} > C_6H_2(NHPh):NPh$ , is regarded as being produced by a condensation, similar to that which takes place in the case of *aposafranine*, from some dianilinoquinoneanilimide,  $NPh:C_6H_2(NHPh)_2:NH$ , initially formed.

*Homoaposafranine*,  $C_6H_4 \begin{smallmatrix} N \\ NPh \end{smallmatrix} > C_6H_2Me:NH$ , obtained by the action of diazoaminobenzene on *o*-toluidine hydrochloride, furnishes a *hydrochloride* which occurs as a microcrystalline, bronze powder; the aqueous solution is reddish-violet and the alcoholic solution is intensely dichroic. *isoHomoaposafranine*, obtained by the action of *o*-toluidine hydrochloride on *p*-aminoazobenzene, closely resembles its isomeride.

*Toluaposafranine*,  $C_6H_3Me \begin{smallmatrix} N \\ N \cdot C_6H_4Me \end{smallmatrix} > C_6H_2Me:NH$ , obtained by the action of *o*-toluidine hydrochloride on *p*-aminoazotoluene, furnishes a reddish-brown *hydrochloride*, which is very soluble in water.

All these *aposafranines* dye cotton and silk, previously treated with tannic acid, in red shades, which become more violet as the molecular weight increases, but they are inferior in tinctorial power when compared with the corresponding safranines. T. A. H.

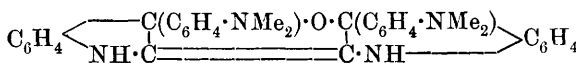
**So-called "Dihydratotetrazine."** MAX BUSCH (*Ber.*, 1907, 40, 2093–2095).—In addition to the evidence cited by Curtius, Darapsky, and Müller (this vol., i, 262, 451), the author (*Abstr.*, 1901, i, 616) showed formerly that the so-called urazines are in reality aminotriazoles. Thus from ethyl phenylmethylphenylcarbazidecarbonylate a triazole, anilinophenylmethylurazole, was obtained, which on elimination of methyl formed diphenylurazine.

The paper further contains a polemical discussion of the views of

Bülöw and Stollé as to the interpretation of urazines as tetrazines or triazoles. E. F. A.

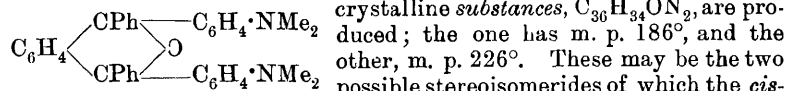
**Extension of the Friedel-Craft Reaction.** ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1907, 144, 947—951).—*tert.*-Aromatic amines and certain *sec.*-amines, for example, diphenylamine, alone or dissolved in a neutral solvent, condense readily in presence of aluminium chloride with a great number of organic compounds, notably the oxalic esters and the ketones. In the latter case, the amine appears to be simply attached to the carbon of the carbonyl group, giving rise to a *tert.*-carbinol group, thus:  $C(OH) \cdot C_6H_4 \cdot NR_2$ , with in some cases the subsequent elimination of one or more mols. of water. In this respect the reaction somewhat resembles the condensations brought about by the action of zinc chloride. The reaction does not take place unless the ketone is distinctly acidic in character; thus, whilst benzophenone condenses readily with dimethylaniline in presence of aluminium chloride, no reaction takes place between Michler's tetramethyl-diaminobenzophenone and the amine.

Indigotin condenses with dimethylaniline to form a *product*, m. p.  $272^\circ$ , which crystallises in orange leaflets, and probably



has the annexed constitution. With benzil the same amine furnishes a *substance*,  $C_{30}H_{30}ON_2$ , m. p.  $214^\circ$ , which crystallises in pale yellow needles, and may have the formula  $O \left\langle \begin{array}{c} CPh \cdot C_6H_4 \cdot NMe_2 \\ CPh \cdot C_6H_4 \cdot NMe_2 \end{array} \right\rangle$ , or

$CPh(C_6H_4 \cdot NMe_2)_2 \cdot CPh$ , or  $CPh_2(C_6H_4 \cdot NMe_2)$  (?). It does not yield a semicarbazone. With *o*-dibenzoylbenzene two isomeric, colourless,



crystalline *substances*,  $C_{36}H_{34}ON_2$ , are produced; the one has m. p.  $186^\circ$ , and the other, m. p.  $226^\circ$ . These may be the two possible stereoisomerides of which the *cis*-form would have the annexed formula, or, as the result of transformation of dihydrobenzoisofuran derivatives first formed (compare Guyot and Catel, *Abstr.*, 1906, i, 761), they may be anthracene compounds of the following constitution,  $C_6H_4 \left\langle \begin{array}{c} CPh \cdot (C_6H_4 \cdot NMe_2) \\ CPh(OH) \end{array} \right\rangle C_6H_3 \cdot NMe_2$

or  $NMe_2 \cdot C_6H_4 \cdot C(OH) \left\langle \begin{array}{c} C_6H_4 \\ C_6H_4 \end{array} \right\rangle CPh \cdot C_6H_4 \cdot NMe_2$ . Ethyl phenylgly-oxalate condenses with dimethylaniline to form *ethyl tetramethyl-diaminotriphenylacetate*,  $CPh(C_6H_4 \cdot NMe_2)_2 \cdot CO_2Et$ , m. p.  $98^\circ$ , which crystallises in colourless leaflets, and when warmed with sulphuric acid evolves carbon dioxide and is transformed into malachite-green. With benzophenone, *p*-dimethylaminotriphenylcarbinol (Ehrlich and Sachs, *Abstr.*, 1904, i, 196) is supposed to be produced, but the product obtained was a brown, viscous mass instead of the crystalline material described under this name by Baeyer and Villiger (*Abstr.*, 1904, i, 786). It yielded when kept, but more readily on treatment with zinc and acetic acid, crystals of O. Fischer's dimethylaminotriphenyl-

methane and dissolved in acids with the production of a fine red colour. Isatin condenses with dimethylaniline under the conditions described to produce the compound,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C}(\text{C}_6\text{H}_4\text{NMe}_2)_2$ , already described by Baeyer and Lazarus (Abstr., 1886, i, 154). Similar products are obtained by the condensation of anthraquinone,  $\beta$ -methylanthraquinone, and  $\beta$ -dimethylaminoanthraquinone with dimethyl- or diethyl-aniline.

T. A. H.

**Azophenols. II.** RICHARD WILLSTÄTTER and MAX BENZ (*Ber.*, 1907, 40, 1578—1584. Compare Abstr., 1906, i, 990).—In a previous communication, the authors showed that *p*-azophenol exists in two forms, which are probably geometrical isomerides. Additional evidence in favour of this view is now submitted; the isomerism persists with the acetyl derivatives.

$\alpha$ -Azophenol exists in two modifications; the form, which is dehydrated by heat, is designated as  $\alpha_1$ , and the form, which is dehydrated at the ordinary temperature under diminished pressure, as  $\alpha_2$ . The  $\alpha_1$ -form does not absorb water from moist air, but quickly absorbs ammonia; the  $\alpha_2$ -form, on the other hand, absorbs  $\text{H}_2\text{O}$ , is not so quickly acted on by ammonia as its isomeride, and, when heated, is transformed into the  $\alpha_1$ -form.

$\beta$ -Azophenol also exists in two varieties which closely resemble one another. The reduction product of quinoneazine is designated as the  $\beta_1$ -variety, whilst the  $\beta_2$ -variety is obtained from a moist ethereal or concentrated sulphuric acid solution of the  $\beta_1$ -variety;  $\beta_1$  is stable, whilst  $\beta_2$  is readily transformed into the  $\alpha$ -form.

The anhydrous  $\alpha$ -form is dark green, whilst the anhydrous  $\beta$ -form is red.

$\alpha$ -Azophenol remains unchanged in alkaline solution, and may be precipitated from it unchanged by the addition of acid. If, however, some of the  $\beta_1$ -form is added to the alkaline solution of the  $\alpha$ -form, the latter is transformed into the stable  $\beta_1$ -form.

The  $\alpha$ - and  $\beta$ -forms are convertible one into the other by means of sulphuric acid.

*p*-Azophenyl acetate,  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OAc}$ , obtained by the acetylation of *p*-azophenol by Thiele's method or by acetylating *p*-azophenol in alkaline solution, separates from glacial acetic acid in yellow prisms and needles, m. p. 198—199°. The specimen of *p*-azophenyl acetate, obtained in the manner indicated, is the  $\alpha$ -form irrespective of whether  $\alpha$ - or  $\beta$ -azophenol is used. The pure  $\beta$ -*p*-azophenyl acetate is present in the freshly-prepared alkaline solution of  $\beta_1$ -*p*-azophenol.

$\beta$ -Azophenol may be converted into  $\alpha$ -azophenol by acetylation, recrystallisation of the product from glacial acetic acid, and subsequent hydrolysis.

*p*-Azophenyl benzoate,  $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$ , separates from benzene or xylene in reddish-yellow leaflets and is characterised by having two sharp melting points, 210.5—211.5° and 249—251°; it forms liquid crystals.

*p*-Azoanisole,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , obtained by methylating



either  $\alpha$ - or  $\beta$ -azophenol by methyl sulphate, separates from methyl alcohol in prisms or leaflets, m. p.  $160.5-162.5^\circ$  (Rotarski gives m. p.  $160-162^\circ$ ).  
A. McK.

**Diazo-oximes.** H. W. BRESLER, W. H. FRIEDEMANN, and JULIUS MAJ (*Annalen*, 1907, 353, 228-241. Compare Abstr., 1892, 163, 1079; 1906, i, 321; Bamberger, Abstr., 1899, i, 589).—This is an investigation of the constitution of the diazobisoximes, which is discussed in the light of the experimental results described below. It is concluded that benzenediazobisacetoxime is represented best by the formula  $\text{CMe}_2\cdot\text{N}\cdot\text{N}(\text{OH})\cdot\text{NPh}\cdot\text{N} < \begin{smallmatrix} \text{O} \\ | \\ \text{CMe}_2 \end{smallmatrix}$ , which is shown to agree with the acid nature as also with the characteristic transformations of the diazobisoximes. The formation of such a substance is pictured as taking place in two stages, the hypothetical intermediate product having the structure  $\text{N}:\text{NPh}\cdot\text{N} < \begin{smallmatrix} \text{O} \\ | \\ \text{CMe}_2 \end{smallmatrix}$ , and the second stage being the addition of acetoxime to the tervalent diazonium nitrogen atom (compare Hantzsch, Abstr., 1900, i, 703).

From an examination of the products obtained when *p*-tolyldiazobisacetoxime is heated carefully, it is concluded that one of the acetoxime groups in the diazobisacetoxime must be readily split off, leaving the unstable complex,  $\text{C}_{10}\text{H}_{13}\text{ON}_3$ , which decomposes partially into *p*-diazotolueneimide and acetone, and for the remainder reacts with a small amount of water, assumed to be present, forming *p*-toluidine, acetone, and nitrous oxide. This view of the reaction, however, does not explain the formation of a considerable volume of nitrogen. When heated with alcohol at  $50-60^\circ$ , *p*-tolyldiazobisacetoxime yields *p*-toluidine and *p* diazotolueneimide. Since *p*-toluidine is the main product in both decompositions, it appeared probable that the grouping  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot$  is present in the diazobisacetoxime molecule which might be formed by the action of acetoxime on the nitrosoamine form of the diazohydrate:  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{NO} + 2\text{CMe}_2\cdot\text{N}\cdot\text{OH} = \text{H}_2\text{O} + \text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{N}(\text{O}\cdot\text{N}:\text{CMe}_2)_2$ . This assumption, however, is not supported by the behaviour of nitrosoamines with oximes; sodium phenylnitrosoamine does not react with acetoxime, whilst sodium *p*-nitrophenylnitrosoamine reacts only slowly, and apparently after isomeric change of the nitrosoamine into the diazo-hydrate, since the free nitrosoamine, which readily undergoes the transformation, reacts with acetoxime in dilute alcoholic solution almost instantaneously.

When reduced with sodium amalgam in cooled alcoholic solution, *p*-tolyldiazobisacetoxime forms *p*-toluidine, isopropylamine, and hydroxylamine; the *p*-toluidine is obtained in an almost quantitative yield.

The action of dilute hydrochloric acid on the diazobisoximes leads to the formation of the aldehyde or ketone, the oxime, and the diazoimide; this reaction has been studied in the case of benzenediazobis-4-dimethylaminobenzaldoxime, which is found to yield diazobenzeneimide, *p*-dimethylaminobenzaldoxime, and *p*-dimethylaminobenzaldehyde in amounts closely approximating to molecular proportions. Similarly, acetoxime, *p*-diazotolueneimide, and acetone are obtained in

molecular proportions by the action of hydrogen chloride on *p*-toluene-diazobisacetoxime in ethereal solution.

The acid character of the diazobisoximes, observed first by Bamberger (*loc. cit.*), is confirmed by the formation of a *copper* salt,  $C_{24}H_{32}O_8N_{10}Cu$ . The red solutions, formed in the coupling of diazohydrates with oximes, which become colourless on dilution, must contain unstable alkali salts of the diazobisoximes; it is found now that *p*-nitrobenzenediazobisacetaldoxime forms, in alkaline solution, a stable red salt, the solution remaining red on addition of an excess of ammonium chloride, and yielding yellow to brown precipitates with metallic salts. G. Y.

[4 : 4'-Diaminodi-*p*-phenoxybenzene and its Azo-derivatives.]

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 178803).—4 : 4'-Diaminodi-*p*-phenoxybenzene,  $C_6H_4(O \cdot C_6H_4 \cdot NH_2)_2$ , m. p.  $170^\circ$ , was obtained by condensing *p*-chloronitrobenzene with the dry potassium derivative of quinol and then reducing the resulting dinitro-compound; it crystallises from alcohol in colourless needles. Its hydrochloride separates in long, colourless, soluble needles, and is precipitated by strong hydrochloric acid. The bisdiazochloride readily combines with 6-amino- $\alpha$ -naphthol-3-sulphonic acid and other naphthol-sulphonic acids to furnish substantive dyes, which have a brilliant red shade and are fast to acids. A series of these azo-derivatives is tabulated in the patent. G. T. M.

**Formation of Hydrols and Aldehydes. Action of Diazo-hydroxides on Amino-derivatives of Di- and Tri-phenylmethane.** ÉMILE SUAIS (*Bull. Soc. ind. Mulhouse*, 1907, 75—78).—Diazo-hydroxides react with dialkylamino-derivatives of di- and tri-phenylmethane, forming hydrols or aldehydes and dialkylaminobenzeneazo-compounds; in the case of tetramethyldiaminotriphenylmethane the reaction takes place according to the scheme: I,  $CHPh(C_6H_4 \cdot NMe_2)_2 + N_2R \cdot OH = OH \cdot CHPh \cdot C_6H_4 \cdot NMe_2 + N_2R \cdot C_6H_4 \cdot NMe_2$ , or, II,  $CHPh(C_6H_4 \cdot NMe_2)_2 + 2N_2R \cdot OH = C_6H_5 \cdot CHO + H_2O + 2N_2R \cdot C_6H_4 \cdot NMe_2$ . The reaction, which takes place in neutral, alcoholic-aqueous solution at the ordinary temperature, has been carried out with the diazo-hydroxides derived from *p*-sulphanilic acid, Dahl's No. III acid, and *m*-nitroaniline, on the one hand, and, on the other, with leucomalachite-green, leucohexamethyl-violet, tetramethyldiaminodiphenyl- $\alpha$ -ethylaminonaphthylmethane, tetramethyldiaminodiphenylmethane, and tetramethyldiaminobenzhydrol.

The following quantitative results were obtained with the diazo-derivative of Dahl's No. III acid; the percentages quoted are those calculated from the above schemes I and II. Leucohexamethyl-violet with 1 mol. of the diazo-hydroxide yields 55—60% of tetramethyldiaminobenzhydrol. Tetramethyldiaminodiphenyl- $\alpha$ -ethylaminonaphthylmethane with 1 mol. of the diazo-hydroxide yields 70% of tetramethyldiaminobenzhydrol. Leucomalachite-green yields with 1 mol. of the diazo-hydroxide 70%, or with 2 mols. 60%, or with excess (3 mols.) 80%, of the amount required by II, of the azo-

compound. Tetramethyldiaminobenzhydrol yields 85% of the azo-compound, the total yield remaining unchanged on addition of a second mol. of the diazo-hydroxide; hence the *p*-dimethylaminobenzaldehyde formed by the first stage does not react with the diazo-hydroxide. Tetramethyldiaminodiphenylmethane yields 80% of the azo-compound with 1 mol., or 70% with 2 mols., of the diazo-hydroxide; as in the first case half of the diphenylmethane base is recovered unchanged, the diazo-hydroxide must attack the two groups,  $\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , simultaneously, or the possible intermediate product, dimethylaminobenzyl alcohol reacts with the diazo-hydroxide more readily than does the diphenylmethane base.

The reaction described offers a practical method of preparing hydrols and aldehydes. G. Y.

**Chemistry of Globulin.** WILLIAM SUTHERLAND (*Proc. Roy. Soc.*, 1907, *B*, 79, 130–154).—The experimental results obtained by Hardy (Abstr., 1906, i, 121) and Mellanby (*ibid*, 122) may be represented by simple formulæ which show that the solution of globulin and its precipitation take place under simple conditions of chemical equilibrium.

For the precipitation of globulin by excess of ammonium sulphate the equation  $p(1+p) = 28.8(c - 0.152)$ , where  $p$  is the fraction which the precipitated globulin is of the whole and  $c$  the concentration of the sulphate in grams per c.c., holds good. Formulæ are applied to the precipitation of globulin by acids from solution in neutral salts, and from these it appears that three compounds of globulin react in producing the precipitate.

A theory of the colloidal state is promulgated. According to this a colloid consists of molecules which are chemically united neighbour to neighbour by the action of valencies which are usually latent. Cases of multiple valency are best accounted for by the electron theory of valency due to Helmholtz, with the assumption that a single atom can contain both negative and positive electrons. According to the author's view the term molecule ceases to have a useful meaning as applied to a colloid and the term *semplar* is used to denote the structure which is repeated like a pattern in three dimensions through a colloid. By suppression of the colloid producing valencies a mass of semplars is converted into a collection of separate molecules. The theory is applied to the various phenomena met with in the study of colloids.

Hardy's experiments on conductivities of globulin solutions can be expressed by means of formulæ which admit of very simple interpretation. At infinite dilution, the hydrochloric acid compound of globulin is completely hydrolysed, the conductivity being that due to the ionised hydrochloric acid, the part due to the globulin being negligible. For other concentrations, the ratio of combined and free hydrochloric acid can be calculated. In the compounds with ammonium and sodium hydroxides, half of the base combines with the globulin in a way which proves it to be an acid, the resulting salt being completely dissociated; the remaining half of the base which is required to dissolve globulin combines with it by addition.

Globulin is shown to have a probable molecular mass 40,000 and basicity 2, or mass 60,000 and basicity 3. A group,  $C_{12}H_{20}O_4N_3$ , related to polypeptides and peptones is shown to be the predominant structure in albumins. The discrepant results of different experimenters on the precipitation of albumin by heavy metals fall into harmony when it is proved that they precipitated different integral numbers of a group such as this in combination with an equivalent of heavy metal.

J. J. S.

**Globulin Precipitated from Human Blood Serum by Acetic Acid.** GEORGES PATEIN (*J. Pharm. Chim.*, 1907, [vi], 25, 470—476).—The precipitate obtained by neutralising the diluted serum with acetic acid is insoluble in water and soluble in acetic acid or sodium carbonate solution and is composed of two globulins, the chief constituent being soluble in 0.6% or more concentrated solutions of sodium chloride and the other in 10% or stronger solutions of the same salt. The precipitate is coagulated in suspension in water or in solution in dilute acetic acid at 56° and in salt solution at 78°. These facts indicate that the material is not a nucleoproteid, a fibrino-globulin, or a casein, and it is further distinguished from the last of these by containing no phosphorus, although it contains some sulphur.

T. A. H.

**Mono-amino-acids of Lactalbumin.** EMIL ABDERHALDEN and HUGO PŘIBRAM (*Zeitsch. physiol. Chem.*, 1907, 51, 409—414).—The lactalbumin was prepared from cow's milk. It was free from phosphorus, and therefore from caseinogen. Whether it was absolutely free from lacto-globulin is uncertain; parts of it at any rate yielded no glycine, and glycine is usually obtained from globulins. A further examination of lacto-globulin will, however, be necessary. The mono-amino-acids obtained in parts per cent. of the albumin were: alanine, 2.5; valine, 0.9; leucine, 19.4; proline, 4.0; aspartic acid, 1.0; glutamic acid, 10.1; phenylalanine, 2.4, and tyrosine, 0.85.

W. D. H.

**Increase in Weight in the Hydrolysis of Casein.** JOHN H. LONG (*J. Amer. Chem. Soc.*, 1907, 29, 295—299).—In a previous paper (this vol., i, 367) it has been shown that when casein has been submitted to prolonged digestion with pepsin and dilute hydrochloric acid, the residue left on evaporating the liquid to dryness contains combined hydrogen chloride. A series of experiments has now been made with the casein of cow's milk in order to determine the rate of increase in weight due to the addition of hydrogen chloride, or water, or both. The mixtures of casein, pepsin, and dilute hydrochloric acid were maintained at 40°, and the weight of the residue was determined at intervals. The results are tabulated, and show that the increase is due to both water and hydrogen chloride. It is found that the products are relatively stable, and that on prolonged heating they lose more water than hydrogen chloride. A large proportion of the water and acid is added during the final evaporation, rather than during the prolonged digestion at 40°. The amount of water added in the actual digestion does not vary much after ten days or so, but the hydrogen

chloride is added more slowly and shows a gradual increase. On the other hand, in the final evaporation, there is a marked increase in the amount of water added in the case of the products of the most prolonged digestions and a relatively small increase in the hydrogen chloride. It is found that 480 mg. of casein finally experience a total increase of 70 mg. of added water and 110 mg. of acid.

It is noteworthy that the sensitiveness of the product to phenolphthalein becomes less as the digestion progresses. The final colour reaction recalls that observed in titrations made in presence of traces of ammonium salts, and evidently indicates the accumulation of amino-compounds, which show an analogous behaviour.

It is suggested that *p*-nitrophenol will probably be found a useful indicator for the estimation of total mineral acids in digestion experiments.  
E. G.

**The Salting-out of Caseinogen and Casein by Sodium Chloride.** SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1907, 9, 311—321).—Two per cent. solutions of sodium caseinogenate and of sodium caseinate were prepared; no precipitation occurs on saturating such solutions with pure sodium chloride. Common salt, however, which contains about 0.4% of calcium and 0.05% of magnesium causes complete precipitation of the proteins in combination with the alkali earths. The calcium ions can be replaced by barium or magnesium, but the quantity of these necessary is about three times that of the calcium ions.  
W. D. H.

**The Relation of Whey-protein to Rennet Action.** SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1907, 9, 322—332).—Pure solutions of caseinogen, prepared by acid precipitation or salting-out, when acted on by rennet, yield about 4% of their nitrogen in the form of whey-protein, which is regarded as a cleavage product of the caseinogen. The mucous membrane of the calf's stomach yields in addition to rennet a protease, which, acting on the casein, yields an increase in the yield of whey-protein. This protease follows the Schutz-Borissow law.  
W. D. H.

**Behaviour of Caseinogen towards Ozone.** CARL D. HARRIES and KURT LANGHELD (*Zeitsch. physiol. Chem.*, 1907, 51, 342—373).—Evidence was obtained that ozonisation of caseinogen leads to the production of comparatively large amounts of the cleavage products of protein. These were separated by lead acetate or by successive treatment with phosphotungstic acid and lead acetate. Little or no leucine was obtained.  
W. D. H.

**Behaviour of Protein Cleavage Products and Certain Sugars with Ozone.** CARL D. HARRIES and KURT LANGHELD (*Zeitsch. physiol. Chem.*, 1907, 51, 373—383).—The fatty amino-acids, including serine, are not altered by ozone. The same is true for amino-acetaldehyde, asparagine, and guanidine. The aromatic cleavage products of protein (phenylalanine, tyrosine, and tryptophan) are altered with the formation of reducing substances. This occurs best in an

alkaline, and least in an acid solution. The chemistry of the change was not made out. The diamino-acids have not yet been examined.

The action of ozone on dextrose is very small; mannitol is changed into mannose and lævulose; dulcitol probably yields galactose.

W. D. H.

**The Monoamino-acids of Crystallised Oxyhæmoglobin.** EMIL ABDERHALDEN and LOUIS BAUMANN (*Zeitsch. physiol. Chem.*, 1907, 51, 397—403).—Globin was prepared from the crystallised oxyhæmoglobin of dog's blood; the amount of hæmatin in the oxyhæmoglobin is 4.2%. The following numbers give the percentages of monoamino-acids obtained from the globin as compared with those previously obtained from globin prepared from the horse:

	Dog.	Horse.
Glycine.....	Traces	—
Alanine .....	3.0	3.0
Valine .....	1.0	—
Leucine .....	17.5	20.9
Proline .....	4.5	1.5
Aspartic acid .....	2.5	3.4
Glutamic acid .....	1.2	1.1
Phenylalanine .....	5.0	3.5

W. D. H.

**Hæmopyrrole.** WILLIAM KÜSTER (*Ber.*, 1907, 40, 2017—2020. Compare Abstr., 1902, i, 845; 1904, i, 647).—The imide obtained by the oxidation of the acid hæmopyrrole is identical with synthetical methylethylmaleinimide. The slightly basic hæmopyrrole also yields an imide from which a small amount of methylethylmaleinimide has been isolated. Hæmopyrrole is thus a mixture of two pyrrole derivatives, the acid constituent is 3-methyl-4-ethylpyrrole, and the basic constituent is 3-methyl-4-ethylpyrroline or 2:4-dimethyl-3-e hylpyrrole or -pyrroline.

J. J. S.

**A New Crystalline Derivative of Hæmin.** WILLIAM KÜSTER and KARL FUCHS (*Ber.*, 1907, 40, 2021—2023).—When dehydrochloridehæmin is extracted for some time with ether in order to remove the last traces of aniline, a mixture of two crystalline products separates in the flask. These may be separated by means of boiling alcohol from which the one compound,  $C_{36}H_{36}O_3N_4$ , termed *ethyl anhydrohæmaterate*, separates as pointed, yellowish-red needles, m. p. 205—210°. The formation of this compound is probably due to the partial esterification of the hæmin to  $C_{36}H_{36}O_4N_4ClFe$ , and the withdrawal of the iron by hydrochloric acid yielding  $C_{36}H_{38}O_4N_4$  from which the new compound is obtained by the elimination of water. It does not dissolve in alkalis, but is soluble in hydrochloric acid.

J. J. S.

**Thymus-nucleic Acid.** WALTER JONES and C. R. AUSTRIAN (*J. Biol. Chem.*, 1907, 3, 1—10).—By the action of nuclease, thymus-

nucleic acid does not yield xanthine; the xanthine formed by more violent hydrolytic methods must therefore originate in guanine groups, or in guanine itself. Hydrolysis at high temperatures destroys a large amount of purine products, especially guanine. The quantities of guanine and hypoxanthine (equivalent to adenine) formed by ferment action are nearly proportional to the molecular weights of the bases. This is evidence that the two bases result from the same nucleic acid.

W. D. H.

#### The Rendering Insoluble of Gelatin by Benzoquinone.

AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEWEYETZ (*Bull. Soc. chim.*, 1907, [iv], 1, 428—431. Compare *Abstr.*, 1906, i, 614, 915, 999).—When a dilute solution of benzoquinone is added to one of gelatin, the latter "sets" in about the same time as when no benzoquinone is present, but the product no longer liquefies on warming. Gelatin can be rendered insoluble by the action of a solution containing 0·001% of benzoquinone, but with so dilute a solution the action proceeds slowly. The product is much more stable than that obtained by the action of formaldehyde on gelatin. Its colour varies from pink to reddish-brown, depending mainly on the colour and strength of the solution of benzoquinone used to produce it. It swells slightly under the action of cold water and remains insoluble in water even after prolonged ebullition. It is not dissociated into its constituents by acids, alkali carbonates or hydroxides or ammonia, but acids and alkalis produce eventually decomposition of the gelatin, this action being the more rapid the more concentrated is the solution of the reagent employed. Ammonia and the alkali carbonates, on the contrary, act very slowly in the cold even in very concentrated solution. T. A. H.

#### Monoamino-acids from Syntonin prepared from Ox-flesh.

ERIL ABDERHALDEN and TAKAOKI SASAKI (*Zeitsch. physiol. Chem.*, 1907, 51, 404—408).—Isolation of the muscle-proteins was not attempted. The syntonin or acid-albumin prepared from ox-flesh, after separation of the humin which is formed yielded the following amino-acids in parts per cent.: glycine, 0·5; alanine, 4; valine, 0·9; leucine, 7·8; proline, 3·3; aspartic acid, 0·5; glutamic acid, 13·6; phenylalanine, 2·5; tyrosine, 2·2.

W. D. H.

#### Relation of Electrolytes to Lecithin and Kephalin.

WALDEMAR KOCH (*J. Biol. Chem.*, 1907, 3, 53—56).—The precipitating action of calcium salts in solutions of lecithin is largely hindered by sodium chloride. According to A. P. Mathews' views, the dissolving action of the chlorine ion will explain this. The greater sensitiveness of kephalin to precipitation by cations can be explained by its more acid properties.

W. D. H.

#### Influence of Ions on Catalysis produced by Pepsin and Trypsin.

WILLIAM N. BERG and WILLIAM J. GIES (*J. Biol. Chem.*, 1907, 2, 489—546).—Beyond the fact well known previously that hydrogen ions favour the action of pepsin, and hydroxyl ions that of trypsin, the present research led to negative results. Disparities in

the velocity, quality, and extent of digestion by pepsin occur in solutions of different acids, whether they are present in equal masses, equal numbers of molecules, of hydrogen atoms, or of hydrogen ions. The action of trypsin is equally irregular.

W. D. H.

**Fermentative Decomposition of Dipeptides.** HANS EULER (*Zeitsch. physiol. Chem.*, 1907, 51, 213—225. Compare Abderhalden and Teruuchi, *Abstr.*, 1906, ii, 464, Abderhalden and Schittenhelm, this vol., i, 104).—The decomposition of glycylglycine by means of erepsin in the presence of sodium hydroxide has been studied as a time reaction by means of electrical conductivity determinations.

The velocity varies considerably with the concentration of the alkali, the maximum being reached when the concentration of the sodium hydroxide is from 0.04—0.06. A considerable proportion of the added alkali is not present as such, but is combined with the glycylglycine and also with the erepsin preparation; if these facts are taken into consideration the optimal concentration of the free alkali is 0.000012. The dissociation constants of glycylglycine, leucylglycine and alanylglycine have been determined as acids and also as bases.

The values are:

	$K_A$	$K_B$
Glycylglycine .....	$1.8 \times 10^{-8}$	$2 \times 10^{-11}$
Leucylglycine .....	$1.5 \times 10^{-8}$	$3 \times 10^{-11}$
Alanylglycine .....	$1.8 \times 10^{-8}$	$2 \times 10^{-11}$

The decomposition of glycylglycine is a reaction of the first order and the velocity constant has the same value until some 50% is decomposed. It then decreases, mainly owing to the decomposition of the erepsin and not to the retarding effects of the products of decomposition. The constant is almost independent of the concentration of the peptide, provided the concentration ratio ferment/substrate is within certain limits, but the constant is practically proportional to the concentration of the enzyme, and Schütz-Borissow's rule does not hold. When extremely small amounts of ferment are present,  $K$  increases more rapidly than the concentration of the ferment.

J. J. S.

**Opium Toxins.** WOLFGANG WEICHARDT and HERMANN STADLINGER (*Biochem. Zeitsch.*, 1907, 3, 431—438)—Protein splitting "antigens" of a fatigue producing character are found not only in the animal, but also in the vegetable, kingdom. That which is present in opium can be obtained in a pure condition by dialysis after removal of the alkaloids and the opinion is expressed that the complex physiological action of opium is in part due to its presence.

W. D. H.

**Oxidising Ferments. I. The Mode of Action of Tyrosinase.** ROBERT CHODAT and STAUB (*Arch. Sci. phys. nat.*, 1907, [iv], 23, 265—277).—The oxidising action of tyrosinase has been studied. A solution of the ferment is most conveniently obtained from *Russula delica* or *Solanum tuberosum*. The red colour which the ferment gives with tyrosine is not obtained with the albumoses, but its production



with glycylytyrosine anhydride indicates that other peptides may give the reaction.

Contrary to Bach's observations, it is found that hydrogen peroxide diminishes the activity of tyrosinase and frequently inhibits its action on tyrosine. Gonnermann's conclusion (*Pflüger's Archiv*, 1900, 82) that tyrosinase is not an oxidising, but a hydrolytic ferment is refuted by the results of experiments in an atmosphere of carbon dioxide; these show clearly that oxygen is necessary for the action, and that the action of the ferment is not simply the production by hydrolysis of an easily oxidisable product.

The rate of oxidation of tyrosine is very much smaller when leucine is added to the solution, but an explanation of this has not yet been obtained. The activity of the ferment increases with temperature up to 61°; at 66° it becomes inactive. At small concentrations the activity is proportional to the concentration of the ferment, but at higher concentrations the rate is expressed by the formula  $kc + b$ , where  $c$  is the concentration, and  $k$  and  $b$  constants. This influence of the concentration is similar to that already observed in the action of laccase (from *Lactarius vellereus*) on pyrogallol.

H. M. D.

**Oxidising Ferments. II. Distribution [Phenomena] in the Action of Peroxydase in Presence of Catalase.** ROBERT CHODAT and J. PASMANIK (*Arch. Sci. phys. nat.*, 1907, 23, 386—393. Compare preceding abstract).—The rate at which iodine is liberated from potassium iodide solution acidified with acetic acid by (1) hydrogen peroxide, (2) hydrogen peroxide + peroxydase, (3) hydrogen peroxide + catalase, and (4) hydrogen peroxide + catalase + peroxydase has been compared. In all the experiments the concentration of the peroxydase was 0.1%, but that of the catalase was varied from 0.00025 to 1.0%. The accelerating effect of the peroxydase is greatly diminished in presence of very small quantities of catalase, but even when the catalase is present in large excess the accelerating influence of the peroxydase on the liberation of iodine from the mixture of peroxide and iodide is clearly distinguishable. With increasing concentration, the retardation resulting from the catalase appears to approximate to a limiting value. Loew's view, that if hydrogen peroxide were formed in the metabolic processes taking place in the cell, it would be immediately destroyed by the catalase even in presence of oxidising ferments, is incompatible with these experimental results. The data rather indicate that distribution phenomena occur when peroxydase and catalase are both present in the system.

H. M. D.

**Oxidising Ferments. III. A Hypothesis as to the Action of Ferments.** ROBERT CHODAT and J. PASMANIK (*Arch. Sci. phys. nat.*, 1907, 23, 394—400. Compare preceding abstracts).—The action of ferments is supposed to be connected with the electrolytic dissociation of water, the degree of dissociation being increased in the presence of ferments which unite with the hydrogen and hydroxyl ions to form complex acid or basic groups capable of specific ferment action. In support of this view it was found that the electrical conductivity of 0.1% solutions of catalase, peroxydase, and pepsin was much smaller

after boiling than before. Other known facts are recorded as evidence in support of the authors' hypothesis. H. M. D.

**Zymoids.** A. R. BEARN and WILHELM CRAMER (*Biochem. J.*, 1907, 2, 174—185. Compare Abstr., 1906, i, 780).—Solutions of enzymes which have been heated at 56—60° for twenty to thirty minutes inhibit the activity of the unheated enzyme. The inhibition disappears by exposure to 100° as a rule. The inhibitory power varies in different preparations of the same enzyme. It is not due to an anti-ferment, but is brought about by a reaction between the substrate and substances present in the inactivated enzyme. These substances dialyse very slowly through parchment paper. In the case of pepsin they are not specific for each species. These facts point to the existence of zymoids which are probably preformed in the enzyme preparations. Zymoids, like enzymes, differ in their resistance towards heat, and different enzyme preparations vary in the amount of zymoids they contain. W. D. H.

**Chemical Reaction Showing Green Luminescence.** EDGAR WEDEKIND (*Chem. Zentr.*, 1907, i, 242; from *Physikal. Zeitsch.*, 1906, 7, 805).—When an ethereal solution of chloropicrin is mixed with magnesium phenyl bromide, a green flame is formed under the ether, which does not, however, take fire. Diphenyl is the only product which has been isolated from the mixture. E. W. W.

**Action of Carbon Dioxide on Magnesium Phenyl Bromide.** GEORG SCHROETER (*Ber.*, 1907, 40, 1584—1585. Compare Abstr., 1903, i, 821).—Meyer and Tögel (Abstr., 1906, i, 757) confirm the observation of the author that under certain conditions triphenylcarbinol and benzophenone are obtained by the action of carbon dioxide on magnesium phenyl bromide. They conclude that the presence of water or alcohol is necessary and that the temperature must be raised during the action of the carbon dioxide. The author maintains that the presence of water is not necessary. The temperature, however, has an important influence, as well as the rate at which the carbon dioxide is passed into the solution of magnesium phenyl bromide.

When a slow current of dry carbon dioxide is passed into a boiling ethereal solution of magnesium phenyl bromide, the product yields benzoic acid, triphenylcarbinol, benzophenone, and diphenyl. When dry carbon dioxide ( $\frac{1}{3}$  mol.) is passed into a cooled ethereal solution of magnesium phenyl bromide (1 mol.), the product yields triphenyl carbinol, benzophenone, and diphenyl, but no benzoic acid. A. McK.

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## Organic Chemistry.

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**Origin of Mineral Oil (Artificial Preparation of Optically Active Petroleum).** CARL NEUBERG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 24, 451—455. Compare Walden, Abstr., 1906, ii, 368).—The fact that many kinds of petroleum from various sources are optically active necessitates a revision of the hypothesis of Engler and Hofer (Abstr., 1888, 928; 1889, 586), since neither fats nor their decomposition products are optically active, and hence cannot give rise to an optically active mineral oil. In continuation of his observation that proteins give rise to optically active fatty acids on decomposition (Abstr., 1906, i, 923), the author has been able to show that by the dry distillation of a mixture of oleic acid and *d*-valeric acid, also by heating such a mixture under pressure, a product is obtained which when purified possesses all the properties of natural petroleum, likewise the same optical rotatory power. Further, the optical rotatory power increases as the boiling point of the fraction increases, and these high boiling fractions give the cholesterol colour reaction (Neuberg, Abstr., 1906, ii, 497), as do the high boiling fractions obtained from natural petroleum.

In conclusion, the author briefly mentions that the acids formed during the putrefaction of cheese frequently do not possess a normal structure as is generally supposed, since besides  $\beta$ -methylbutyric acid and  $\gamma$ -methylvaleric acid, the optically active acids,  $\alpha$ -methylbutyric acid and  $\beta$ -methylvaleric acid are also found in putrid cheese. No aminobutyric acid is found in the putrefaction products of casein, so that the butyric acid, which is present to the extent of one-third of the total acids formed, is undoubtedly produced by the decomposition of glutamic acid. It is also very probable that several optically active acids are formed during the putrefaction of gelatin.

W. H. G.

**Catalytic Dehydration of Alcohols by Amorphous Phosphorus and Phosphates.** JEAN B. SENDERENS (*Compt. rend.*, 1907, 144, 1109—1111).—In the presence of commercial amorphous phosphorus in the form of an impalpable purple powder,  $D = 2.165$ , the alcohols are decomposed at  $180^\circ$  (approx.) into olefine and water together with traces of hydrogen phosphide. Thus ethyl alcohol begins to decompose at  $215^\circ$ , and at  $230$ — $240^\circ$  gives a mixture of 95% of ethylene and 5% of hydrogen phosphide. Propyl alcohol gives similar results, whilst butyl alcohol at  $205^\circ$  gives 97% of butylene and 3% of hydrogen phosphide. All specimens of amorphous phosphorus are, however, not equally active, but it can be replaced by various phosphates, of which aluminium phosphate is the most active and is the basis of a general method for the preparation of open chain and *cyclo*-olefines. Ethyl alcohol begins to decompose at  $330^\circ$  and gives pure ethylene in abundance at  $380^\circ$ . *n*-Propyl alcohol decomposes

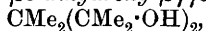
into propylene and water at 300—340°. *n*-Butyl alcohol at 520° gives 27% of *isobutylene* and 73% of  $\alpha$ -butylene; *isobutyl* alcohol at 310°, a mixture of 68·5% of *isobutylene* and 31·5% of  $\alpha$ -butylene. Trimethylcarbinol at 200° gives pure *isobutylene*; *isopropyl* alcohol at 300°, propylene; *isoamyl* alcohol at 300—350°, a mixture of  $\alpha$ -*isoamylene* and  $\gamma$ -*amylene* with traces of  $\beta$ -methyl- $\Delta^{\beta}$ -butylene and  $\alpha$ -*amylene*; *tert.*-*amyl* alcohol,  $\beta$ -methyl- $\Delta^{\beta}$ -butylene; *n*-octyl alcohol,  $\alpha$ -octylene, b. p. 122—123°; and *sec.*-octyl alcohol, an octylene, b. p. 120·5—121·5°. The method is readily applicable to the *cycloparaffin* alcohols, and theoretical yields of the corresponding *cyclo*-olefines are obtained at 300—350° from *cyclohexanol*, the three methyl*cyclo*-hexanols, 1:3:4-dimethyl*cyclohexanol*, and menthol. The silicates have similar, but less powerful, catalytic properties, whilst silica has the singular property of being a dehydrogenating catalyst when in the crystalline condition and a dehydrating catalyst when amorphous.

E. H.

**Isomerisation Point of *sec.*- and *tert.*-Pinacolyl Alcohol Derivatives.** MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 575—586).—In continuation of previous work on the isomerisation of pinacolyl derivatives (Abstr., 1906, i, 477, 518, 551, 784; this vol., i, 459), the author has compared the action of potassium acetate on *sec.*-pinacolyl bromide and the hydrobromide of  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene. The former furnishes 39·3% of the symmetrical hydrocarbons,  $\text{CMe}_2\cdot\text{CMe}_2$  and  $\text{CHMe}_2\cdot\text{CMe}\cdot\text{CH}_3$ , and a residue, which contains *tert.*-pinacolyl acetate and a bromide, which may be the compound  $\text{CMe}_3\cdot\text{CHMeBr}$ . The hydrobromide of  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene under the same conditions yields a similar proportion of the two symmetrical hydrocarbons, and the residue is almost wholly composed of *tert.*-pinacolyl acetate. From these results the inferences are drawn that by the action of hydrogen bromide on *sec.*-pinacolyl alcohol about 94% of  $\text{CBrMe}_2\cdot\text{CHMe}_2$  and about 6% of the unsymmetrical bromide,  $\text{CMe}_3\cdot\text{CHMeBr}$ , are formed.

T. A. H.

**Synthesis and Decomposition of  $\beta\delta$ -Dihydroxy- $\beta\gamma\gamma\delta$ -tetramethylpentane.** A. N. SLAVJANOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 140—160).—The investigation was undertaken with the object of preparing hexamethyl*cyclopropane* by the action of hydrogen bromide on the glycol, which, according to Grignard, should be obtained by the action of magnesium methyl iodide on ethyl dimethylacetate (*Ann. Chim. Phys.*, 1901, [vii], 24, 463). This attempt was, however, not successful, but the glycol,  $\beta\delta$ -dihydroxy- $\beta\gamma\gamma\delta$ -tetramethylpentane,



was isolated and its properties investigated. It forms colourless, feathery crystals, m. p. 76·5°, b. p. 223—225°/753 mm., of burning taste and camphoraceous odour, is sparingly soluble in water and very unstable in the presence of mineral and even dilute organic acids; this probably explains why Grignard, who worked in acid solution, was unable to obtain the substance  $\text{CEt}_2(\text{CMe}_2\cdot\text{OH})_2$ . *iso*Butyric acid and  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid were obtained as by-products in the preparation of the pentane. The same substance is obtained when

dimethylmalonic ester is substituted for dimethylacetoacetic, but the yield is less. The products of dehydration of the glycol consist chiefly of acetone and  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene. When treated with phosphorus and bromine, the glycol yields  $\beta\gamma$ -dibromo- $\beta\gamma$ -dimethylbutane. With hydrobromic acid, the mono-bromo-derivative,  $\text{CHMe}_2\cdot\text{CMe}_2\text{Br}$ , is formed. Z. K.

**Friedel's Pinacolin-pinacone and the Constitution of Ordinary Pinacolin.** MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 535—543. Compare this vol., i, 459).—When pinacolin is reduced with sodium there is formed in addition to *sec*-pinacolyl alcohol (methyl-*tert*-butylcarbinol) a solid product, which Friedel called pinacolin-pinacone; this according to Couturier (*Abstr.*, 1893, i, 245) is decomposed by dilute acids into pinacolin and  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene. This opens up the question as to whether Friedel's pinacolin-pinacone is itself a symmetrical compound or gives rise to a symmetrical hydrocarbon as a decomposition product owing to initial isomerisation.

The author finds that in addition to the two products named, a third substance, b. p. 200—225°, is produced when pinacolin is reduced with sodium, but it is not certain that this may not be produced from an impurity in the pinacolin used. Pinacolin-pinacone, b. p. 255—258°, m. p. 71—72°, crystallises from light petroleum. When heated with acetic anhydride in a closed vessel it yields pinacolin and *sec*-pinacolyl acetate. With acetyl chloride, *sec*-pinacolyl acetate, and with phosphorus trichloride, *sec*-pinacolyl chloride is produced, accompanied in each case by a second substance, a liquid hydrocarbon,  $\text{C}_{12}\text{H}_{20}$ , b. p. 180° (approx.), which has a feeble characteristic odour and readily absorbs bromine.

The formula suggested by Couturier for pinacolin-pinacone affords an explanation of the first of these reactions, thus :

$\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{CMe}(\text{OH})\cdot\text{CMe}_3 \rightarrow \text{CMe}_3\cdot\text{CHMe}\cdot\text{OH} + \text{CMe}_3\cdot\text{COMe}$ ,  
but does not account for the formation of the hydrocarbon  $\text{C}_{12}\text{H}_{20}$ . These reactions indicate therefore that pinacolin furnishes unsymmetrical products on reduction with sodium. T. A. H.

**Explosive Mixtures of Air and Ethyl Ether.** JEAN MEUNIER (*Compt. rend.*, 1907, 144, 1107—1108. Compare this vol., i, 460).—By the use of smaller containing vessels (190 c.c. and 252 c.c. instead of 1 litre) the author obtains the values of 0.058 gram and 0.059 gram per litre for the lower limit of inflammability of ethyl ether in air, thus agreeing with the value 0.06 gram per litre obtained by Le Chatelier and Boudouard (*Abstr.*, 1898, ii, 574). The higher result previously obtained is probably due to incomplete mixing in the larger vessel. When the proportion of ethyl ether is 0.06 gram per litre, it burns without noise. With a higher proportion, explosion occurs, the explosion being violent between the limits 0.1 and 0.175 gram per litre, and the maximum violence occurring with the proportion 0.12—0.15 gram per litre. As the amount of ethyl ether increases above 0.175 gram per litre, the combustion becomes calmer and ceases with 0.195 gram per litre. Similar results are obtained with carbon

disulphide, but in this case the higher limit amounts to 0.9 gram per litre.  
E. H.

**Compounds of Aluminium Bromide with Ethyl Ether.** WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 163—167).—In view of the interest which attaches to complex aluminium compounds as well as ethereal compounds in regard to chemical constitution, it seemed desirable to obtain compounds of aluminium bromide with ether by a process which would exclude the formation of any by-products. Quite colourless, freshly distilled aluminium bromide was introduced as a layer in the reacting vessel and absolutely pure; dry ethyl ether was then introduced by means of a capillary reaching to the bottom of the vessel. On evaporating the ether in a vacuum, dry, colourless crystals of the formula  $\text{AlBr}_3 \cdot \text{OEt}_2$ , m. p.  $47^\circ$ , were obtained. The substance is very unstable and readily soluble in ether, bromine, benzene, &c. Unlike the non-electrolytic solutions of aluminium bromide in the same solvents, the solutions of the complex substance show no evidence of chemical reaction and are electrolytes; it is therefore probable that the aluminium in this compound has formed a complex ion. The experiments also indicate that with the formation of stable, complex ions in the compounds of aluminium, those of its reactions which depend on the formation of complex ions are either considerably weakened or altogether disappear.  
Z. K.

**Reaction between Titanium Tetrachloride and Ethyl Ether.** HENRY R. ELLIS (*Chem. News*, 1907, 95, 241).—Anhydrous ethyl ether was added slowly to titanium tetrachloride cooled in ice; reaction took place at once and the mixture ultimately set to a mass of yellow crystals resembling rhombic sulphur. After twenty-four hours, the solid was distilled; the first fraction consisted of ether, hydrogen chloride, and a small quantity of a yellow liquid which crystallised; the second fraction,  $34\text{--}60^\circ$ , consisted of a yellow oil which solidified to yellow crystals; the third fraction,  $60\text{--}100^\circ$ , was a yellow liquid which solidified to small, yellowish-white crystals; and the last fraction,  $170\text{--}196^\circ$ , consisted of orange crystals, m. p. about  $70^\circ$ . The residue, which formed a brown powder resembling hydrated oxides of manganese, was washed with light petroleum and analysed; it contained 34.4% of titanium and 18% of chlorine. The other substances slowly decompose with evolution of hydrogen chloride and ethyl chloride.  
P. H.

**Methyl Ethers of Allyl- and Propargyl-carbinols.** ROBERT LESPIEAU (*Compt. rend.*, 1907, 144, 1161—1162).—By alternately adding to magnesium covered with dry ether successive small quantities of allyl bromide and methyl chloride, a mixture of diallyl and the ether  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$  is obtained. Complete separation of the latter is impossible by fractional distillation, but is easily effected after conversion into the bromo-derivatives.

The ether,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$ , b. p.  $90\text{--}91^\circ/13\text{ mm.}$ ,  $101\text{--}102^\circ/25\text{ mm.}$ ,  $209\text{--}211^\circ/760\text{ mm.}$  (decomp.),  $D_0^{20} 1.811$ , is con-

verted by hydrogen bromide into  $\gamma\delta$ -dibromo-*n*-butyl alcohol, is reduced by zinc dust and alcohol to the unsaturated ether  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$ , and by treatment with sodium ethoxide gives a mixture of the ether  $\text{CH}_2\text{:CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$ , b. p. 142—143°,  $D_0$  1.356, and the ether  $\text{CHBr}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$ , b. p. 149—151°,  $D_0$  1.358. Both the latter ethers react with aqueous or alcoholic potash giving the acetylenic ether  $\text{CH}\text{:C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$ , having b. p. 86—87°,  $D_0$  0.8579, and giving a yellow precipitate with ammoniacal cuprous chloride solution. E. H.

**Tetramethylethylene** [ $\beta\gamma$ -Dimethyl- $\Delta^2$ -butylene] **Oxide**. MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 586—590).—It has frequently been asserted that the formation of pinacolin,  $\text{CMe}_3\cdot\text{COME}$ , from pinacone,  $\text{OH}\cdot\text{CMe}_3\cdot\text{CMe}_2\cdot\text{OH}$ , takes place through the isomerisation of some tetramethylethylene oxide,  $\text{O} \begin{smallmatrix} \diagup \text{CMe}_2 \\ \diagdown \text{CMe}_2 \end{smallmatrix}$ , first formed, but this transformation has not yet been realised experimentally.

The method recommended by Eltekoff (*Abstr.*, 1883, 567) for the preparation of the oxide does not in the author's experience give good results, and he has used instead that suggested by Friedel, which consists in treating pinacone with dry hydrogen chloride and distilling the product over potassium hydroxide. The rectified distillation product was finally separated into eight fractions. From that boiling at 90—100° a portion boiling at 92.5—99° was isolated. This had a peculiar odour, was partially transformed into pinacone in contact with water, and on reduction with sodium in presence of an aqueous solution of potassium hydroxide yielded some *tert*-pinacolyl alcohol mixed with the *sec*-alcohol; the presence of the latter may be due either to isomerisation or to impurities in the liquid reduced. The fraction, b. p. 109—115°, on reduction gave mainly *tert*-pinacolyl alcohol, and no indication of the occurrence in it of the alcohol  $\text{CH}_2\text{:CMe}\cdot\text{CMe}_2\cdot\text{OH}$  was obtained. The portion boiling below 90° consisted mainly of hydrocarbons and gave gummy precipitates with hydrobromic acid. The fraction boiling between 90° and 109° gave with this reagent pinacone bromide,  $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br}$ , and with hydrochloric acid an oily product. T. A. H.

**New Method of Synthesis of Diprimary Compounds containing an Odd Number of Carbon Atoms:  $\alpha\eta$ -Dimethoxyheptane.** JULES L. HAMONET (*Compt. rend.*, 1907, 144, 1217—1219. Compare *Abstr.*, 1904, i, 467).—The  $\delta$ -chloro- $\alpha\eta$ -dimethoxyheptane described previously (*Abstr.*, 1906, i, 58) does not form a magnesium compound, but the chlorine can be replaced by hydrogen by the action of sodium on the ethereal solution containing hydrogen chloride. The resulting  $\alpha\eta$ -dimethoxyheptane,  $\text{CH}_3\cdot([\text{CH}_2]_3\cdot\text{OMe})_2$ , is a very mobile liquid, b. p. 189—190°,  $D_{15}^{20}$  0.860, having an agreeable fruity odour. The  $\delta$ -bromo- $\alpha$ -amyloxybutane and  $\epsilon$ -bromo- $\alpha$ -amyloxy-pentane previously described (*Abstr.*, 1904, i, 467, 705) and Dionneau's  $\zeta$ -bromo- and  $\zeta$ -iodo- $\alpha$ -ethoxyhexane (*Abstr.*, 1906, i, 134) would, by reacting with ethyl formate, give similar halogen ethers, from which sodium would

withdraw the bromine giving diprimary compounds containing  $C_9$ ,  $C_{11}$ , and  $C_{13}$  respectively. The method is probably applicable to all the homologues  $RO(CH_2)_nBr$ . E. H.

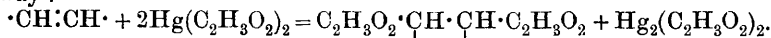
**Crystalline "Acidates" (Compounds of Magnesium Bromide and Iodide with Organic Acids).** BORIS N. MENSCHUTKIN (*Zeitsch. anorg. Chem.*, 1907, **54**, 89—96; *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1335—1346. Compare Abstr., 1906, i, 131, 132; this vol., i, 271).—The compounds in question have been prepared mainly by the action of the anhydrous acids on the dietherates of the salts. In some cases the solubility of the compounds in the corresponding free acids have been determined from  $0^\circ$  to the respective melting points.

The compounds  $MgBr_2 \cdot 6CH_2O_2$  (m. p.  $88^\circ$ ) and  $MgBr_2 \cdot 6C_2H_4O_2$  (m. p.  $112^\circ$ ) occur in colourless, extremely hygroscopic crystals. The solubility curve of the former in formic acid shows no distinct bend, whilst that of the latter in acetic acid rises steeply to about  $80^\circ$ , beyond which point it becomes much flatter, indicating a much more rapid increase of solubility with temperature above the latter point.

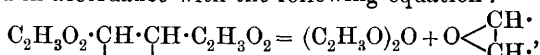
The following compounds with magnesium iodide have been prepared:  $MgI_2 \cdot 6C_2H_4O_2$ , m. p.  $142^\circ$ ;  $MgI_2 \cdot 6C_3H_6O_2$ , m. p.  $55-56^\circ$ , and  $MgI_2 \cdot 6C_4H_8O_2$ , m. p.  $68^\circ$ . The solubility curve of the acetic acid compound has the same form as that of the corresponding compound with magnesium bromide. The compounds with formic and valeric acids could not be obtained in crystalline form.

The compounds with calcium chloride, referred to in the latter part of the paper, have been described previously (this vol., i, 272). G. S.

**Interaction of Olein and Mercuric Acetate in Acetic Acid.** ALEXANDRE LEYS (*Bull. Soc. chim.*, 1907, [iv], 1, 543—548. Compare Abstr., 1905, i, 433, ii, 655; this vol., i, 379).—As the result of determinations of the amount of mercurous acetate formed in the interaction of olein or fats containing unsaturated acids, with mercuric acetate, in presence of acetic acid, under the conditions already described (this vol., i, 379), the author suggests that the principal reaction may be regarded as taking place in the following way:

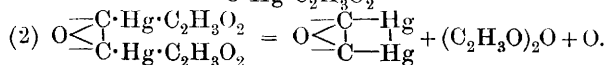
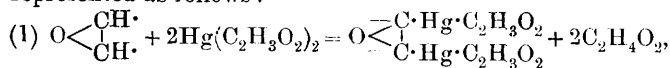


The diacetate so formed is decomposed to some extent by the boiling acetic acid in accordance with the following equation:



and it is to this reaction that the noticeable browning of the liquid is due.

The eventual fixation of some mercury is explained by reactions represented as follows:





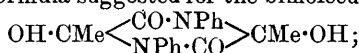
The mercurialised groups in the two chief products of these reactions, by the action of the oxygen set free in the second reaction, may be transformed into  $\cdot\text{CO}\cdot\text{CO}\cdot$  with the liberation of mercurous acetate and mercury respectively.

T. A. H.

**Transformation of the Esters of  $\alpha$ -Bromo-Fatty Acids into Esters of  $\alpha$ -Iodo-Fatty Acids.** F. BODROUX and FÉLIX TABOURY (*Compt. rend.*, 1907, 144, 1216—1217. Compare Bodroux, *Abstr.*, 1905, i, 585).—On adding the ester of an  $\alpha$ -bromo-fatty acid to an ethereal solution of magnesium iodide, obtained by treating magnesium turnings with iodine in presence of excess of ether, an energetic reaction takes place and the corresponding iodo-ester is formed in an almost theoretical yield. In this manner, ethyl bromoacetate is converted into ethyl iodoacetate, a liquid, b. p.  $85^{\circ}$ — $86^{\circ}$ /25 mm.,  $D_{25}^{24}$  1.762; ethyl  $\alpha$ -bromopropionate into ethyl  $\alpha$ -iodopropionate, a liquid, b. p.  $85^{\circ}$ /38 mm.,  $D_{17}^{17}$  1.662, and ethyl  $\alpha$ -bromobutyrate into ethyl  $\alpha$ -iodobutyrate, a liquid with b. p.  $100^{\circ}$ — $101^{\circ}$ /21 mm.,  $D_{17}^{17}$  1.570. These three esters emit irritating vapours at the ordinary temperature, and are decomposed rapidly by heat and light with liberation of iodine.

E. H.

**Amides of Pyruvic Acid.** ALFRED WOHL and L. H. LIPS (*Ber.*, 1907, 40, 2312—2315).—It is shown that the methylanilide and the diethylamide of pyruvic acid are stable and do not tend to polymerise in the same manner as the anilide (Nef, *Abstr.*, 1892, 1441; Bischoff and Walden, *ibid.*, 1893, i, 511), thus indicating that it is the hydrogen atom attached to nitrogen which takes part in the polymerisation. The formula suggested for the bimolecular anilide is



it forms a sodium derivative with two equivalents of sodium hydroxide.

The crude *methylanilide*,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ , after extraction with concentrated hydrochloric acid solidifies and then crystallises from water in snow-white needles, m. p.  $152^{\circ}$ — $153^{\circ}$ . The *diethylamide*,  $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$ , is an oil, b. p.  $100^{\circ}$ /18.3 mm., and dissolves readily in cold water, but separates when the solution is warmed or is made strongly alkaline.

J. J. S.

**Hydroxyfumaric and Hydroxymaleic Acids.** ALFRED WOHL (*Ber.*, 1907, 40, 2282—2293. Compare Wohl and Oesterlin, *Abstr.*, 1901, i, 365; Michael, *Abstr.*, 1906, i, 179; Michael and Bucher, *ibid.*, 1896, i, 599).—Both acids in alcoholic solution readily yield intense colorations with ferric chloride and both are readily oxidised by permanganate. The properties described in the following abstracts are in harmony with the enolic nature of the two acids. The readiness with which the one form is transformed into the other, when compared with other examples of *cis-trans* isomerism, may be accounted for by the intermediate formation of the ketonic form. The salts are probably derived from the ketonic form, as they differ considerably from the acids as regards stability. All the salts when acidified yield

the acid of lower m. p. Hydroxymaleic acid decomposes at  $152^{\circ}$  (not  $146^{\circ}$  as previously given) and hydroxyfumaric acid at  $184^{\circ}$ .

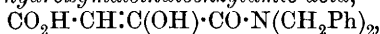
J. J. S.

**Oxalacetic Acid.** ALFRED WOHL and CARL H. LIPS (*Ber.*, 1907, 40, 2294—2300).—Hydroxymaleic acid is formed when the pyridine salt of hydroxymaleic anhydride (Wohl and Oesterlin, *Abstr.*, 1901, i, 365) is decomposed with 12% sulphuric acid, and hydroxyfumaric when 30% acid is used. *Dibenzylamine hydroxymaleate*,  $C_{13}H_{19}O_5N$ , is obtained when absolute alcoholic solutions of the base and of hydroxyfumaric acid are mixed. It crystallises from acetone, but is insoluble in cold alcohol; m. p.  $127-128^{\circ}$  (decomp.). When decomposed with hydrochloric acid, it yields hydroxymaleic acid, and the same salt is formed by the union of dibenzylamine and hydroxymaleic acid.

*Hydroxymaleinanilic acid*,  $CO_2H \cdot CH:C(OH) \cdot CO \cdot NHPh$ , is obtained by the addition of an excess of an absolute alcoholic solution of aniline to the pyridine salt at  $-20^{\circ}$  to  $-15^{\circ}$ , and is isolated by the addition of 5*N*-hydrochloric acid. It crystallises from benzene in snow-white crystals, m. p.  $112-113^{\circ}$  (decomp.). The sodium salt has m. p.  $156-158^{\circ}$  (decomp.), and dissolves sparingly in absolute alcohol, and also in water (20 parts) at  $22^{\circ}$ . *Hydroxyfumaranilic acid*,  $C_{10}H_9O_4N$ , is obtained in a similar manner from the pyridine salt, but using 10*N*-sulphuric acid and extracting with ether. It crystallises from benzene and has m. p.  $141-142^{\circ}$  (decomp.). The two isomerides may be transformed each into other. The addition of 10*N*-sulphuric acid to an alcoholic ethereal solution of the maleic derivative at  $-20^{\circ}$  converts it into the fumaric, and the addition of 5*N*-hydrochloric acid to the aniline salt of the fumaric compound at  $-20^{\circ}$  yields the maleinanilic acid.

In the presence of aniline the alcoholic solutions of the two acids are unstable, and even at  $-13^{\circ}$  begin to evolve carbon dioxide.

Dibenzylamine reacts with the pyridine salt in alcoholic solution at  $60-70^{\circ}$ , yielding *hydroxymaleindibenzylamic acid*,



which separates from benzene in colourless crystals, m. p.  $147^{\circ}$  (decomp.).

J. J. S.

**Anhydride and Anil of Hydroxymaleic Acid.** ALFRED WOHL and W. FREUND (*Ber.*, 1907, 40, 2300—2308).—*Hydroxymaleic anhydride*,

$\begin{array}{c} CH \cdot CO \\ | \quad | \\ OH \cdot C - CO \end{array} > O$ , may be obtained by the action of hydrogen chloride on an absolute ethereal solution of its pyridine salt provided moisture is rigorously excluded during all the operations, namely, shaking, filtration, and removal of the ether. It separates from its chloroform solution on the addition of light petroleum in the form of yellow needles. When heated in a closed capillary tube it decomposes at  $82-83^{\circ}$  (corr.), yielding a solid which melts and decomposes at  $120^{\circ}$ .

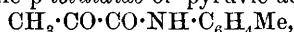
*Hydroxymaleic acid anil*,  $\begin{array}{c} CH \cdot CO \\ | \quad | \\ OH \cdot C - CO \end{array} > NPh$ , is obtained by the

action of acetyl chloride on the anilic acid (preceding abstract) at 40—43°. When pure it is quite white, but in the presence of moisture turns yellow, owing to the formation of an anhydride, the same decomposition occurs rapidly when the anil is heated at 120°. Aniline transforms the anil into anilinomaleic acid anil.

*Acetoxymaleic acid anil*,  $\text{OAc} \cdot \text{C} \begin{matrix} \text{CH} \cdot \text{CO} \\ \text{CO} \end{matrix} \text{NPh}$ , obtained together with xanthoxalanil (Ruhemann, *Trans.*, 1906, 89, 1236, 1847) by the action of acetyl chloride or acetic anhydride and sulphuric acid on hydroxymaleinanilic acid, crystallises from carbon disulphide, and has m. p. 125°. The yellow xanthoxalanil is transformed into a red modification when rubbed or heated, and this modification yields the yellow compound when crystallised from glacial acetic acid. When heated with aniline on the water-bath, the xanthoxalanil yields *anilino-dimaleic acid anil*,  $\text{C}_{26}\text{H}_{17}\text{O}_4\text{N}_3$ , which decomposes above 260°.

*Hydroxymalein-p-tolilic acid*,  $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$ , begins to decompose at 99° when slowly heated or melts and decomposes at 114° when rapidly heated. The *p-tolil*,  $\text{C}_{11}\text{H}_9\text{O}_2\text{N}$ , is more stable in moist air than the anil, but when heated at 160° yields the anhydride, *xanthoxaltolil*,  $\text{C}_{22}\text{H}_{16}\text{O}_5\text{N}$ , which exists in yellow and red modifications, m. p. 263—264° (decomp., corr.).

*p-Toluidinoacryl-p-toluidide*,  $\text{C}_{17}\text{H}_{18}\text{ON}_2$ , crystallises from alcohol in colourless needles, m. p. 150°, and dissolves readily in ether, benzene, acetone, or water. The *p-toluidide* of pyruvic acid,



has m. p. 109°.

J. J. S.

[Constants of] **Hydroxymaleic and Hydroxyfumaric Acid.**  
ALFRED WOHL and P. CLAUSSNER (*Ber.*, 1907, 40, 2308—2312).  
—A modification of Wohl and Oesterlin's method (*Abstr.*, 1901, i, 365) for the preparation of hydroxyfumaric acid is described. The following physical constants for the isomeric acids have been determined:

	Hydroxymaleic.	Hydroxyfumaric.
Molecular heat of combustion at constant volume .....	286.58 Cal.	275.78 Cal.
Heat of formation calc. ....	230.3 „	241.1 „
Dissociation constant <i>K</i> .....	0.2505	0.276

Molecular refraction in propyl alcoholic solution :

<i>D</i> line .....	24.90	25.32
<i>C</i> „ .....	24.90	25.21
<i>F</i> „ .....	25.35	25.35

Do. in aqueous solution :

<i>D</i> line .....	23.90	23.94
<i>C</i> „ .....	24.28	24.35

These values agree fairly well with those required for the enolic form of oxalacetic acid.

J. J. S.

**Partial Racemism.** VI. ALBERT LADENBURG and LEO FISCHL (*Ber.*, 1907, 40, 2279—2281. Compare Abstr., 1903, i, 575).—When a solution containing molecular proportions of brucine and racemic acid is crystallised from water below 50°, a crystalline salt is obtained,  $C_{23}H_{26}O_4N_2 \cdot C_4H_6O_6 \cdot 2\frac{1}{2}H_2O$ , and the acid obtained from this is optically inactive. It is the partially racemic acid salt, brucine hydrogen racemate. When the crystals separate at a temperature above 50°, they have quite a different appearance, and the recovered acid is levorotatory. According to Pasteur, the *l*-tartrate contains  $5H_2O$ , whereas the *d*-tartrate is anhydrous. That the crystals separating at the lower temperature are not a mere mixture of the *d*- and *l*-acid tartrates has been shown by sp. gr. and solubility determinations.

100 parts of water dissolve at

	20°.	25°.	35°.	44°.	56°.
Tartrate mixture .....	1·986	2·177	2·860	3·628	4·638
Racemate .....	1·411	1·638	2·539	3·629	4·983

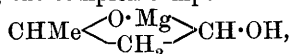
The two curves cut at 44°, and at this temperature the solubility of the racemate is not affected by the addition of an excess of *d*- or *l*-tartrate. In neutral solution, racemic acid is not resolved at the ordinary temperature by brucine. The racemate has the composition  $(C_{22}H_{26}O_4N_2)_2 \cdot C_4H_6O_6 \cdot 9H_2O$ , and is not resolved at temperatures up to 100°.

J. J. S.

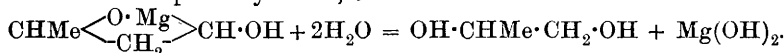
**Ethylthioglycollic [Ethylthiolacetic] Acid.** LUDWIG RAMBERG (*Ber.*, 1907, 40, 2588—2589. Compare Klason, *Ber.*, 1875, 8, 121).—Ethylthiolacetic acid is obtained quantitatively from sodium mercaptide and sodium chloroacetate in concentrated aqueous solution, the acid being liberated by the addition of excess of sulphuric acid. It has b. p. 164°/83 mm. and 117—118°/11 mm., m. p. -8·7°,  $D_{20}^{20}$  1·1518, and  $D_4^{20}$  1·1497. The value  $K$  is 0·0183.

C. S.

**Action of Magnesium Amalgam on Aldehydes.** ANDRÉ KLING and PAUL ROY (*Compt. rend.*, 1907, 144, 1111—1114. Compare L. Meunier, Abstr., 1902, i, 335).—Magnesium amalgam acts on aliphatic aldehydes producing the aldol condensation, followed by a reduction of the aldol formed. In presence of the amalgam, the aldehyde seems to act in the two desmotropic forms  $CH_3 \cdot CHO$  and  $CH_2 \cdot CH \cdot OH$ , forming the complex compound



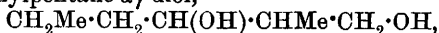
which is decomposed by water, thus:



This hypothesis is supported by the fact that the reaction does not take place when (as with chloral) tautomerism from the  $R \cdot CH_2 \cdot CHO$  to the  $R \cdot CH \cdot CH \cdot OH$  form is impossible.

Trioxymethylene does not react with magnesium amalgam. Acetaldehyde reacts very violently, giving a 15% yield of a glycol,  $C_4H_{10}O_2$ , b. p. 203—204°, which Meunier considered to be  $\beta$ -butanediol, but which the authors by a differentiation method previously

described (Kling and Viard, Abstr., 1904, i, 545) have decided is the glycol  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ . Propaldehyde gives a mixture of Talberg's  $\beta$ -methylpentane- $\alpha$ -diol,



and its propionic ester. From benzaldehyde, magnesium and benzyl benzoate and a small quantity of isohydrobenzoin are obtained.

E. H.

**Nonaldehyde Semicarbazone.** CARL HARRIES and HANS O. TÜRK (*Ber.*, 1907, 40, 2756).—Bagard (this vol., i, 384) finds the semicarbazone of synthetic nonaldehyde to melt at  $100^\circ$ , whereas the authors (this vol., i, 11) found that from oleic acid ozonide to have m. p.  $84^\circ$ . They now find that if the nonaldehyde be purified previously by means of the sodium bisulphite compound, the semicarbazone has m. p.  $100^\circ$ .

E. F. A.

**Chemical Action of Light. XI.** GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1907, 40, 2415—2424. Compare Abstr., 1906, i, 10).—It has been shown (Abstr., 1903, i, 562) that acetone in aqueous solution under the influence of sunlight is hydrolysed with the formation of acetic acid and methane. The present investigation was undertaken with the object of ascertaining whether other ketones in solution are similarly affected by sunlight. It is found that in aqueous solution, methyl ethyl ketone is hydrolysed into acetic acid and ethane, whilst lævulic acid yields propionic acid and in all probability also formic acid and methyl alcohol, but not acetic acid. Lævulic acid in alcoholic solution is probably converted into its ethyl ester and partially into  $\gamma$ -hydroxyvaleric acid, the formation of which is accompanied by the oxidation of part of the alcohol to acetaldehyde. Menthone, dissolved in dilute alcohol, yields decoic acid and an aldehyde, which is probably identical with Wallach's menthonicitronellaldehyde (Abstr., 1897, i, 427).

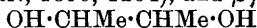
W. H. G.

**Dihydroxytetramethylacetone.** LOUIS HENRY (*Compt. rend.*, 1907, 144, 1200—1202).—By the action of magnesium methyl bromide (5 mols.) on ethyl mesoxalate (1 mol.), dihydroxytetramethylacetone,  $\text{CO}(\text{CMe}_2\cdot\text{OH})_2$ , is formed, although the carbonyl group is more readily attacked by organo-magnesium compounds than is the carbethoxy-group, and sufficient magnesium methyl bromide is used to react with all three groups. Dihydroxytetramethylacetone forms white needles, m. p.  $117$ — $118^\circ$ , b. p.  $238$ — $240^\circ$ . The differences between its melting and boiling points and those of pinacone are very nearly the same as those between glycol and  $\alpha\gamma$ -dihydroxyacetone and between  $\beta\gamma$ -dimethylbutane (diisopropyl) and diisopropyl ketone respectively.

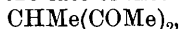
E. H.

**Direct Hydrogenation of Aliphatic Diketones.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, 144, 1086—1089. Compare Sabatier and Senderens, Abstr., 1903, i, 733; Darzens, Abstr., 1905, i, 66).—When diacetyl is submitted to hydrogenation in presence of reduced nickel at  $140$ — $150^\circ$ , it is completely transformed

into a mixture of almost equal volumes of Pechmann's dimethylketol,  $\text{OH}\cdot\text{CHMe}\cdot\text{COMe}$  (Abstr., 1890, 1234), and  $\beta\gamma$ -butanediol,



(Eltokoff). Acetylacetone when similarly hydrogenated at  $150^\circ$  gives a mixture of acetaldehyde, acetone, ethyl alcohol, *isopropyl* alcohol, and Claisen's  $\beta$ -hydroxy- $\delta$ -ketopentane,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COMe}$  (Abstr., 1899, i, 667). The latter, which has  $D_0^{15} 0.9677$ ,  $n_D^{15} 1.4292$ , is formed to an extent corresponding with one-quarter of the acetylacetone used. Thus three-quarters of the acetylacetone are decomposed according to the reaction  $\text{COMe}\cdot\text{CH}_2\cdot\text{COMe} + \text{H}_2 = \text{MeCHO} + \text{COMe}_2$ , the acetaldehyde and acetone partially undergoing subsequent hydrogenation to ethyl and *isopropyl* alcohols, whilst the remaining quarter undergoes the normal reaction. The latter reaction occurs less and less as the temperature is raised. In the case of methylacetylacetone,

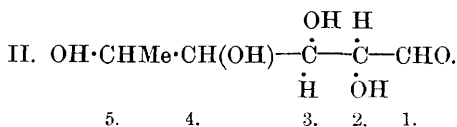
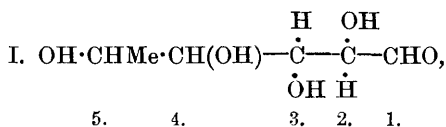


hydrogenation at  $170^\circ$  proceeds almost entirely according to a reaction analogous to the first above, the products being acetaldehyde, ethyl alcohol, methyl ethyl ketone, *isobutyl* alcohol, and a very small quantity of a liquid boiling above  $190^\circ$ . Acetonylacetone, when hydrogenated at  $190^\circ$ , is completely converted into water,  $\beta\epsilon$ -hexylene

oxide,  $\begin{matrix} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2\cdot\text{CHMe} \end{matrix} \text{O}$  (compare Béhal, Abstr., 1889, 839), having  $D_0^{17} 0.833$ ,  $n_D^{17} 1.4051$ , and a small quantity of *isopropyl* alcohol. In this case the change proceeds according to the normal reaction, giving  $\beta\delta$ -dihydroxyhexane,  $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{OH}$ , of which the greater proportion is dehydrated, forming water and hexylene oxide, whilst a small quantity is further hydrogenated to *isopropyl* alcohol. E. H.

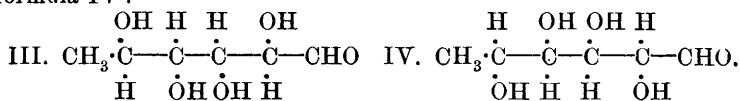
**Fucose.** WILLY MAYER and BERNHARD TOLLENS (*Ber.*, 1907, 40, 2434—2440. Compare Abstr., 1905, i, 746).—With the object of ascertaining the configuration of fucose, the products obtained by the oxidation of fucose and fucohexonic acid have been investigated. Fucose when oxidised with nitric acid does not yield mucic acid, but a trihydroxyglutaric acid which seems to be identical with that obtained by Ruff (Abstr., 1899, i, 324) by the oxidation of *d*-arabinose. Fucohexonic acid, prepared by the addition of hydrocyanic acid to fucose and subsequent hydrolysis, was obtained only in the form of its *lactone*,  $\text{C}_7\text{H}_{12}\text{O}_6$ , crystallising from alcohol in white plates, m. p.  $160^\circ$ , which gave  $[\alpha]_D + 33.3^\circ$  eight days after the solution had been prepared.

The *barium*, *calcium*, and *cadmium* salts of the acid have been prepared, likewise the *phenylhydrazone*,  $\text{C}_{13}\text{H}_{20}\text{O}_6\text{N}_2$ , which forms rhombic leaflets, m. p.  $218^\circ$ . When oxidised with nitric acid, fucohexonic acid yields oxalic acid and other acids which have not been identified, but no mucic acid, from which it follows that the two hydroxyl



groups attached to the two carbon atoms nearest the aldehyde group in fucose must be situated on opposite sides of the molecule as in I or II.

If now the hydroxyl group attached to carbon atom 4 be situated on the same side as that attached to carbon atom 3, then fucose would possess the configuration present either in *d*- or *l*-arabinose, but the trihydroxyglutaric acid obtained by the oxidation of fucose is undoubtedly identical with that obtained by the oxidation of *d*-arabinose, so that formula I is more probable than formula II. The hydroxyl group attached to carbon atom 5 is probably situated on the opposite side to that on which the hydroxyl group attached to carbon atom 4 is situated, so that fucose would have the formula III. This is quite analogous to the formula assigned to *l*-galactose, and that the two compounds possess a similar structure is highly probable, since the specific rotatory power of fucose is  $-75.5^\circ$ , whilst that of *l*-galactose is  $-81^\circ$ . Since rhodose is the optical isomeride of fucose (Müther and Tollens, *Abstr.*, 1904, i, 226), it follows that it must possess the formula IV:



W. H. G.

**Nature and Structure of Starch.** E. JENTYS (*Bull. Acad. Sci. Cracow*, 1907, 203—252).—The starch grains occurring in potato, rice, wheat, and sorghum are not homogeneous, but consist of a mixture of colloids composed of reducing sugars and aromatic substances related to the tannins, and glucosidic in character. The stratified starch grains occurring in chloroplastids, leucoplastids, &c., are of different composition at various parts. Stratification is the result of separation from a liquid mixture of carbohydrates and tannin like substances. The coloration of starch by iodine is due to the presence of aromatic substances, of which one gives a blue tint, another red, a third yellow, and the characteristic colour reactions with iodine usually ascribed to the various dextrans are due to the gradual decomposition of these compounds by diastase, the compound which gives the blue colour disappearing before that giving the red colour, and so on. Sorghum and other starches, which give a red coloration with iodine, differ only from ordinary starch in containing more tannin-like substances which give a red colour with iodine.

The conversion of starch into sugar is not a hydrolytic process, but consists in a separation of reducing sugars from aromatic substances. In the action of enzymes on starch the aromatic substances are probably merely separated, but in the action of acids they are decomposed.

T. A. H.

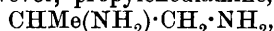
**Crystallography of Halogen Salts of Aliphatic Ammonium Bases.** L. WAGNER (*Zeitsch. Kryst. Min.*, 1907, 43, 148—201).—Crystallographic descriptions are given of each of the two dimorphous modifications of the chlorides, bromides, and iodides of the primary,

secondary, tertiary, and quaternary methyl- and ethyl-amines. Their morphotropic relations are compared with regard to their topic axes.

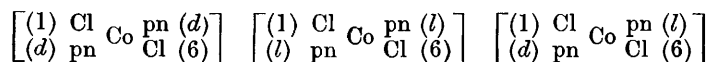
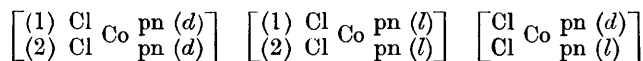
L. J. S.

**Substituted Mercurammonium Compounds.** K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 230—240).—These compounds were prepared by adding Nessler solution to alkaline solutions of the pure amines. *Mercuriodomethylamine* is formed when the experiment is conducted in the cold, but if the solution is heated the precipitate changes from lemon-yellow to yellow, and has the constitution  $\text{IHg}\cdot\text{NHMe}$ . By analogy with these two compounds it is considered that the substance to which Buisson (*Abstr.*, 1906, ii, 704) gives the formula  $\text{Hg}_9\text{N}_4\text{I}_6$  is really a mixture of two definite compounds, the proportions of which depend on the conditions of the experiment. *Mercuriodoethylamine*, possibly  $\text{HgI}_2\cdot\text{Hg}_2(\text{NHET})_2$ , is fairly stable when pure. *Mercuriodopropylamine* yields colloidal solutions, and is quite different from any of the other mercurammonium compounds; it can probably be represented as  $\text{HgI}\cdot\text{Hg}\cdot\text{Hg}\cdot\text{NI}\cdot\text{NHPr}, 12\text{H}_2\text{O}$ . *Mercuriododiethylamine* separates after a time as a white, crystalline, very unstable substance. Ž. K.

**Stereoisomeric Dichlorodipropylenediamine Cobalt Salts.** ALFRED WERNER and A. FRÖHLICH (*Ber.*, 1907, **40**, 2225—2235).—The stereoisomeric *cis*- and *trans*-dichlorodipropylenediamine cobalt salts of the type  $[\text{Cl}_2\text{Cpn}_2]\text{X}$  are described [ $\text{pn} = \text{C}_3\text{H}_6(\text{NH}_2)_2$ ], the corresponding salts derived from ethylenediamine already having been described. Since, however, propylenediamine,



as distinct from ethylenediamine, contains an asymmetric carbon atom, a new aspect is introduced, and for the complete elucidation of the phenomena of isomerism in this field a considerable amount of further experimental data will be required. The following combinations are possible for the group  $[\text{Cl}_2\text{Cpn}_2]$ , namely:



An additional factor, which still further increases the possibilities of isomerism, lies in the unsymmetrical constitution of propylenediamine itself.

The authors predict the possible existence of four inactive praseo-salts of the type in question, and six inactive violeo-isomerides. Of these, two praseo-salts and three violeo-salts should be resolvable into optically active components.

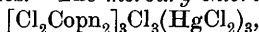


Of these possible isomerides, the authors, so far, have obtained only one praseo- (*trans*-) salt and one violeo- (*cis*-) salt. These compounds, like the corresponding ethylenediamine compounds, are intensely green, but are much more soluble; the chemical behaviour is similar.

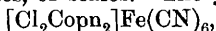
An aqueous solution of propylenediamine hydrochloride was gradually added to an aqueous solution of cobalt chloride and the mixture oxidised by passing air through it. Hydrochloric acid was then added, and, after twenty-four hours, *trans*-dichlorodipropylenediamine acid chloride,  $[\text{Cl}_2 \text{ Co pn}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ , separated as dark green, rhombic plates. When heated at  $105^\circ$ , the *trans*-salt loses water, and is converted into the isomeric violeo-chloride.

The *trans*-chloride,  $[\text{Cl}_2 \text{ Co pn}_2]\text{Cl}$ , obtained by dissolving the preceding compound in 95% alcohol and then adding ether, separates in bright green leaflets. Its aqueous solution is green, but after some hours becomes pink, probably owing to the formation of the aquo-compound. When the aqueous solution is heated, it assumes a carmine-red colour, and, when evaporated on the water-bath, gives the violet violeo-salt. The action of various acids and of a large number of salts on the chloride in question is described.

The *bromide*,  $[\text{Cl}_2 \text{ Copn}_2]\text{Br} \cdot \text{H}_2\text{O}$ , obtained by the addition of potassium bromide to the preceding chloride, is a pale green, crystalline powder. It cannot be purified by recrystallisation from water, since its aqueous solution on heating is converted into the aquo-salt. The *iodide*,  $[\text{Cl}_2 \text{ Copn}_2]\text{I}$ , is yellowish-green and very unstable. The *nitrate*,  $[\text{Cl}_2 \text{ Copn}_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ , obtained by the addition of potassium nitrate to the chloride, forms pale green crystals. The *thiocyanate*,  $[\text{Cl}_2 \text{ Copn}_2]\text{SCN}$ , is pale green. The *dithionate*,  $[\text{Cl}_2 \text{ Copn}_2]\text{S}_2\text{O}_6$ , forms glistening, green needles. The *permanganate*,  $[\text{Cl}_2 \text{ Copn}_2]\text{MnO}_4$ , has the colour of potassium permanganate. The *hydrogen sulphate*,  $[\text{Cl}_2 \text{ Copn}_2]\text{SO}_4\text{H}$ , obtained by addition of not too much sulphuric acid to the chloride, separates in green needles and forms a *silver* salt,  $([\text{Cl}_2 \text{ Copn}_2]\text{SO}_4\text{Ag})_2 \cdot \text{AgNO}_3$ , which crystallises in malachite-green, glistening scales. The *platinichloride*,  $[\text{Cl}_2 \text{ Copn}_2]_2\text{PtCl}_6$ , obtained by the addition of platinic chloride to the chloride, forms dark green, hexagonal prisms. The *platinosochloride*,  $[\text{Cl}_2 \text{ Copn}_2]_2\text{PtCl}_4$ , obtained by the addition of potassium platinosochloride to the chloride, is a pale green, microcrystalline powder. The *aurichloride*,  $[\text{Cl}_2 \text{ Copn}_2]\text{AuCl}_4$ , forms grass-green needles. The *mercury chloride* compound,



forms green rhoms, needles, or scales. The *ferricyanide*,



is a green powder.

*cis*-Dichlorodipropylenediaminecobalt chloride,  $[\text{Cl}_2 \text{ Copn}_2]\text{Cl}$ , obtained either from the acid or neutral praseo-chlorides already described by heating at  $105^\circ$ , is a violet powder. Its aqueous solution is dark violet, but gradually assumes a violet-red tint owing to the formation of aquo-salt. The action on the *cis*-salt of various acids and salts is described. The *dithionate*,  $[\text{Cl}_2 \text{ Coen}_2]\text{S}_2\text{O}_6$ , prepared by the addition of sodium dithionate to the violeo-chloride, forms green crystals; some dithionate of the aquo-series separates in red crystals at the same time.

A. McK.

**Action of Nitrous Acid on Pentamethylenediamine.** NIKOLAUS J. DEMJANOFF and M. DOJARENKO (*Ber.*, 1907, 40, 2589—2594).—This reaction has been studied by Gustavson and Demjanoff (compare Abstr., 1889, 950) and Demjanoff (Abstr., 1894, i, 500), but in consequence of Haworth and Perkin's statement that compounds are produced containing four atoms of carbon (compare *Trans.*, 1894, 65, 95), the experiments have been repeated. The decomposition of the pentamethylenediamine and the isolation of the products in the form of bromides, alcohols, and glycols have been performed as in the earlier papers. Two bromides of the composition  $C_5H_8Br_4$  have been obtained in the crystalline state, with m. p.  $86^\circ$  and  $112.5\text{--}113^\circ$  respectively, but the quantities were too small for further investigation. Since, however,  $\alpha$ : $\omega$ -dichloro- or di-iodo-pentanes and alcoholic potassium hydroxide yield a hydrocarbon, the bromide of which has m. p.  $86^\circ$  and appears to be identical with one of the preceding bromides, the authors conclude that the latter is the tetrabromide of divinylmethane; the other bromide, m. p.  $112.5\text{--}113^\circ$ , appears to be piperylene tetrabromide.

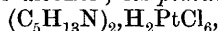
The alcohols were fractionally distilled, and the main fraction, b. p.  $130\text{--}136^\circ$ , consists of a mixture of  $\Delta^6$ -penten- $\alpha$ -ol and  $\Delta^7$ -penten- $\alpha$ -ol; by oxidation with potassium permanganate, formic, acetic, oxalic, and succinic acids are obtained.

The main fractions of the glycols have b. p.  $225\text{--}230^\circ$  and  $234\text{--}236^\circ$  respectively, and the composition  $C_5H_{12}O_2$ . They consist of a mixture of pentan- $\alpha\epsilon$ -diol and pentan- $\alpha\delta$ -diol; this was proved by converting the first-mentioned fraction through the bromide into the nitrile, which by hydrolysis yielded pimelic acid and a small quantity of another acid, which is apparently  $\alpha$ -methyladipic acid.

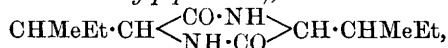
C. S.

**Natural Isomeride of Leucine. II. Constitution and Synthesis of *iso*Leucine ( $\alpha$ -Amino- $\beta$ -methylvaleric Acid).** FELIX EHRLICH (*Ber.*, 1907, 40, 2538—2562. Compare Abstr., 1904, i, 560).—The approximate separation of *isoleucine* from valine (compare Fischer, Matsubara, and Hilpert, Abstr., 1906, i, 561) when, as is often the case, the latter is present in considerable quantity, may be effected by heating the mixture with barium hydroxide solution under pressure, preparing the copper salts, and either shaking with cold methyl alcohol or boiling with ethyl alcohol; the copper salt of *isoleucine* dissolves, whilst the other is insoluble.

On dry distillation, *d-isoleucine* yields: (1) partially racemised *d*-amylamine, identical with that prepared by Marckwald (Abstr., 1904, i, 362) from *d*-amyl alcohol; its *platinichloride*,



forms golden-yellow, rhombic plates decomposing at  $240^\circ$ ; its *sulphate*,  $(C_5H_{13}N)_2, H_2SO_4$ , decomposes at about  $295^\circ$ . (2) *isoLeucinimide* (*iso*-2:5-*diketo*-3:6-*diisobutylpiperazine*),



which separates from alcohol in spherical aggregates of slender, colourless needles, m. p.  $280\text{--}281^\circ$ , and has the normal molecular weight

in boiling alcohol. This compound has a slight dextrorotation in alcoholic solution, and probably consists of a mixture of several of the four possible stereoisomerides. From these results and the observation that the phenylcarbimide derivative of *isoleucine* yields a hydantoin compound (compare Abstr., 1904, i, 362), the conclusion is drawn that *isoleucine* is an amino-acid containing two asymmetric carbon atoms, and is identical with one of the four possible optically active  $\alpha$ -amino- $\beta$ -methylvaleric acids,  $\text{CHMeEt}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ . This constitution is supported by fermenting sugar in presence of *isoleucine*, the latter being converted into *d*-amyl alcohol (compare Ehrlich, this vol., i, 383) which, on oxidation, yields the dextrorotatory  $\alpha$ -methylbutyric acid,  $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ . Further proof is afforded by the synthesis of *isoleucine* (see also Bouveault and Locquin, Abstr., 1905, i, 636) from *d*-amyl alcohol by oxidising to *d*-valeraldehyde, converting the latter into aminovaleronitrile by the action of hydrogen cyanide and ammonia, and hydrolysing the nitrile. In this way is obtained a mixture of about equal proportions of *isoleucine* and the stereoisomeric *alloisoleucine*. An almost identical mixture is obtained by the action of barium hydroxide solution on natural *d*-*isoleucine* under pressure, so that *alloisoleucine* must differ from *isoleucine* only in the space-arrangement of the  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{NH}_2$  part of the molecule (compare Fischer, this vol., i, 192).

*alloisoLeucine* strongly resembles *isoleucine* in external appearance and in the properties of its derivatives. Its taste is, however, sweet instead of bitter (compare Fischer and Warburg, Abstr., 1906, i, 72; Fischer, Matsubara, and Hilpert, Abstr., 1906, i, 561), and it is levorotatory, its  $[\alpha]_D^{20}$  having the values  $-14.4^\circ$  and  $-36.95^\circ$  for aqueous and hydrochloric acid solutions respectively.

The naturally occurring dextrorotatory *isoleucine* and all its natural and synthetic derivatives are designated by the prefix *d*- (compare Marckwald, Abstr., 1902, i, 418), whilst the *alloisoleucine* prepared from *d*-*isoleucine* by a change in the spacial arrangement of the groups round the  $\alpha$ -carbon atom is named *d'*-*alloisoleucine* (compare Fischer, this vol., ii, 148).

*d*-Valeraldehyde ( $\beta$ -methylbutane- $\alpha$ -al),  $\text{CHMeEt}\cdot\text{CHO}$ , prepared by the oxidation of *d*-amyl alcohol (93%), is a clear, highly refractive liquid, b. p.  $90-92^\circ/760$  mm., and, assuming the product obtained to contain 93% of the active aldehyde, has  $[\alpha]_D^{20} +23.56^\circ$ . If rapidly dried and kept away from the air, the aldehyde remains unchanged for a long time, but it is rapidly oxidised in the air to *d*-valeric acid.

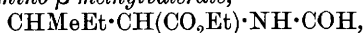
T. H. P.

**Resolution of  $\alpha$ -Amino- $\beta$ -methylvaleric Acid into its Optical Isomerides. Properties of the Optically Active Acids and their Derivatives. Identification with Ehrlich's *isoLeucine*.** RENÉ LOCQUIN (*Bull. Soc. chim.*, 1907, [iv], 1, 595—601, 601—607. Compare Ehrlich, Abstr., 1903, i, 796; 1904, i, 560; 1906, i, 807; Bouveault and Locquin, 1905, i, 636; 1906, i, 938).—Attempts to resolve *r*- $\alpha$ -amino- $\beta$ -methylvaleric acid into its optical isomerides by (1) crystallisation of quinine, quinidine, brucine, strychnine, or

cinchonine salts of (a) its benzoyl derivative or (b) of the benzene- or *p*-toluene-sulphonate, or (2) the corresponding camphoramic acid, were unsuccessful.

The resolution was finally effected by crystallisation of the brucine salt of the formyl derivative, the procedure adopted being that described by Fischer and Warburg (Abstr., 1906, i, 72) for leucine.

*Ethyl  $\alpha$ -formylamino- $\beta$ -methylvalerate*,



b. p.  $163^\circ/17$  mm.,  $D_4^{20}$  1.056, is prepared by heating the ethyl ester of the amino-acid with formic anhydride. It is hydrolysed by water at  $165$ — $175^\circ$ , yielding  $\alpha$ -amino- $\beta$ -methylvaleric acid. The latter, when heated with formic acid at  $170^\circ$  during several hours, furnishes  $\alpha$ -formyl-amino- $\beta$ -methylvaleric acid, and this on solution in dry alcohol and addition of brucine in the same solvent furnishes a precipitate of the brucine salt (m. p.  $150$ — $154^\circ$ ) of the *laevo*-acid still containing a small amount of the *r*-acid, which is readily separated by recrystallisation from warm water. The brucine salt of the *dextro*-acid is obtained by evaporating the mother liquor.

The optically active  $\alpha$ -amino- $\beta$ -methylvaleric acids, m. p.  $156$ — $157^\circ$ , separate from water in superb, translucent crystals. The *l*-acid, after being twice recrystallised from water, had  $[\alpha]_D^{20} - 27.76^\circ$  in alcohol and the *d*-acid  $[\alpha]_D^{20} + 28.26^\circ$  under the same conditions. A sample of formylisoleucine, prepared by Ehrlich, had, according to the latter, m. p.  $154$ — $156^\circ$  and  $[\alpha]_D^{20} + 25.41$  after a single crystallisation from water.

The optically active  $\alpha$ -amino- $\beta$ -methylvaleric acids crystallise from water in brilliant spangles and have m. p.  $280$ — $290^\circ$ . The *l*-acid has  $[\alpha]_D^{20} - 10.55^\circ$  in water,  $-31.37^\circ$  in dilute hydrochloric acid, and  $-40.86^\circ$  in concentrated acid. The *d*-acid has  $[\alpha]_D^{20} + 11.29^\circ$  in water and  $+40.61^\circ$  in concentrated hydrochloric acid.

The lower figures given by Ehrlich for *isoleucine* are probably due to the presence of some *l*-leucine or other impurity in his product.

The *benzoyl* derivative of the *l*-acid, m. p.  $118^\circ$ , crystallises in needles and has  $[\alpha]_D^{20} - 26.03$  in  $N/2$ -sodium hydroxide solution (compare Ehrlich, Abstr., 1903, i, 796).

The *benzenesulphonate* of the *r*-acid, m. p.  $169^\circ$ , forms small crystals; that of the *dextro*-acid, m. p.  $149^\circ$ ,  $[\alpha]_D^{20} - 11.63^\circ$  in  $N/3$ -sodium hydroxide solution, crystallises from benzene. T. A. H.

**Metallic Dithiocarbamates; Preparation of Aliphatic Thiocarbimides.** MARCEL DELÉPINE (*Compt. rend.*, 1907, 144, 1125—1127).—In the general method for the preparation of fatty thiocarbimides (Hofmann, *Ber.*, 1868, 1, 25; Ponzio, Abstr., 1896, i, 636) represented by the equations:  $\text{CS}_2 + 2\text{RNH}_2 = \text{R} \cdot \text{NH} \cdot \text{CS}_2 \cdot \text{NH}_3\text{R}$ ;  $2\text{R} \cdot \text{NH} \cdot \text{CS}_2 \cdot \text{NH}_3\text{R} + 2\text{HgCl}_2 = 2\text{RNH}_3\text{Cl} + (\text{R} \cdot \text{NH} \cdot \text{CS}_2)_2\text{Hg} + \text{HgCl}_2 \rightarrow 2\text{HgS} + 2\text{HCl} + 2\text{RN} \cdot \text{CS}$ , the author prevents the loss of amine as hydrochloride in the first reaction by substitution of a molecule of sodium hydroxide for one molecule of amine, and avoids the formation of hydrochloric acid in the second reaction by using dibasic lead acetate

instead of mercuric chloride. Thus the improved method is based on the scheme:  $\text{RNH}_2 + \text{CS}_2 + \text{NaOH} = \text{NHR} \cdot \text{CS}_2 \cdot \text{Na} + \text{H}_2\text{O}$ ;  $\text{NHR} \cdot \text{CS} \cdot \text{SNa} + \text{OH} \cdot \text{Pb} \cdot \text{OAc} = \text{RN} : \text{CS} + \text{H}_2\text{O} + \text{PbS} + \text{NaOAc}$  (compare Goldschmidt and Schulhof, *Abstr.*, 1886, 557; Losanitsch, *Abstr.*, 1892, 55). The sodium hydroxide can be replaced by potassium or barium hydroxide, and, as the sodium alkyl dithiocarbamates are soluble in water, this solvent can be used instead of the alcohol or ether necessary with the anhydrous amines. The method gives good results with methyl-, propyl-, and isobutyl-amines, but is not so satisfactory with benzylamine. The solutions of the dithiocarbamates on evaporation give well crystallised salts, which undergo double decomposition with metallic salts. Many of the metallic derivatives formed give the thiocarbimide on boiling with water, and those of iron, nickel, cobalt, and manganese dissolve in ether, chloroform, benzene, and carbon disulphide, giving intensely coloured solutions.

The secondary amines react similarly, giving sodium salts of the constitution  $\text{NRR}' \cdot \text{CS} \cdot \text{SNa}$ , which also crystallise well and give metallic salts. The latter are generally soluble in organic solvents, and their solubility in these and insolubility in water increase with the complexity of the alkyl radicles present. The salts of most metals except those of the alkalis and alkaline earths are precipitated by sodium diisobutyl dithiocarbamate.

The sodium mono- and dialkyl dithiocarbamates react, as well as the salts of the amines in the reactions previously described, for the formation of the thiuram disulphides and the mono- and dialkyl dithiocarbamic and iminodithiocarbonic esters.

E. H.

**Complex Compounds of Organic Imides. IV. The Biuret Reaction.** LEO TSCHUGAEFF (*Ber.*, 1907, 40, 1973—1980. Compare *Abstr.*, 1904, i, 478; 1905, i, 865; 1906, i, 814; Ley and Werner, this vol., i, 302).—Abnormally coloured complex metallic salts of succinimide are obtained when an alkali hydroxide, copper acetate, and excess of the imide interact in aqueous alcoholic solution. They are all of the type  $\text{Cu}(\text{Su})_4 \cdot \text{M}_2 \cdot n\text{H}_2\text{O}$  or  $\text{Cu}(\text{Su})_2 \cdot 2\text{MSu} \cdot n\text{H}_2\text{O}$  [ $\text{Su} = \text{C}_2\text{H}_4 \cdot \text{CO}_2 \cdot \text{N}$ ]. The sodium and lithium salts are coloured blue and ultramarine-blue respectively, the potassium, rubidium, and caesium salts are all reddish-violet. These compounds are stable in the solid state, but are hydrolysed by water.

Nickel yields a series of similar complex salts of a yellow colour.

Attention is drawn to the similarity in colour and behaviour towards water of the above compounds, and the complex copper derivatives of biurets (Schiff, this vol., i, 206); they differ in composition only in that the biuret compounds contain two molecules of imide, the succinimide derivatives containing four. The conclusion is therefore drawn that the succinimide salts possess the general co-ordinate formula  $[\text{Cu}(\text{Su})_4] \cdot \text{M}_2$ .

W. R.

**Cuprammonium Salts. III.** DAVID W. HORN (*Amer. Chem. J.*, 1907, 37, 467—483. Compare *Abstr.*, 1906, ii, 231).—The dependence

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of the complexity of a cuprammonium compound on the concentration of ammonia, copper salt, and water in the system which it forms is indicated.

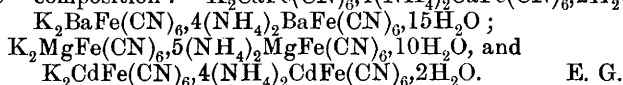
The salt,  $\text{Cu}(\text{SCN})_2 \cdot 2\text{NH}_3$ , obtained by dissolving cupric thiocyanate in dilute ammonia or by digesting cuprous thiocyanate and dilute ammonia in contact with air, or by treating solutions of potassium or ammonia thiocyanates with dilute ammonia and solutions of cupric salts, forms greyish-blue needles. The salt,  $\text{Cu}(\text{SCN})_2 \cdot 4\text{NH}_3$ , obtained by the addition of potassium or ammonium thiocyanate to a solution of copper sulphate in concentrated ammonia, forms purple-blue crystals, and is identical with the compound already described by Richards and Merigold.

The solubility of copper thiocyanate in ammonia at  $25^\circ$  and  $40^\circ$  respectively was determined, and the results interpreted by aid of the phase rule.

A. McK.

### Some Ferrocyanides of Calcium, Barium, and Magnesium.

FRANK B. DAINS (*J. Amer. Chem. Soc.*, 1907, 29, 727—729).—When potassium ferrocyanide is added to a solution of a calcium salt in presence of a large excess of ammonia, a precipitate is produced which is usually regarded as potassium calcium ferrocyanide. An investigation of this precipitate and of similar barium, magnesium, and cadmium salts has shown that these salts contain ammonium and have respectively the composition:



E. G.

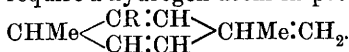
**The Benzene Problem.** IWAN VON OSTROMISLENSKY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1351—1387).—A critical survey of the theories which have so far been advanced as to the structure of the benzene nucleus leads to the conclusion that the one which is most probably correct is that of Kekulé, its only weak point being the absence of isomerides in some of the substituted derivatives, as, for instance, in the ortho-compounds. Contrary to Ladenburg's view (*Ber.*, 1869, 2, 140), it is considered that the impossibility of obtaining such substances is not entirely beyond dispute. With a view to elucidating this question and also of testing Knoevenagel's theory of motor-isomerism (*Abstr.*, 1903, i, 785), a partially successful attempt has been made to obtain the  $\alpha$ - and  $\beta$ -modifications of compounds such as *o*-nitrotoluene, *o*-bromotoluene, *o*-chlorophenol, &c., as well as some of the tri-substituted derivatives. By treating 1-chloro-2:4-dinitrobenzene with ammonia, a new 2:4-dinitrophenol has been obtained, m. p.  $85.1^\circ$ , and differing from the ordinary *o*-dinitrophenol in many of its properties. Reasons are advanced for assuming that these two modifications are not tautomeric forms, but are really due to the different positions of the double linkings in the ring. An attempt is also made to apply crystallographic methods to the solution of the benzene problem, and also, although unsuccessfully, to separate the different modifications by methods analogous to those used by Pasteur. From this point of view the centric formula seems to be altogether untenable; on the other

hand, the experimental data are not yet sufficient to lead the author to any quite definite conclusion. Z. K.

**Separation of Aromatic Hydrocarbons by the Fractional Precipitation of their Alcoholic Solution.** K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1388—1392. Compare Abstr., 1905, i, 405).—In order that the separation of hydrocarbons by means of fractional precipitation should receive a wide application, it is essential that the choice of solvent and precipitant should not be a mere matter of chance, but should depend on certain definite constants which at once indicate their applicability.

The necessary constants are: (1) the solubility of the substances in solvent and in precipitant separately; (2) the solubility of each substance in a mixture of equal volumes of solvent and precipitant. The precipitation will be the more complete the greater the value of  $m/2p$ , and the less  $m'/2p'$  (where  $m$  and  $m'$  = the solubilities of the substances in the solvent,  $p$  = the solubility of one of them in the mixture);  $p/n$  (where  $n$  = the solubility of one substance in the precipitant) is termed the "characteristic coefficient." The solvent and precipitant must mix with one another. The method has been applied successfully to the separation of a mixture of benzene and toluene, alcohol and water being used as solvent and precipitant. Z. K.

**Menthatriene: Determination of Constitution by Optical Methods.** AUGUST KLAGES (*Ber.*, 1907, **40**, 2360—2373. Compare Klages and Sommer, Abstr., 1906, i, 566; Rupe and Liechtenhahn, *ibid.*, 374; Brühl, Trans., 1907, **91**, 115).—The constitution of the 2-alkylmenthatrienes is discussed and it is considered that the optical properties exclude the possibility of formulæ containing a trimethylene or a pentamethylene ring. On the other hand, the molecular dispersions,  $M_v - M_a$ , found exceed those calculated by the same amount, 0.25—0.26, as is the case with the corresponding *p*-cymenes, in which the conjugated ethylene linkings are inactive, whereas the molecular dispersions of similarly constituted compounds containing active conjugated ethylene linkings exceed the calculated dispersions by larger amounts: 0.44 for  $\Delta^{1:3}$ -dihydro-*m*-xylene, 0.67 for  $\Delta^{1:3}$ -dihydro-3-ethyl-1:5-xylene. Hence the menthatrienes cannot contain conjugated ethylene linkings, and, since their optical properties require a hydrogen atom in position 4, they must have the constitution



2-Phenylmenthatriene cannot be obtained in a state of purity as it readily undergoes transformation into 2-phenyl-*p*-cymene; three specimens, boiling at the same temperature, had  $\alpha_D + 66^\circ$ ,  $+ 100^\circ$ , and  $+ 88^\circ$  respectively. The product obtained on reduction of the specimen,  $\alpha_D + 88^\circ$ , with sodium and alcohol, yielded a small amount of an oil, b. p.  $261^\circ/752$  mm., with a changed rotatory power and odour; it could not be separated completely from the 2-phenyl-*p*-cymene constituting the remainder of the product. In yielding a reduction product with sodium and alcohol, 2-phenylmenthatriene resembles phenyl- $\Delta^1$ -cyclohexene which contains the grouping  $\text{CPh:CH}$

and differs from the 2-alkylmenthatrienes and also from such substances as 2-phenyl- and 3-phenyl-1-methyl- $\Delta^1$ -cyclohexenes, which contain an ethylene linking, but not the above grouping. These *cyclohexenes* can be reduced by hydriodic acid, the products having molecular refractions and dispersions similar to those of the normal benzene hydrocarbons, the molecular dispersion found exceeding the calculated by 0.253 for phenylcyclohexane and by 0.241 for benzylcyclohexane. This exaltation of the molecular dispersion for 2-phenylmenthatriene, +0.98 for a specimen having  $\alpha_D + 110.2^\circ$ , is greater than for phenylcyclohexenes containing the grouping CPh:C: 0.622 for phenyl- $\Delta^1$ -cyclohexene, 0.697 for 2-phenyl-1-methyl- $\Delta^1$ -cyclohexene, but less than for phenylcyclohexadiene containing active conjugated ethylene linkings: 1.911 for 3-phenyl-1-methyl- $\Delta^{1:3}$ -cyclohexadiene, 1.744 for 3-phenyl- $\Delta^{1:3}$ -dihydro-1:5-xylene. The exaltation of the molecular dispersion is normal for hydrocarbons containing one ethylene linking and a phenyl group attached to a saturated carbon atom: 0.227 for benzyl- $\Delta^1$ -cyclohexene, 0.300 for 3-benzyl-1-methyl- $\Delta^1$ -cyclohexene.

As a derivative of diphenyl, 2-phenyl-*p*-cymene has an exaltation of the molecular dispersion, 0.79, greater than that for 2-benzyl-*p*-cymene, 0.49.

Refractive indices are given for the sodium *D*-line, and for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hydrogen lines; those for the *D*-line only are quoted here.

2-Methylmenthatriene,  $D_4^{15}$  0.8776,  $[\alpha]_D^{21} + 69.12^\circ$ ,  $n_D^{15}$  1.50217,  $M_\gamma - M_\alpha = 1.94$ . 2-Methyl-*p*-cymene,  $D_4^{15.5}$  0.8740,  $n_D^{15.5}$  1.50001,  $M_\gamma - M_\alpha = 1.94$ .

2-Ethyl-*p*-cymene, formed by Fittig's reaction from 2-iodo-*p*-cymene, b. p.  $100^\circ/17$  mm.,  $D_4^{15.7}$  0.8706,  $n_D^{15}$  1.49670,  $M_\gamma - M_\alpha = 2.07$ ; the corresponding *sulphonanilide*, m. p.  $150-151^\circ$ . 2-Ethyl-*p*-cymene, from 2-ethylmenthatriene,  $D_4^{15.6}$  0.8708,  $n_D^{15.6}$  1.49878,  $M_\gamma - M_\alpha = 2.07$ . 2-Ethylmenthatriene,  $D_4^{15}$  0.8880,  $n_D^{15}$  1.50847,  $M_\gamma - M_\alpha = 2.07$ .

2-Propyl- $\Delta^{6:8(9)}$ -menthadiene-2-ol (2-propylcarveol),  $C_{13}H_{22}O$ , prepared by the action of magnesium propyl bromide on carvone, is a colourless, viscid oil with a feeble odour, b. p.  $125^\circ/15$  mm.,  $D_4^{21}$  0.9178,  $[\alpha]_D^{21} + 49.16^\circ$ ,  $n_D^{21}$  1.4885.

2-Propylmenthatriene,  $C_{13}H_{20}$ , prepared by treating the product of the action of magnesium propyl bromide on carvone with an ice-cold mixture of glacial acetic acid and acetic anhydride, is obtained as a mobile oil, b. p.  $107-108^\circ/13$  mm.,  $D_4^{15}$  0.8804,  $[\alpha]_D^{22} + 86.20^\circ$ ,  $n_D^{15}$  1.50273,  $M_\gamma - M_\alpha = 2.22$ , and decolorises bromine instantaneously.

2-Propyl-*p*-cymene,  $C_{13}H_{20}$ , formed in a 60% yield by heating 2-propylmenthatriene with 3% hydrochloric acid, b. p.  $226^\circ/766$  mm. (corr.) or  $106-107.5^\circ/13$  mm.,  $D_4^{15}$  0.8685,  $n_D^{15}$  1.49585,  $M_\gamma - M_\alpha = 2.21$ . The *sulphonic acid* crystallises in colourless needles, m. p.  $69-71^\circ$ ; the *sulphonyl chloride* crystallises in rhombic plates, m. p.  $61^\circ$ ; the *sulphonanilide*,  $C_{19}H_{25}O_2NS$ , forms strongly refracting plates, m. p.  $138^\circ$ . 2-Propyl-*p*-cymene is converted by the action of bromine and aluminium bromide into pentabromotoluene, m. p.  $283^\circ$ .

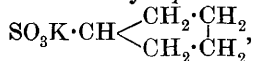
2-Phenylmenthatriene,  $D_4^{15}$  0.9752,  $[\alpha]_D^{13.8} + 110.2^\circ$ ,  $n_D^{15}$  1.56914,  $M_\gamma - M_\alpha = 3.63$ . 2-Phenyl-*p*-cymene, b. p.  $143^\circ/14$  mm.,  $D_4^{15}$  0.9776,  $n_D^{15}$  1.56797,  $M_\gamma - M_\alpha = 3.44$ ; the *sulphonic acid* forms glistening crystals containing water of crystallisation, m. p.  $109-115^\circ$ ; the



*sulphonyl chloride* forms small leaflets, m. p.  $173^{\circ}$ ; the *sulphonanilide*,  $C_{22}H_{23}O_2NS$ , crystallises in plates, m. p.  $209^{\circ}$ . The action of bromine and aluminium bromide on 2-phenyl-*p*-cymene leads to the formation of *octabromo-o-methyldiphenyl*,  $C_{13}H_4Br_8$ , which crystallises in yellow needles, m. p.  $345-350^{\circ}$ .

2-Benzyl-*p*-cymene,  $C_{17}H_{20}$ , b. p.  $176-177^{\circ}/17$  mm. or  $296-297^{\circ}/743$  mm.,  $D_4^{15}$  0.9690,  $n_D^{15}$  1.55650,  $M_{\gamma} - M_{\alpha} = 3.25$ , is formed from 2-benzylidenementhadiene,  $[\alpha]_D^{21} + 177.35^{\circ}$ . 2-Benzyl-*p*-cymenedisulphonic acid crystallises in leaflets, m. p.  $71-72^{\circ}$ ; the *disulphonyl chloride*, m. p.  $134^{\circ}$ , crystallises from light petroleum; the *disulphonanilide*,  $C_{28}H_{25}O_2NS$ , forms colourless crystals, m. p.  $88-103^{\circ}$ . *Nonabromo-o-methyldiphenylmethane*,  $C_{14}H_5Br_9$ , formed by the action of bromine and aluminium bromide on 2-benzyl-*p*-cymene, crystallises in yellow needles, m. p.  $281^{\circ}$ . G. Y.

**Alicyclic Compounds containing Sulphur.** WALTHER BORSCHÉ and W. LANGE (*Ber.*, 1907, 40, 2220-2225. Compare *Abstr.*, 1905, i, 765; 1906, i, 165).—*Potassium cyclopentanesulphonate*,



obtained by forming the sulphinic acid by the action of sulphur dioxide on magnesium *cyclopentyl* bromide and then oxidising it with permanganate, crystallises in leaflets. It was converted into the *sulphonyl chloride* from which the acid was obtained as colourless, hygroscopic crystals, which, in ethereal solution, combine with aniline to form *cyclopentanesulphonanilide*,  $C_5H_9 \cdot SO_2 \cdot NHPh$ , separating from dilute alcohol in needles, m. p.  $89.5-90.5^{\circ}$ .

For the preparation of 1-methylcyclohexane-3-sulphonic acid, methylcyclohexane-3-ol was converted into 3-chloromethylcyclohexane by heating with fuming hydrochloric acid for five hours at  $100^{\circ}$ . By the action of sulphur dioxide on the Grignard reagent, prepared from the latter compound, a sulphinic acid was obtained, which was oxidised by permanganate to form *potassium methylcyclohexane-3-sulphonate*,  $C_7H_{13}O_3SK$ , which separates from water in leaflets and from absolute alcohol in silvery scales. The corresponding *sulphonyl chloride* has b. p.  $143-144^{\circ}/14$  mm. (decomp.), and, when warmed with water, gives the *acid*,  $C_7H_{14}O_3S \cdot 2H_2O$ , which separates from dilute alcohol in hygroscopic needles, m. p.  $93-94^{\circ}$ .

As by-products from the Grignard reaction mentioned, the following were obtained: unchanged methylhexanol, 3:3'-dimethyldicyclohexyl, m. p.  $263-264^{\circ}$ , and 3:3'-dimethyldicyclohexyl sulphoxide. The latter was converted by oxidation into the corresponding sulphone.

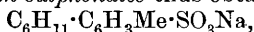
*Methylcyclohexyl 3-hydrosulphide*,  $SH \cdot CH \begin{array}{l} \diagup CH_2 \cdot CHMe \\ \diagdown CH_2 - CH_2 \end{array} CH_2$ , obtained by the action of sulphur on magnesium methylcyclohexyl chloride, is a colourless liquid, b. p.  $172-174^{\circ}$ . A. McK.

**Some Derivatives of Phenylcyclohexane.** NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1295-1303. Compare *Abstr.*, 1902, i, 20).—Phenylcyclohexane when heated with nitric acid, D 1.075, in sealed tubes yields chiefly 1-nitrophenylcyclohexane,

$\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CPh} \cdot \text{NO}_2$ , m. p. 54.5—56°, which crystallises in long needles, also a mixture of other *nitro*-derivatives,  $\text{C}_6\text{H}_{10}\text{Ph} \cdot \text{NO}_2$ , m. p. 86—89°, and small quantities of hydrocyanic, benzoic, glutaric, and succinic acids.

The corresponding 1-*amine*, b. p. 180.5—182.5°/66 mm., is obtained by heating the *nitro*-derivative with tin and hydrochloric acid; it is insoluble in water, and absorbs carbon dioxide from the air, forming a solid *carbonate*. The following salts are described: *hydrochloride*, m. p. 230—230.5°; *nitrate*, m. p. 173° (decomp.); *sulphate*, m. p. 226—227.5°; *nitrite*, decomposing at 70—80°; *acetate*, m. p. 154—155.5°; and *platinichloride*,  $(\text{C}_{12}\text{H}_{15}\text{NH}_2)_2\text{H}_2\text{PtCl}_6$ , m. p. 177°. The compound  $\text{NHPh} \cdot \text{CN} \cdot \text{NH} \cdot \text{C}_6\text{H}_{10}\text{Ph}$ , m. p. 156°, is also described. 1-*Phenylcyclohexane-1-ol*,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CPh} \cdot \text{OH}$ , obtained by heating 1-amino-1-phenylcyclohexane with nitrous acid, forms monoclinic crystals [ $a : b : c = 1.9033 : 1 : 1.8227$ ;  $\beta = 79^\circ 19'$ ], m. p. 62—63.5°, b. p. 151°/20 mm. Z. K.

**The Hydrocarbon  $\text{C}_{13}\text{H}_{18}$ .** NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1304—1316. Compare preceding abstract).—Friedel and Craft's reaction is equally applicable to the chlorine compounds of the *cyclohexanes* as it is to those of the aliphatic derivatives, and the phenylcyclohexanes so produced have all the properties of aromatic compounds with a fatty side-chain. The chlorocyclohexane, when treated with toluene and aluminium chloride, yields a mixture of isomeric *tolylcyclohexanes*, which could not be separated by fractional distillation. The mixture was therefore treated with sulphuric acid, then neutralised with sodium hydroxide; of the mixture of *sodium sulphonates* thus obtained, one,



could be isolated by reason of its complete insolubility in benzene. When treated with concentrated hydrochloric acid, it yields *m-tolylcyclohexane*, b. p. 257—257.3°/754 mm.,  $n_D^{20} 1.5236$ ,  $D_4^{20} 0.9365$ . This, when oxidised with dilute nitric acid, yields *isophthalic acid*. The soluble sodium sulphonates when treated with phosphorus pentachloride yield a mixture of the compounds  $\text{R} \cdot \text{SO}_2\text{Cl}$ ; neither these nor the corresponding *amides*,  $\text{RSO}_2 \cdot \text{NH}_2$ , could be crystallised, but the chlorides on treatment with aniline yield a mixture of *anilides*, one of which is a crystalline substance insoluble in petroleum,  $\text{C}_6\text{H}_{11} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2 \cdot \text{NHPh}$ , m. p. 186.5—187.5°. When treated with

hydrochloric acid, it forms *p-tolylcyclohexane*,  $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_{11}$ , b. p. 259.8—260°/750 mm.,  $n_D^{18} 1.5232$ ,  $D_4^{18} 0.9365$ , which with nitric acid yields *terephthalic acid*. Its odour and properties are similar to the meta-derivative. The other anilides when heated in sealed tubes with fuming hydrochloric acid yielded a mixture of complex hydrocarbons. 3-*Phenyl-1-methylcyclohexane*,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHPh} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{CH}_2$ , obtained by the action of benzene on chloromethylcyclohexane in the presence of aluminium chloride, is a liquid with an odour resembling

that of lemon, b. p.  $249^{\circ}/730$  mm.,  $D_4^{18}$  0.9425,  $n_D^{18}$  1.5246; its properties are similar to those of the other isomerides of the hydrocarbon  $C_{13}H_{18}$ . Z. K.

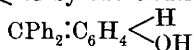
**Triphenylmethyl.** II. JULIUS SCHMIDLIN (*Ber.*, 1907, 40, 2316—2329. Compare *Abstr.*, 1906, i, 392; this vol., i, 26).—*p*-Benzoyltriphenylmethane has been obtained from *p*-tolylphenyl ketone by conversion into the  $\omega$ -dibromo-derivative (Bourcet, *Abstr.*, 1897, i, 566) and condensing this with benzene and aluminium chloride. The product melts at  $165.5$ — $166^{\circ}$  (corr.) and is identical with the substance obtained by the action of benzaldehyde on the  $\alpha$ -form of magnesium triphenylmethyl chloride. When a fresh benzene solution of the  $\alpha$ -magnesium compound is decomposed by dilute hydrochloric acid, no trace of hydrogen is evolved.

The reaction between triphenylmethyl chloride and magnesium in dry ether, if necessary, with the addition of benzene, and in the presence of a little iodine, has been investigated. The liquid after boiling for some time was decomposed with dilute sulphuric acid and the amounts of magnesium sulphate and triphenylmethyl (as peroxide) determined. In many experiments the amount of magnesium sulphate was less than that corresponding with the triphenylmethyl, assuming the latter to be formed according to the equation  $CPh_3 \cdot MgCl + HCl = MgCl_2 + CPh_3 + H$ . When, however, the heating is continued for fifty to one hundred minutes, the amount of sulphate is in excess of the triphenylmethyl. An explanation of these phenomena is offered.

Both  $\alpha$ - and  $\beta$ -compounds yield triphenylmethyl when treated with triphenylmethyl chloride, but in order to obtain a good yield it is essential that the ether used in the preparation of the magnesium compound should be absolutely dry. The dryness of the ether is indicated by the formation of a voluminous precipitate when the ethereal solution of triphenylmethyl chloride has been heated with magnesium and a little iodine for an hour. Although the  $\alpha$ - and  $\beta$ -compounds yield different products with benzaldehyde and the same derivative with triphenylmethyl chloride, experiments have shown that it is the same  $\beta$ -derivative which yields  $\beta$ -benzopinacoline with benzaldehyde, and triphenylmethyl with triphenylmethyl chloride. Similar experiments with the  $\alpha$ -compound did not give conclusive evidence. J. J. S.

**Tautomerism in the Triphenylmethane Series.** FRIEDRICH KEHRMANN and FRANZ WENTZEL (*Ber.*, 1907, 40, 2755—2756. Compare Gomberg, this vol., i, 504).—The authors claim that Gomberg's interpretation of the nature and cause of the basic character of the tautomeric carbinol salts is not essentially different from their theory (*Abstr.*, 1901, i, 638).

They compare  $CPh_2 \cdot \text{C}_6H_4 < \begin{smallmatrix} H \\ Cl \end{smallmatrix}$  with ammonium chloride and regard it as derived either by the addition of hydrogen chloride to the radicle  $CPh_2 \cdot C_6H_4 <$  or by substitution from the base



E. F. A.

**Terpenes and Ethereal Oils. LXXXV. Behaviour of the Nitrites of Primary Bases and Enlargement of Rings in Carbocyclic Systems.** OTTO WALLACH (*Annalen*, 1907, 353, 318—334).—It is found that the nitrites of primary aliphatic bases can be prepared by the action of commercial, alkaline sodium nitrite on the concentrated aqueous solution of the hydrochloride, that is, in the complete absence of free acid. The resulting nitrite may be isolated if less soluble than the hydrochloride, and is then sufficiently stable to permit of recrystallisation from boiling water, but is decomposed on addition of traces of a free acid. The nitrites of primary alicyclic amines are even more stable (Wallach and Griepenkerl, *Abstr.*, 1892, 1238). *l*-Menthylamine nitrite crystallises in needles, decomposes at about 139°, and yields menthol when boiled with water containing a drop of acetic acid. *Pinylamine nitrite* forms stout crystals, decomposes at about 125°, and when treated with acids yields chiefly pinocarveol.

Stable, sparingly soluble nitrites of secondary bases have been described previously (*loc. cit.*; *Abstr.*, 1906, i, 514).

Primary aromatic amines, which form sparingly soluble nitrates, yield also sparingly soluble nitrites. *m*-4-Xylidine nitrite is formed in white crystals, which when dried become yellow and decompose to a reddish-brown oil; the crystals yield *m*-4-xylidine with aqueous alkalis, phenol when boiled with dilute acetic acid, or a solution of the diazo-sulphate when treated with sulphuric acid.

The decomposition of nitrites of primary alicyclic amines in boiling aqueous solution on addition of a free acid, takes place mainly in two directions: (1) the formation of a hydrocarbon, and (2) the formation of an alcohol, or of two or more isomeric alcohols. Thus, whilst *l*-menthylamine nitrite gives *l*-menthol, *d*-menthylamine nitrite yields chiefly menthene. *iso*Thujylamine nitrite is converted almost completely into a hydrocarbon, whilst under the same conditions thujylamine nitrite yields much alcohol. It is found now that when boiled with water and acetic acid, the nitrites of cyclylmethylamines (compare this vol., i, 616) yield small amounts of hydrocarbons and of the alcohols corresponding to the amines, together with the alcohols of the next higher ring system (compare Demjanoff, *Abstr.*, 1904, i, 410). As the cyclylmethylamines are prepared from *cycloketones* and *cycloketones* are formed by oxidation of the alcohols produced by the decomposition of the nitrites, the whole series of reactions constitutes a method of enlarging carbocyclic systems. In this manner, *cyclohexanone* is formed from *cyclopentanone*, *cycloheptanone* (suberone) from *cyclohexanone*, and *azaleone* (*cyclooctanone*) from *suberone*.

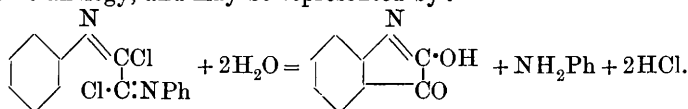
*Azaleone* (Mager, *Abstr.*, 1893, i, 558; Derlon, *Abstr.*, 1898, i, 638; Miller and Tschitschkin, *Abstr.*, 1899, i, 789) crystallises when cooled, m. p. 25—26°, b. p. 195—197°,  $D^{20}$  0.9581,  $n_D$  1.4694; the semicarbazone, m. p. 163—164.5°. The ketone yields suberic acid on oxidation with chromic and sulphuric acids.

The following constants are given for the pure ketones and their derivatives: *cyclopentanone*, b. p. 129°,  $D^{20}$  0.948,  $n_D$  1.4366; semicarbazone, 206°; dibenzylidene derivative, m. p. 189°. *cycloHexanone*,

b. p. 155°,  $D^{21}_D$  0.947,  $n_D$  1.4503; semicarbazone, m. p. 165—166°; dibenzylidene derivative, m. p. 117—178°. *cyclo*Heptanone, b. p. 180°,  $D^{21}_D$  0.9500,  $n_D$  1.4604; semicarbazone, m. p. 163°; dibenzylidene derivative, m. p. 108°. G. Y.

**Imino-chlorides of Oxalic Acid.** RUDOLPH BAUER (*Ber.*, 1907, 40, 2650—2662).—Imino-chlorides of the type  $R \cdot N : CCl : CCl : NR$  have been prepared by Wallach and Bischoff by the action of phosphorus pentachloride on the substituted oxamides. A much better method is to heat the materials in a solvent such as benzene or toluene. The imino-chlorides prepared are well characterised substances, and, although similar in properties to those obtained from monobasic acids, are more stable. Diphenyloxalimino-chloride,  $NPh : CCl : CCl : NPh$ , is obtained in 70% yield when toluene is used as solvent; with benzene no imino-chloride was isolated. It crystallises in straw-yellow needles, m. p. 115°, and is stable in dry air; moisture, however, slowly converts it into oxanilide (compare Wallach, *Abstr.*, 1881, 718). A 90% yield of di-*o*-tolyloxalimino-chloride (oxalotoluidiminochloride) is obtained when benzene is used as solvent (Bischoff, *Abstr.*, 1894, i, 514). The di-*p*-tolyl- and di-*m*-tolylimino-chlorides have m. p. 107° and 72° and are yellow.

These imino-chlorides, when added to pure concentrated sulphuric acid at the temperature of the water-bath, yield isatin or methylisatins; no intermediate product has as yet been isolated. This reaction has no analogy, and may be represented by:



The yield of isatin is 15%, of *o*- and *p*-methylisatins, 49% and 19%, whilst it is very small in the case of the meta-compound. 7-Methylisatin,  $C_9H_7O_2N$ , crystallises in red, hair-like needles, m. p. 266°; the phenylhydrazone,  $C_{15}H_{13}ON_3$ , forms golden-yellow needles, m. p. 242°, and the oxime,  $C_9H_8O_2N_2$ , yellow needles, m. p. 235°. 4-Methylisatin forms red leaflets, m. p. 155°. The methylisatin, obtained from the di-*m*-tolyloxalimino-chloride, has m. p. 165°, and may be identical with Findeklee's 6-methylisatin, m. p. 169° (*Abstr.*, 1906, i, 43).

The imino-chlorides react with bases like acid chlorides; with alcoholic ammonia, diphenyloxalimino-chloride gives diphenyloxalamidine; aniline yields tetraphenyloxalamidine,  $NPh : C(NHPh) : C(NHPh) : NPh$ , m. p. 153°, and crystallising in light yellow prisms; its picrate has m. p. 182°. With phenylhydrazine, tetraphenyloxalaldehydrazidine,  $NPh : C(NH \cdot NHPh) : C(NH \cdot NHPh) : NPh$ , is obtained in yellow needles, m. p. 200°; ferric chloride oxidises it to a dark red osotetrazone.

Diphenyloxalimino-chloride is decomposed by alcoholic potassium hydroxide; with the di-*o*-tolyl derivative, however, a mixture is obtained, the less soluble constituent of which is diethyl di-*o*-tolylimino-oxalate,  $C_7H_7 : N : C(OEt) : C(OEt) : N : C_7H_7$ , m. p. 92°; the more soluble is ethyl *o*-tolylimino-*o*-tolylloxamate,  $C_7H_7 : NH : CO : C(OEt) : N : C_7H_7$ , m. p. 91°.

Tetra-*o*-tolylloxalamidine,  $C_{30}H_{30}N_4$ , forms light yellow plates from a mixture of light petroleum and benzene; m. p. 169°. W. R.

**Platinum Compounds of Phenylcarbylamine and of Benzonitrile.** LUDWIG RAMBERG (*Ber.*, 1907, 40, 2578—2588. Compare Hofmann and Bugge, this vol., i, 489).—The *substance*  $[\text{Pt}(\text{CNPh})_2\text{Cl}_2]_x$ , obtained by adding slowly an aqueous suspension of phenylcarbylamine to a solution of an excess of potassium platinosulphate, is a violet-blue, amorphous powder which does not dissolve unchanged in the usual solvents. By heating at 110—115° or by prolonged boiling with chloroform or acetone, it changes into the colourless *chloride*,  $\text{Pt}(\text{CNPh})_2\text{Cl}_2$ , m. p. 257—258°; this forms well-defined, monoclinic crystals [ $a : b : c = 1.1113 : 1 : 0.8391$ ;  $\beta = 101^\circ 53'$ ], and by treatment with concentrated sulphuric acid at 110—115° yields colourless needles of a *substance* of unknown composition, which is reconverted into the chloride,  $\text{Pt}(\text{CNPh})_2\text{Cl}_2$ , by treatment with potassium chloride, and forms the iodide,  $\text{Pt}(\text{CNPh})_2\text{I}_2$ , by the action of potassium iodide, a mixture of the bromide and chloride by the action of potassium bromide, and a mixture of the chloride and of the thiocyanate by the action of potassium thiocyanate.

The brownish-violet *compound*,  $[\text{Pt}(\text{CNPh})_2\text{Br}_2]_x$ , is obtained in a similar manner to the corresponding chloride, and, like the latter, changes into colourless *dibromobisphenylcarbylamineplatinum*,  $\text{Pt}(\text{CNPh})_2\text{Br}_2$ , m. p. 245°, which forms monoclinic crystals [ $a : b : c = 1.1303 : 1 : 0.8496$ ;  $\beta = 103^\circ 9'$ ], and is not attacked by concentrated sulphuric acid in the cold.

*Di-iodobisphenylcarbylamineplatinum*,  $\text{Pt}(\text{CNPh})_2\text{I}_2$ , m. p. 241°, prepared as mentioned above, separates from chloroform in yellow, monoclinic crystals [ $a : b : c = 0.554 : 1 : 0.369$ ;  $\beta = 99^\circ 19'$ ], and occasionally in slender needles, which change rapidly into the stable form; by the addition of iodine to a warm solution of the iodide in chloroform, black needles of a *hexaiodide*,  $\text{Pt}(\text{CNPh})_2\text{I}_6$ , are obtained.

*Dinitritobisphenylcarbylamineplatinum*,  $\text{Pt}(\text{CNPh})_2(\text{NO}_2)_2$ , is prepared from phenylcarbylamine and potassium platinonitrite in aqueous solution; it separates from acetone in slender, yellow needles, which lose acetone and become dark red; the red crystals turn yellow at 100—110° and decompose at 155—160° without melting.

*Dichlorobisbenzonitrileplatinum*,  $\text{Pt}(\text{NCPH})_2\text{Cl}_2$ , prepared by the prolonged heating of benzonitrile and a solution of potassium platinosulphate at 60—70°, separates from acetone in small, yellow prisms or leaflets, has m. p. 219—220° (decomp.), and is deposited from chloroform or benzene solution in crystals containing 2 mols. of the solvent. The substance is easily soluble in hot benzonitrile, and on cooling, small, yellow needles separate which have the same composition and m. p. as the original chloride, but are more soluble in acetone; this solvent changes them partially into the original substance. Concentrated sulphuric acid dissolves the chloride with effervescence; the clear solution yields with potassium chloride the original chloride, and with potassium iodide the corresponding iodide mixed with the chloride. A yellow, crystalline *substance*,  $\text{Pt}(\text{NCPH})_2\text{Cl}_4$ , m. p. 114—115° (decomp.), is precipitated when chlorine is passed into a solution of the chloride in chloroform.

*Dibromobisbenzonitrileplatinum*,  $\text{Pt}(\text{NCPH})_2\text{Br}_2$ , m. p. 218—220°, is obtained by the prolonged heating of benzonitrile (2 mols.), a solution of potassium platinochloride (1 mol.), and potassium bromide (>4 mols.) at 60—70°. The substance separates from acetone in orange-yellow plates or prisms, and from chloroform with  $2\text{CHCl}_3$ ; like the chloride it exists in two isomeric forms and yields a red, crystalline additive compound,  $\text{Pt}(\text{NCPH})_2\text{Br}_4$ .

The nature of the isomerism of these platinum derivatives is not yet elucidated. C. S.

**Two New Methods for the Preparation of *cyclo*Butanol.** NIKOLAUS J. DEMJANOFF and M. DOJARENKO (*Ber.*, 1907, 40, 2594—2597).—Silver *cyclobutanecarboxylate*, iodine, and powdered glass are heated on the water-bath and the product distilled under 40—60 mm. pressure. The distillate contains *cyclobutanecarboxylic acid* and its ester with *cyclobutanol*. The latter,  $\text{C}_4\text{H}_7\cdot\text{CO}_2\cdot\text{C}_4\text{H}_7$ , b. p. 198.5—199°/750 mm., is a colourless, mobile liquid, which has  $D_{15}^{16}$  1.0033 and  $n_D^{19}$  1.4551; by hydrolysis with 25% potassium hydroxide at 110—120°, the ester yields *cyclobutanol*, b. p. 123°/733 mm.,  $D_{15}^{16}$  0.9226, and  $n_D^{19}$  1.4339, which yields succinic acid by oxidation with nitric acid.

The same alcohol and ester are obtained by the electrolysis of a solution containing potassium *cyclobutanecarboxylate*, potassium carbonate, and potassium hydrogen carbonate.

*cyclo*Butanol and phenylcarbimide react to form a *phenylurethane*,  $\text{C}_4\text{H}_7\text{O}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 110—111°, which separates from dilute alcohol in glistening prisms. C. S.

**Condensation of Epichlorohydrin with Phenols.** PAUL COHN and ROBERT PLOHN (*Ber.*, 1907, 40, 2597—2602. Compare Cohn and Friedländer, *Abstr.*, 1904, i, 866; Lindemann, *Abstr.*, 1891, 1198).—

*Phenyl glycid ether*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{O} \end{smallmatrix}$ , m. p. 82°, is obtained by heating together a solution of sodium phenoxide and epichlorohydrin, by adding concentrated sodium hydroxide to equal molecular quantities of epichlorohydrin and phenol, or by heating the same two substances with alcoholic sodium ethoxide. 2:4:6-Tribromophenyl glycid ether has m. p. 85°, and p-tolyl glycid ether, 88°.

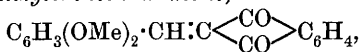
Dichlorohydrin and potassium phenoxide yield phenyl glycid ether, and Rössing's so-called acetyldiphenylglyceryl ether (*Abstr.*, 1886, 345) is also the same substance. C. S.

**Derivatives of Quinol Dimethyl Ether.** HUGO KAUFFMANN and KARL BURR (*Ber.*, 1907, 40, 2352—2358).—The auxochromic effect of the methoxyl group is found to be intensified when two methoxyls are present in the para-position to one another.

$\beta$ -Cyano-2:5-dimethoxystilbene,  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}\cdot\text{OPh}\cdot\text{CN}$ , formed

by condensation of 2:5-dimethoxybenzaldehyde with phenylacetonitrile in alcoholic sodium hydroxide solution, crystallises in intensely yellow needles, m. p. 69°, and forms yellow solutions with greenish-blue fluorescence in dissociating, but less intensely-coloured solutions with a more violet fluorescence in other, solvents. The corresponding chromogen, cyanostilbene, is colourless.

2:5-Dimethoxybenzylideneindandione,

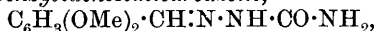


prepared by heating 1:3-diketohydrindene with 2:5-dimethoxybenzaldehyde in alcoholic solution, crystallises in orange-red needles, m. p. 149°, and forms yellow to yellowish-red solutions with greenish-yellow fluorescence. The chromogen, benzylideneindandione, is light yellow.

2:5-Dimethoxycinnamic acid forms yellowish-green crystals, m. p. 147° (143°: Schnell, Abstr., 1884, 1164), and gives a brownish-yellow colour with concentrated sulphuric acid. The chromogen is colourless. *Ethyl 2:5-dimethoxycinnamate*,  $\text{C}_{13}\text{H}_{16}\text{O}_4$ , is obtained as a strongly refracting, yellowish-green liquid with blue fluorescence, b. p. 216°/20 mm.,  $D_{26}^{26}$  1.1357, has a brilliant fluorescence in very dilute solutions, and forms a yellow solution in concentrated sulphuric acid. The liquid chromogen is colourless.

2:5-Dimethoxybenzylidenemalonic acid,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CH} : \text{C}(\text{CO}_2\text{H})_2$ , prepared by heating 2:5-dimethoxybenzaldehyde with malonic acid in glacial acetic acid solution on the water-bath, crystallises in yellow prisms with greenish-yellow fluorescence, m. p. 188° (decomp.), and forms in alcohol a yellow solution with blue fluorescence which becomes colourless, but with violet fluorescence, on addition of an alkali. The chromogen, benzylidenemalonic acid, is colourless.

2:5-Dimethoxybenzylidenesemicarbazone,



crystallises in white needles, m. p. 208°, and dissolves in glacial acetic acid or hot alcohol, forming solutions with violet fluorescence. This is believed to be the first semicarbazone the fluorescence of which can be observed directly.

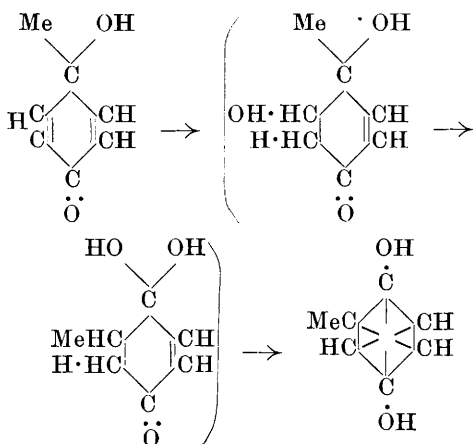
2:2':5:5'-Tetramethoxybenzylideneazaine,  $\text{N}_2[\text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2]_2$ , crystallises in yellow needles, m. p. 160°, detonates when highly heated, and forms red salts which have a red fluorescence when observed through a blue screen.

2:5-Dimethoxybenzylideneaniline,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CH} : \text{NPh}$ , is obtained as a strongly refracting, viscid, yellow oil, b. p. 239°/20 mm.,  $D_{23.5}^{23.5}$  1.1422, and dissolves in organic solvents, forming solutions which are not fluorescent; the salts are intensely yellow, and show a yellow fluorescence when observed through a blue screen. G. Y.

**Action of Hydroxylamine on 2:4-Dimethylquinol and its Ethers.** EUGEN BAMBERGER and L. RUDOLF (*Ber.*, 1907, 40, 2236—2258. Compare this vol., i, 519, 520).—The transformation of quinols into ketonic quinol or resorcinol derivatives is undoubtedly accompanied by the formation of intermediate products. To take one case, the simplest ketonic quinol transformation, namely, the conversion



of ketonic compound into toluquinol, is expressed by the following scheme :

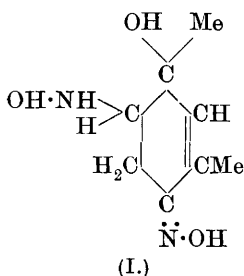


To support this hypothesis it was desirable to prove the presence of such additive compounds. The additive compounds of water and alcohol cannot be isolated. In the present communication the property possessed by quinols of uniting with hydroxylamine or phenylhydrazine is, however, shown and the structure of the intermediate products proved.

The action of hydroxylamine on ketonic 2 : 4-dimethylquinol and on its

ethyl and methyl ethers has been studied. The action on the quinol itself is represented by the equation :  $\text{OH} \cdot \text{C}_8\text{H}_9\text{O} + 2\text{NH}_2 \cdot \text{OH} = \text{H}_2\text{O} + \text{OH} \cdot \text{C}_8\text{H}_{13}\text{N}_2\text{O}_3$ . The hydroxyl group does not play a part in this reaction, since the action of the ketonic quinol ethers is represented by  $\text{OR} \cdot \text{C}_8\text{H}_9\text{O} + 2\text{NH}_2 \cdot \text{OH} = \text{H}_2\text{O} + \text{OR} \cdot \text{C}_8\text{H}_{13}\text{N}_2\text{O}_3$ .

The product of the action of hydroxylamine on ketonic xyloquinol has the property of a hydroxylamino-compound,  $\text{R} \cdot \text{NH} \cdot \text{OH}$ , and is represented by the formula (I). It possesses the properties typical of a  $\beta$ -substituted hydroxylamine.



It is soluble not only in alkalis, but also in mineral acids, it exhibits reducing properties towards Fehling's solution, &c., and it combines with diazo-salts, benzaldehyde, and acetone respectively. It forms a tribenzoyl derivative insoluble in alkali hydroxides. It is reduced by stannous chloride to a xylenediamine. The compound in question is accordingly designated as *hydroxylaminohydroxyketodimethyltetrahydrobenzene oxime*; it separates

from alcohol in glistening needles and decomposes at about  $169^\circ$ . When its alcoholic solution is boiled with benzaldehyde, glistening leaflets of the *benzylidene* compound,  $\text{C}_{15}\text{H}_{18}\text{O}_3\text{N}_2$ , separate, m. p.  $218^\circ$  (decomp.). The alkaline solution of the latter compound reduces Fehling's solution very slowly in the cold. The *o*-nitrobenzylidene derivatives form colourless, nacreous needles, decomposing at  $239^\circ$ . The *m*-nitrobenzylidene derivative forms glistening, colourless plates, decomposing at  $216.5^\circ$ . The *p*-nitrobenzylidene derivative forms orange-yellow, glassy, quadratic plates, decomposing at  $207^\circ$ . The *o*-nitrodiazobenzene derivative,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{N}(\text{OH}) \cdot \text{C}_6\text{H}_4\text{Me}_2(\text{OH}) \cdot \text{N} \cdot \text{OH}$ , forms orange-yellow, glistening, rhombic plates, m. p.  $196.5^\circ$ . The *p*-nitrodiazobenzene derivative separates in yellow, glistening leaflets, m. p.

220·5°. The *tribenzoyl* derivative forms glistening needles, m. p. 149—150°.

Since the oxime in question is of the type  $\text{CHRR}'\cdot\text{NH}(\text{OH})$ , it readily loses two atoms of hydrogen on oxidation by Caro's acid, being converted into *hydroxydiketodimethyltetrahydrobenzene dioxime*, m. p. 176° (decomp.), when heated quickly. This substance has not basic properties, but is distinctly acidic, and with benzoyl chloride gives, accordingly to the conditions, either a dibenzoyl derivative, soluble in alkali, or a tribenzoyl derivative soluble in alkali. The *dibenzoyl* derivative forms silky needles, m. p. 141° (decomp.), whilst the *tribenzoyl* derivative forms silky needles, m. p. 153° (decomp.).

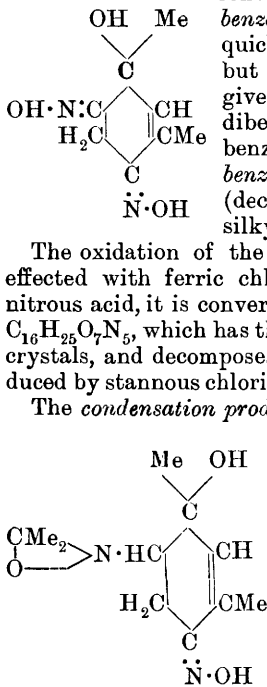
The oxidation of the hydroxylaminoquinol monoxime may also be effected with ferric chloride. When the monoxime is acted on by nitrous acid, it is converted into a compound with the probable formula  $\text{C}_{16}\text{H}_{25}\text{O}_7\text{N}_5$ , which has the properties of a nitrosoamine, forms glistening crystals, and decomposes at about 183·5°. The monoxime was also reduced by stannous chloride to form 1:3-dimethylphenylene-4:6-diamine.

The *condensation product*, obtained from acetone and the hydroxylaminoquinoloxime in the presence of a trace of hydrochloric acid, forms glistening, hexagonal plates, m. p. 195·5° (decomp.). It is at once decomposed by mineral acids to regenerate acetone and the original oxime. Its *dibenzoyl* derivative has m. p. 145—146° and does not dissolve in alkalis. The condensation product in question is readily soluble in alkalis, does not reduce cold Fehling's solution, or condense with phenylhydrazine or with *p*-nitrophenylhydrazine.

In the presence of hydrogen ions, it is without action on diazo-salts in neutral solution; however, 2 mols. combine with 1 mol. of diazo-compound with the elimination of 1 mol.  $\text{H}_2\text{O}$ . With *p*-nitrodiazobenzene nitrate, it forms the compound,  $\text{C}_{28}\text{H}_{39}\text{O}_8\text{N}_7$ , an amorphous substance, m. p. 150° (decomp.). Its solution in sodium hydroxide is raspberry-coloured, whilst its alcoholic solution gives a green coloration with ferric chloride. With *o*-nitrodiazobenzene nitrate, it forms the compound,  $\text{C}_{28}\text{H}_{39}\text{O}_8\text{N}_7$ , which also could not be obtained crystalline; its solution in alkalis is carmine-red, whilst its alcoholic solution gives a dark green coloration with ferric chloride.

The condensation product also combines with benzaldehyde to form the compound  $\text{C}_{15}\text{H}_{18}\text{O}_3\text{N}_2$ , which crystallises in glistening leaflets, m. p. 218°.

*Hydroxylaminoketoethoxydimethyltetrahydrobenzene oxime*, obtained from ketonic 2:4-dimethylquinol ethyl ether, hydroxylamine, and methyl alcohol, forms colourless, nacreous leaflets, m. p. 161°. Its aqueous solution reduces cold Fehling's solution. It condenses with benzaldehyde to form a *benzylidene* derivative,  $\text{C}_{17}\text{H}_{22}\text{O}_3\text{N}_2$ , which crystallises in glistening needles, m. p. 192—192·5°, is soluble in alkalis, but not in acids, and reduces Fehling's solution very slowly.



*Ketomethoxyhydroxylaminodimethyltetrahydrobenzene oxime*,  $C_9H_{16}O_3N_2$ , obtained from 2:4-dimethylquinol methyl ether, hydroxylamine, and methyl alcohol, forms glistening needles, m. p. 156.5—157°. Its behaviour towards Fehling's solution, acids, and alkalis is similar to that of the analogous ethoxy-compound just described. A. McK.

**2:5:2':5'-Tetramethoxystilbene.** HUGO KAUFFMANN and KARL BURR (*Ber.*, 1907, 40, 2358—2360).—2:5:2':5'-*Tetramethoxystilbene*,  $C_6H_3(OMe)_2 \cdot CH:CH \cdot C_6H_3(OMe)_2$ , formed by reduction with zinc dust and boiling alcoholic ammonia of the *product*, m. p. 123°, obtained on condensation of quinol dimethyl ether with chloral by means of concentrated sulphuric acid in glacial acetic acid solution cooled with ice, crystallises in light yellow needles, m. p. 99°, b. p. 140—180°/16 mm., and has a strong blue fluorescence. Whilst the exceptionally strong fluorescence of this substance is in agreement with Kauffmann's theoretical views, its yellow colour is of importance as proof that the methoxyl group is an auxochrome. G. Y.

**Some *p*-Nitrobenzyl-mercaptals and -mercaptols.** A. SCHAEFFER and A. MURÚA (*Ber.*, 1907, 40, 2007—2008).—*p*-Nitrobenzyl mercaptan is a good qualitative reagent for ketones or aldehydes, and may be used to separate these substances. The condensation products obtained from it are well characterised, stable substances. The method of preparation consists in dissolving zinc *p*-nitrobenzyl mercaptide in alcohol saturated with hydrogen chloride and adding the calculated quantity of the aldehyde or ketone. After remaining for twenty-four hours at 0°, the products of condensation crystallise out. *p*-Nitrobenzyl-ethylidenemercaptal,  $CH_3 \cdot CH(S \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_2$ , forms colourless, microscopic leaflets, m. p. 82°; *p*-nitrobenzylsalicylidenemercaptal,

$C_{21}H_{18}O_5N_2S_2$ , colourless prisms, m. p. 152°; *p*-nitrobenzyl-*p*-isopropylbenzylidenemercaptal,  $C_{24}H_{24}O_4N_2S_2$ , needles, m. p. 84°; *p*-nitrobenzylphenylpropenyl-mercaptal,  $CHPh \cdot CH_2 \cdot CH(S \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_2$ , small prisms, m. p. 140°. Menthone yields the *mercaptol*,  $C_{24}H_{30}O_4N_2S_2$ , crystallising in small needles, m. p. 171°, and pulegone the corresponding *mercaptol*,  $C_{24}H_{28}O_4N_2S_2$ , m. p. 133°. *p*-Nitrobenzylfurfurylidenemercaptal,

$C_{19}H_{14}O_5N_2S_2$ , could not be obtained by the above method, but was prepared by boiling an alcohol solution of mercaptan and furfuraldehyde. It crystallises in leaflets, m. p. 87°. W. R.

**Dibenzylideneacetone and Triphenylmethane. II. Distyrylchlorocarbinol.** FRITZ STRAUS and FRITZ CASPARI (*Ber.*, 1907, 40, 2689—2709. Compare Straus and Ecker, *Abstr.*, 1906, i, 859).—Moist silver oxide acting on distyryldichloromethane in ethereal solution replaces one of the chlorine atoms by hydroxyl, forming distyrylchlorocarbinol,  $CCl(CH:CHPh)_2 \cdot OH$ , which bears the same relationship to the keto-chloride as triphenylcarbinol does to triphenylchloromethane. The chlorocarbinol forms colourless needles, m. p. 50°, and dissolves in concentrated sulphuric acid with a characteristic bluish-violet coloration. Hydrogen chloride or acetyl chloride reconvert it into distyryldichloromethane, whilst alcoholic hydrogen chloride or glacial acetic acid changes it to dibenzylideneacetone.

The elimination of hydrogen chloride could not be brought about even by such active reagents as pyridine, alcoholic potassium hydroxide, boiling alcoholic silver nitrate, or sodium acetate.

On heating for a time above the melting point at  $60^\circ$ , the chlorocarinol is converted into an anhydride,  $C_{34}H_{28}OCl_2$ , crystallising in colourless needles, which sinter at  $150^\circ$ , m. p.  $160^\circ$ , and there is no elimination of hydrogen chloride.

The *methyl ether*,  $CCl(CH:CHPh)_2 \cdot OMe$ , of the chlorocarinol results when this is left standing with a little methyl alcohol. It crystallises in colourless, glistening plates or broad needles, m. p.  $54-55^\circ$ , and decomposes slowly on keeping. Concentrated sulphuric acid converts it into the sulphate,  $CCl(CH:CHPh)_2 \cdot OSO_3H$ , which dissolves with the characteristic violet coloration. Methyl-alcoholic hydrogen chloride, in the cold or warm acetic acid, rapidly converts it into the ketone, but in the absence of mineral acids the methyl ether can be boiled with silver nitrate without changing. In benzene solution, hydrogen chloride regenerates the keto-chloride, chlorine being substituted for methoxyl.

*Di-p-chlorostyrylchlorocarinol*, prepared in the manner already described for the monochloro-derivative, forms long, colourless needles, m. p.  $101-102^\circ$ , which become very electric when rubbed. It dissolves in concentrated sulphuric acid or liquid sulphur dioxide with an indigo-blue coloration and blood-red fluorescence, and shows all the reactions described for the monochlorocarinol; the methyl ether has m. p.  $94^\circ$ , and is identical with the compound obtained by the action of sodium methoxide (compare Abstr., 1906, i, 859). The *anhydride* separates in glistening, colourless crystals, m. p.  $165-167^\circ$  (decomp.).

Benzophenone chloride,  $CPh_2Cl_2$ , and silver oxide, under the same conditions, form benzophenone, both chlorine atoms being eliminated.

The behaviour of the derivatives of distyrylchloromethane makes it necessary to regard them as triphenylmethane derivatives in which chlorine replaces a phenyl residue.

E. F. A.

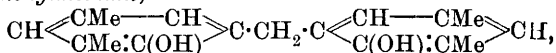
**Cholesterol. IX.** ADOLF WINDAUS (*Ber.*, 1907, 40, 2637—2639).—By heating cholesterol with sodium amyloxide in amyl alcohol solution for eight hours, an isomeric alcohol saturated towards bromine is produced. This is identical with the  $\alpha$ -cholestanol obtained by Abderhalden and Diels and by Neuberg (Abstr., 1906, i, 272, 356), but as the substance is obtained from the amyloxide and is not obtainable by using energetic reducing agents, it is concluded that it is not a reduction product of cholesterol, an isomeric change having occurred which involves the formation of the ring compound, *cylcholesterol*,  $C_{27}H_{46}O$ . This supports the conclusion previously arrived at, that the oxidation products of cholesterol are also ring compounds (this vol., i, 212).

W. R.

**The Lederer-Manasse Synthesis of Phenol Alcohols.** KARL AUWERS (*Ber.*, 1907, 40, 2524—2537).—The author has carried out a number of syntheses of phenol alcohols by the method given by

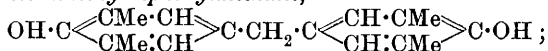
Lederer (Abstr., 1894, i, 577) and Manasse (Abstr., 1894, i, 575), and has studied the manner in which the course of the synthesis varies with the nature of the phenol employed and with the conditions of working.

All his results confirm the observation made by the discoverers of the synthesis that the latter yields ortho- and para-, but not meta-, derivatives. The use of a strong alkali, such as sodium hydroxide, as condensing agent favours, at any rate with the homologous phenols, the formation of para-compounds. Thus the interaction of *p*-xylenol, sodium hydroxide, and formaldehyde at the ordinary temperature yields *p*-hydroxy- $\psi$ -cumyl alcohol (Auwers and Ercklentz, Abstr., 1899, i, 35) in almost quantitative yield. In other cases, 50% or more of the para-derivative is obtained, and, at most, very small proportions of the isomeride. The action of the stronger alkalis differs also from that of the weaker ones, such as calcium hydroxide, in that the phenol alcohol formed is often accompanied by a larger or smaller quantity of a dihydroxydiphenylmethane derivative, which is less soluble in most solvents than the principal product (compare Manasse, Abstr., 1903, i, 28). Thus, by the action of formaldehyde and calcium hydroxide on *as-m*-xylenol at 50°, a good yield of *o*-hydroxymesityl alcohol [OH : Me<sub>2</sub> : CH<sub>2</sub>·OH = 1 : 4 : 6 : 2] is generally obtained. In some cases, however, and especially if the heating is too intense or too prolonged, this alcohol is accompanied by 2 : 2'-*dihydroxy*-3 : 5 : 3' : 5'-*tetramethyldiphenylmethane*,



which forms the main product when the condensation is effected by means of sodium hydroxide, even in very dilute solution. This compound crystallises from light petroleum in long, colourless needles, m. p. 145—146°, and gives no coloration with ferric chloride. Its *diacetyl* derivative, C<sub>22</sub>H<sub>24</sub>O<sub>4</sub>, crystallises from aqueous alcohol in slender needles, m. p. 86°. This diphenylmethane derivative is probably formed by the action of the alkali on the phenolalcohol first formed (compare Auwers, Abstr., 1904, i, 487; also Kann, *Inaug. Diss.*, Marburg, 1905, 22).

The nature of the phenol used has a still greater effect than that of the condensing agent in determining the formation of diphenylmethane derivatives. For instance, with  $\beta$ -naphthol, this synthesis yields dihydroxydinaphthylmethane as sole product. The same is the case with *m*-2-xylenol, which, when treated with formaldehyde and either sodium hydroxide or a weaker base, yields always 4 : 4'-*dihydroxy*-3 : 5 : 3' : 5'-*tetramethyldiphenylmethane*,

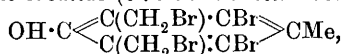


this compound, which is also formed by boiling *p*-hydroxymesityl-piperidine [OH : Me<sub>2</sub> : CH<sub>2</sub>·C<sub>5</sub>NH<sub>10</sub> = 1 : 2 : 6 : 4] with dilute sodium hydroxide solution, crystallises from aqueous methyl alcohol in colourless, glassy needles, m. p. 175°, and when oxidised with chromic acid in acetic acid solution yields the xyloquinone described by Noeltling and Baumann (Abstr., 1885, 892). Its *diacetyl* derivative, C<sub>21</sub>H<sub>24</sub>O<sub>4</sub>, crystallises from methyl alcohol in slender needles, m. p. 142°.

The Lederer-Manasse synthesis fails in the cases of *p*-bromo-*o*-cresol and of other halogenated and nitro-phenols. This failure cannot be attributed to steric hindrance, but seems to depend on a specific chemical action of the halogens and the nitro-group, or possibly of any negative substituent.

The formation of dialdehydes from monohydric phenols by Reimer's synthesis takes place with difficulty, but the corresponding dihydric alcohols are readily formed from many simple phenols by means of the Lederer-Manasse synthesis. Thus when *p*-cresol is treated with formaldehyde and sodium hydroxide solution, it yields (1) *p*-homosaligenin and (2) 2 : 6-dimethylol-*p*-cresol,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CH}_2\text{OH})_2$ , which is identical with the compound, m. p.  $133^\circ$ , obtained by Lederer (Abstr., 1894, i, 577) from *p*-cresol and formaldehyde, and regarded by him as an isomeride of *p*-homosaligenin. The action of hydrogen bromide converts 2 : 6-dimethylol-*p*-cresol into vic.-hydroxymesitylene dibromide ( $2^1 : 6^1$ -dibromomesitol-1),  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CH}_2\text{Br})_2$ , which crystallises from light petroleum in silky needles, m. p.  $116-117^\circ$ . Treatment of this dibromo-derivative with bromine yields, not as expected,

$\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_3(\text{CH}_2\text{Br})_2$  [ $\text{OH} : \text{Br}_3 : (\text{CH}_2\text{Br})_2 = 1 : 3 : 4 : 5 : 2 : 6$ ] (compare Auwers and Anselmino, Abstr., 1900, i, 159), but dibromo-vic.-hydroxymesitylene bromide ( $3 : 5 : 2^1 : 6^1$ -tetrabromomesitol-1),



which crystallises from light petroleum in a felted mass of white needles, m. p.  $152-152.5^\circ$ . When boiled for a few minutes with methyl alcohol, this tetrabromo-derivative yields the compound,

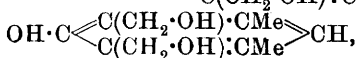
$\text{OH} \cdot \text{C} \begin{array}{c} \diagup \text{C}(\text{CH}_2 \cdot \text{OMe}) \cdot \text{CBr} \diagdown \\ \diagdown \text{C}(\text{CH}_2 \cdot \text{OMe}) \cdot \text{CBr} \diagup \end{array} \text{CMe}$ , which separates in white, silky

needles, m. p.  $63-64^\circ$ . When  $2^1 : 6^1$ -dibromomesitol-1 is heated on the water-bath with bromine and a little water, it is converted into tetrabromo-*p*-cresol  $\psi$ -bromide (compare Zincke and Wiederhold, Abstr., 1902, i, 284). In this case, contrary to what happens with about a dozen other phenols examined, the two side-chains in the ortho-position are removed, whilst that in the para-position remains.

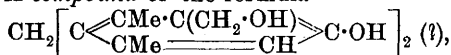
With phenols containing both *o*- and *p*-hydrogen, the Lederer-Manasse reaction follows a very complicated course. This is also the case with phenols in which ortho substitution takes place relatively easily, as these yield, not only the two monohydric alcohols, but one or two dihydric alcohols and also diphenylmethane derivatives. Thus from the products of the interaction of *m*-xylenol, formaldehyde, and sodium hydroxide, the following compounds have been isolated: (1) *p*-hydroxy-hemimellitethyl alcohol (4-hydroxy-2 : 6-dimethylbenzyl alcohol),



which crystallises from ethyl acetate in silky needles or from aqueous acetone in stout, rhombic plates, m. p.  $174-175^\circ$ . (2) A dialcohol of *s*-*m*-xylenol,  $\text{OH} \cdot \text{C} \begin{array}{c} \diagup \text{CH} \text{---} \text{CMe} \diagdown \\ \diagdown \text{C}(\text{CH}_2 \cdot \text{OH}) \cdot \text{CMe} \diagup \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{OH}$  or



which crystallises from benzene in glassy prisms and leaflets, m. p. 138° (decomp.). (3) A compound of the formula



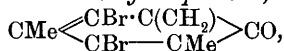
m. p. about 190°; on treatment with bromine in chloroform solution, it gives a tetrabromo-derivative,  $\text{CH}_2[\text{C}_6\text{BrMe}_2(\text{CH}_2\text{Br})\cdot\text{OH}]_2$ , which crystallises from acetic acid in stellate aggregates of slender, shining needles, m. p. 232—234°. T. H. P.

**Action of Bromine and Chlorine on Phenols. Substitution Products,  $\psi$ -Bromides, and  $\psi$ -Chlorides. XXI.  $o$ - $\psi$ -Haloids and  $o$ -Methylenequinones from  $o$ -Oxymesityl Alcohol.** KARL FRIES and K. KANN (*Annalen*, 1907, 353, 335—356. Compare Zincke and Hedenström, this vol., i, 124; Auwers and Büttner, Abstr., 1899, i, 36).—The bromo-derivatives of  $o$ -hydroxybenzyl bromide resemble those of  $p$ -hydroxybenzyl bromide and are true  $\psi$ -bromides. The typical reactions take place, however, more slowly with the ortho- than with the para-compounds, and the intermediately formed methylenequinones have not been isolated, although such substances have been shown to be capable of existence by Fries and Hübner (Abstr., 1906, i, 190); the 1:2-naphthamethylenequinones studied by these authors differed from the  $p$ -methylenequinones described by Zincke in their indifference to additive reagents. As this difference might be caused by the naphthalene nucleus, the authors have studied the preparation of  $o$ -methylenequinones from  $o$ -hydroxymesityl alcohol, and found that 2:6-dibromo-1:3-xylo-4:5-methylenequinone is even more stable and indifferent than the 1:2-naphthamethylenequinones. These results render the formation of the  $o$ -methylenequinones as intermediate products in the transformations of the  $o$ - $\psi$ -haloids extremely doubtful.

**I. Dibromo- $o$ -hydroxymesityl Bromide and its Derivatives.**—Dibromo- $o$ -hydroxymesityl  $\psi$ -bromide (Auwers, Abstr., 1906, i, 355) gives the reactions of the  $\psi$ -bromides, and is converted by the action of aqueous alkalis into an insoluble product which melts at high temperatures, and is probably a polymeride of dibromo- $o$ -methylenequinone. Dibromo- $o$ -acetoxymesityl bromide,  $\text{OAc} \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{CH}_2\text{Br}$ , forms stout crystals, m. p. 130°. Dibromo- $o$ -mesityl alcohol,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , crystallises in needles, m. p. 146°. The methyl ether,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , forms stout crystals, m. p. 66°.

The reduction of dibromo- $o$ -hydroxymesityl bromide with zinc and hydrochloric acid leads to the formation of dibromomesitol and tetra-bromodi- $o$ -hydroxydimesityl,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OH}$ , which forms stout crystals, m. p. 261—262°. The diacetate,  $\text{C}_{22}\text{H}_{22}\text{O}_4\text{Br}_4$ , m. p. 245°. Dibromomesityl acetate,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{Br}_2$ , m. p. 103°.

2:6-Dibromo-1:3-xylo-5:4-methylenequinone,



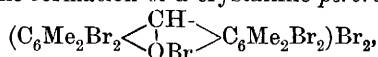
prepared by shaking dibromo- $o$ -hydroxymesityl bromide in ethereal petroleum solution with 10% sodium acetate solution, crystallises in

yellow prisms, m. p. 168°, and gives an intense brownish-red coloration with concentrated sulphuric acid. When reduced with zinc and hydrogen chloride in ethereal solution, it yields tetrabromodi-*o*-hydroxydimesityl.

II. *o*-Hydroxymesityl Chloride and its Derivatives.—*o*-Hydroxymesityl  $\psi$ -chloride,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CH}_2\text{Cl}$ , formed by the action of hydrogen chloride on *o*-hydroxymesityl alcohol in benzene solution, crystallises in long needles, m. p. 58°, yields the *o*-hydroxy-alcohol when treated with aqueous acetone, and when shaken in ethereal solution with sodium carbonate or acetate is converted into the polymeride of 1:3-xylo-5:4-methylenequinone,  $(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{O})_3$ , crystallising in white needles, m. p. 198–199°.

*Di-2-hydroxydi-3:5-xylylmethane*,  $\text{CH}_2(\text{C}_6\text{H}_2\text{Me}_2\cdot\text{OH})_2$ , formed by boiling *o*-hydroxymesityl alcohol with 3% sodium hydroxide, or by boiling *as-m*-xylenol with formaldehyde and hydrochloric acid, crystallises in slender needles, m. p. 146°, and is readily soluble in aqueous alkalis. The diacetate,  $\text{C}_{21}\text{H}_{24}\text{O}_4$ , m. p. 86–87°.

The action of bromine on dihydroxydixylylmethane in chloroform solution leads to the formation of a crystalline *perbromide*,



m. p. 190°, together with dibromo-*o*-hydroxymesityl bromide and a product which is soluble in alkalis and is probably a brominated xylenol.

When treated with nitrous acid, *o*-hydroxymesityl alcohol yields 5-nitro-1:3:4-xylenol, m. p. 78°, and a substance,  $\text{C}_9\text{H}_{11}\text{O}_4\text{N}$ , which crystallises in needles, m. p. 97°, and forms intensely red alkali salts and a diacetate,  $\text{C}_{18}\text{H}_{15}\text{O}_6\text{N}$ , m. p. 74°.

The action of nitrous acid on dibromo-*o*-hydroxymesityl alcohol leads to the formation of 2:6-dibromo-5-nitro-*m*-4-xylenol,  $\text{NO}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH}$ , which crystallises in yellow needles, m. p. 158°. The acetate,  $\text{C}_{10}\text{H}_9\text{O}_4\text{NBr}_2$ , m. p. 90°.

The carbinol group of *o*-hydroxymesityl alcohol is replaced by the nitro-group in the same manner by the action of fuming nitric acid.

G. Y.

**Action of Bromine and Chlorine on Phenol. Substitution Products,  $\psi$ -Bromides, and  $\psi$ -Chlorides. XXII. *o*- $\psi$ -Bromides and *o*-Methylenequinones from *o*-Hydroxyisoduryl Alcohol.** THEODOR ZINCKE and C. VON HOHORST (*Annalen*, 1907, 353, 357–379).—*o*-Hydroxyisoduryl alcohol (4- $\psi$ -cumenol-3-carbinol) behaves in the same manner as *o*-hydroxymesityl alcohol (see preceding abstract). In this case the halogen-free quinone, *o*-isodurylenequinone has been obtained.

$\psi$ -Cumenol alcohol (Manasse, Abstr., 1903, i, 28) yields a nitro-derivative when treated with sodium nitrite in glacial acetic acid solution; the diacetate,  $\text{C}_{14}\text{H}_{18}\text{O}_4$ , crystallises in flat needles, m. p. 50.5–51.5°. When boiled with 5% sodium hydroxide, the alcohol yields di-*o*- $\psi$ -cumenolmethane,  $\text{CH}_2(\text{C}_6\text{HMe}_3\cdot\text{OH})_2$ , which is formed also by the action of formaldehyde and alcoholic hydrogen chloride on  $\psi$ -cumenol. It crystallises in white needles, m. p. 171–172°, forms a



sparingly soluble *alkali* salt, and yields a deep red *perbromide*. The *diacetate*,  $C_{23}H_{28}O_4$ , crystallises in small leaflets, m. p. 130—131°.

*o-Hydroxyisoduryl ψ-bromide*,  $OH \cdot C_6HMe_3 \cdot CH_2Br$ , formed by the action of hydrogen bromide on the alcohol in benzene solution, crystallises in white needles, m. p. 107—107·5°, gives a yellow coloration when heated with alkalis, and is converted by boiling, more slowly by cold, water into *o-ψ-cumenolmethane* and formaldehyde, or by dilute alkalis in ethereal solution into the methylenequinone, or by acetic anhydride into the diacetate of *o-hydroxyisoduryl alcohol*.

*o-Hydroxyisoduryl ψ-chloride*,  $C_{10}H_{13}OCl$ , crystallises in white needles, m. p. 99—100°, and gives the same reactions as the *ψ-bromide*.

*o-Acetoxyisoduryl ψ-bromide*,  $OAc \cdot C_6HMe_3 \cdot CH_2Br$ , forms white needles, m. p. 127—128°. The *ψ-chloride* crystallises in white needles, m. p. 116—117°.

*o-Hydroxyisoduryl methyl ether*,  $C_{11}H_{16}O_2$ , crystallises in stout, colourless needles, m. p. 44—45°; the *acetate* is an oil. *o-Hydroxyisoduryl acetate* forms white needles, m. p. 57—58°.

When shaken in ethereal solution with dilute alkalis, the *ψ-bromide* yields *o-isodurylenequinone*  $CMe \begin{smallmatrix} \swarrow CMe \cdot C(CH_2) \\ \searrow CH = CMe \end{smallmatrix} > CO$ , and its *polymeride*,  $(C_{10}H_{12}O)_3$ . The *quinone* crystallises in yellow, monoclinic prisms, m. p. 128—129°, gives a deep red coloration with concentrated sulphuric acid, does not react with methyl alcohol, glacial acetic acid, acetic anhydride, alkalis in acetone solution, or hydrogen bromide in glacial acetic acid solution, and when exposed in solution to sunlight is gradually converted into its *polymeride*. This crystallises in colourless, rhombic plates, m. p. 173—174°, and is indifferent to the action of reagents.

*6-Bromo-o-hydroxyisoduryl ψ-bromide*,  $OH \cdot C_6Me_3Br \cdot CH_2Br$ , formed by the action of bromine on *o-hydroxyisoduryl alcohol* in chloroform solution, crystallises in white needles, m. p. 111—112°, and is not identical with Auwer's compound (Abstr., 1906, i, 354). The *acetate* of the *ψ-bromide*,  $C_{12}H_{14}O_2Br_2$ , forms needles or leaflets, m. p. 135—136°. The *diacetate*,  $OAc \cdot C_6Me_3Br \cdot CH_2 \cdot OAc$ , crystallises in white needles, m. p. 88—88·5°.


*6-Bromo-o-hydroxyisoduryl acetate*,  $OH \cdot C_6Me_3Br \cdot CH_2 \cdot OAc$ , crystallises in rhombic plates, m. p. 91—92°, and is insoluble in alkalis. The *methyl ether*,  $OH \cdot C_6Me_3Br \cdot CH_2 \cdot OMe$ , crystallises in white needles, m. p. 94—94·5°, and forms an *acetate*,  $C_{13}H_{17}O_3Br$ , crystallising in stout needles, m. p. 63—64°.



When shaken in ethereal solution with dilute sodium hydroxide, the *ψ-bromide* yields *6-bromo-o-isodurylenequinone*,  $CH_2 \cdot C_6Me_3Br \cdot O$ , and its *polymeride*,  $(C_{10}H_{11}OBr)_3$ . The *quinone* crystallises in white needles, m. p. 142—142·5°. The *polymeride* crystallises in yellowish-white needles, m. p. 255—257°. The *quinone* and its *polymeride* are completely unreactive.


The action of acetone and water on the *ψ-bromide* leads to the formation of *6-bromo-o-hydroxyisoduryl alcohol* and, as the main product, a *condensation product* of the alcohol with acetone.

*6-Bromo-o-hydroxyisoduryl alcohol*,  $OH \cdot C_6Me_3Br \cdot CH_2 \cdot OH$ , crystallises in small, white needles, m. p. 128—129°.

The condensation product,  $\text{C}_6\text{Me}_3\text{Br} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CMe} \cdot \text{OH} \end{array}$ , forms stout prisms or rhombohedra, m. p. 81—82°, and yields an acetate,  $\text{C}_{15}\text{H}_{19}\text{O}_3\text{Br}$ , crystallising in white needles, m. p. 86—87°. G. Y.

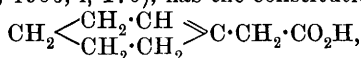
**Terpenes and Ethereal Oils. LXXXIV. Carboxylic Acids of Cyclic Hydrocarbons and their Transformation Products.** OTTO WALLACH (*Annalen*, 1907, 353, 284—317. Compare this vol., i, 541).—Acids and bases which are derived from the simplest cyclic hydrocarbons and have the carboxyl and amino-groups respectively situated in a side-chain are but little known. The present work was undertaken to fill this gap in our knowledge. The author proposes the term *cyclyl* for the univalent groups, *cyclopentyl*, *cyclohexyl*, corresponding to the *cyclohydrocarbons*; thus ·CH<sub>2</sub>·CO<sub>2</sub>H,

·CH<sub>2</sub>·CO<sub>2</sub>H, &c., are *cyclylacetic acids*, whilst ·CH<sub>2</sub>·NH<sub>2</sub>,

·CH<sub>2</sub>·NH<sub>2</sub>, &c., are *cyclylmethylamines*.

*Cyclylacetic acids* and their homologues are prepared readily by condensation of cyclic ketones with ethyl bromoacetate and its homologues, treatment of the resulting hydroxy-ester with hydrogen bromide, and reduction of the bromo-ester, so obtained, or of the corresponding bromo-acid. The *cyclylacetic acids* yield amides, from which are obtained the *cyclylmethylamines* directly by Hofmann's reaction, or the *cyclylethylamines* by conversion into, and reduction of, the *cyclylacetonitriles*.

I. *Compounds from cycloHexanone; Isomeric cycloHexeneacetic Acids.*—It is found that, on loss of water, *cyclohexanolacetic acid* (Wallach and Isaac, *Abstr.*, 1906, i, 564) yields two *cyclohexeneacetic acids*; one of these, m. p. 38°, which has been described previously (*Abstr.*, 1906, i, 176), has the constitution



whilst the new isomeride, m. p. 91—92°, is  $\Delta^{\alpha}$ -*cyclohexeneacetic acid*,  $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , since on oxidation with potassium permanganate it yields *cyclohexanone*; it crystallises in long needles and distils slowly in a current of steam. Both *cyclohexeneacetic acids* yield a *hydrobromide*, m. p. 89—90°. 1 :  $\alpha$ -*Dibromocyclohexylacetic acid*,  $\text{C}_8\text{H}_{12}\text{O}_2\text{Br}_2$ , m. p. 133—134°, formed from  $\Delta^{\alpha}$ -*cyclohexeneacetic acid*, is converted into an oil by the action of alkali carbonates. 1-*Chlorocyclohexylacetic acid*,  $\text{C}_6\text{H}_{10}\text{Cl} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , separates from methyl alcohol in crystals, m. p. 83°. 1-*Iodocyclohexylacetic acid*,  $\text{C}_6\text{H}_{10}\text{O}_2\text{I}$ , forms transparent prisms, m. p. 99—100° (becoming brown).

The oil, b. p. 178—185°, formed by the action of sodium carbonate on 1 : 2-dibromocyclohexylacetic acid, distils in a current of steam and is probably a brominated lactone (compare *Abstr.*, 1906, i, 176). A *lactone* is obtained also when  $\Delta^1$ -*cyclohexeneacetic acid* is boiled

with sulphuric acid. These properties confirm its constitution as a  $\beta\gamma$ -unsaturated acid.  $\Delta^1$ -cycloHexeneacetamide,  $C_6H_9 \cdot CH_2 \cdot CO \cdot NH_2$ , prepared by the successive action of phosphorus pentachloride and ethereal ammonia on the acid, separates from methyl alcohol in crystals, m. p. 152—153°.

The product,  $C_7H_{10}O$ , b. p. 175°, obtained on oxidation of  $\Delta^1$ -cyclohexeneacetic acid (Abstr., 1906, i, 176), is now considered to be an aldehyde; when purified by conversion into its semicarbazone,  $C_8H_{13}ON_3$ , m. p. 203—204°, and liberation by means of oxalic acid, it has an odour of benzaldehyde, reduces silver oxide in boiling water, and is oxidised by chromic and sulphuric acids, yielding glutaric acid. Since the semicarbazone of 2-methyl- $\Delta^2$ -cyclohexenone has m. p. 211—212°, and that of  $\Delta^1$ -tetrahydrobenzaldehyde has m. p. 212—213°, the constitution of the aldehyde from the cyclohexeneacetic acid requires further investigation.

cycloHexylacetic acid,  $C_6H_{11} \cdot CH_2 \cdot CO_2H$ , prepared by the action of hydrogen bromide on ethyl cyclohexanolacetate and treatment of the product with zinc dust, is freed from unsaturated acids by oxidation of the latter with potassium permanganate; it solidifies when cooled, m. p. 30—31°, b. p. 245—247°. The silver salt,  $C_8H_{13}O_2Ag$ , is sparingly soluble. The amide,  $C_7H_{13} \cdot CO \cdot NH_2$ , m. p. 168°, crystallises from dilute methyl alcohol. The nitrile,  $C_6H_{11} \cdot CH_2 \cdot CN$ , b. p. 215—217°, distils with steam, and on reduction yields  $\beta$ -aminoethylcyclohexane,  $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot NH_2$ , b. p. 188—189°. The hydrochloride, m. p. 252—253°; the platinichloride decomposes at 253—254°; the carbamide,  $C_8H_{15} \cdot NH \cdot CO \cdot NH_2$ , m. p. 85—86°; the trimethylammonium iodide,  $C_8H_{15} \cdot NMe_3I$ , m. p. 221—222°.

cycloHexanemethylamine,  $C_6H_{11} \cdot CH_2 \cdot NH_2$ , b. p. 162—164° (Demjanoff, Abstr., 1904, i, 410), formed by the action of bromine and potassium hydroxide on the acetamide, absorbs carbon dioxide yielding a solid carbonate; the hydrochloride, m. p. above 210°; the carbamide,  $C_7H_{13} \cdot NH \cdot CO \cdot NH_2$ , m. p. 225°.

*Ketones from cycloHexylacetic Acid.*—Dihexahydrobenzyl ketone,  $CO(CH_2 \cdot C_6H_{11})_2$ , formed by distilling calcium cyclohexylacetic acid at 120—130° under reduced pressure, solidifies at low temperatures, is an oil at the ordinary temperature, and has a feeble odour. The semicarbazone,  $C_{16}H_{29}ON_3$ , m. p. 142—145°.

Hexahydrobenzyl methyl ketone, b. p. 198—200°, formed from cyclohexylacetic acid, may be identical with Freundler's ketone (Abstr., 1906, i, 283); the semicarbazone, m. p. 165—166° (182.5°: Freundler, loc. cit.).

## II. Compounds from Suberone.—cycloHeptylacetic acid,



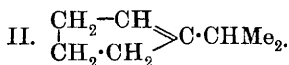
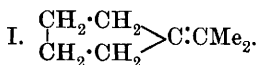
prepared by the successive action of hydrogen bromide and zinc dust on ethyl suberolacetate (Abstr., 1901, i, 156), is obtained as an oil, b. p. 165°/19 mm.; the silver salt,  $C_9H_{15}O_2Ag$ , is sparingly soluble. cycloHeptylacetic acid,  $C_7H_{13} \cdot CH_2 \cdot CO \cdot NH_2$ , crystallises in leaflets, m. p. 146—148°. cycloHeptanemethylamine,  $C_7H_{13} \cdot CH_2 \cdot NH_2$ , b. p. 193—195°,  $D_{20}^{25}$  0.8840,  $n_D$  1.4719, absorbs carbon dioxide and volatilises slowly with ether. The hydrochloride, m. p. 229—232°; the platinichloride,  $(C_8H_{18}N)_2PtCl_6$ , was analysed; the carbamide,

$C_7H_{18} \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$ , crystallises in leaflets, m. p. 127—129°; the *trimethylammonium iodide*,  $C_8H_{15} \cdot NMe_3I$ , m. p. 223°.

III. *Compounds from cyclopentanone*.—[With KARL FLEISCHER.]—*cyclopentylacetic acid*,  $C_5H_9 \cdot CH_2 \cdot CO_2H$ , prepared from ethyl *cyclopentanolacetate* (Wallach and Speranski, Abstr., 1902, i, 800), is obtained as an oil, b. p. 226—230° (139—140°/26 mm.: Verwey, Abstr., 1896, i, 671), and has an odour resembling that of the fatty acids. The *amide*,  $C_5H_9 \cdot CH_2 \cdot CO \cdot NH_2$ , m. p. 143—145°. *cyclopentanemethylamine*,  $C_5H_9 \cdot CH_2 \cdot NH_2$ , b. p. 139—145°, absorbs carbon dioxide and is readily soluble in water; the *hydrochloride* is deliquescent; the *platinichloride*,  $(C_6H_{14}N_2)_2PtCl_6$ , was analysed.

*Ethyl cyclopentanolisobutyrate*,  $\begin{array}{c} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{array} > C(OH) \cdot CMe_2 \cdot CO_2Et$ , formed from *cyclopentanone* and ethyl  $\alpha$ -bromoisobutyrate, is obtained as an oil, b. p. 108—113°/11 mm., containing small amounts of the unsaturated *ester*, into which it is converted completely when heated with potassium hydrogen sulphate at 150—160°. This on hydrolysis yields *cyclopenteneisobutyric acid*,  $\begin{array}{c} CH_2-CH \\ | \quad | \\ CH_2 \cdot CH_2 \end{array} > C \cdot CMe_2 \cdot CO_2H$ , b. p. 148—150°/27 mm.; the *ammonium salt* is readily soluble; the *silver salt*,  $C_9H_{13}O_2Ag$ , was analysed. The unsaturated acid forms crystalline additive products,  $\begin{array}{c} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{array} > CX \cdot CMe_2 \cdot CO_2H$ , with hydrogen haloids. 1-*Chlorocyclopentylisobutyric acid*,  $C_9H_{15}O_2Cl$ , m. p. 122·5—123·5°. 1-*Bromocyclopentylisobutyric acid*, m. p. 113—114° (decomp.). 1-*Iodocyclopentylisobutyric acid*, m. p. 107—108° (decomp.).

When distilled under atmospheric pressure, *cyclopenteneisobutyric acid* yields a *hydrocarbon*, b. p. 136—137°,  $D^{20}_D$  0·817,  $n_D$  1·4581, which is probably a mixture of I with a small amount of II. With nitrosyl chloride it forms an intense blue oil, which is volatile

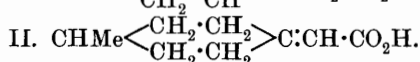
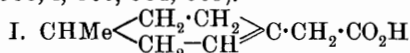


with steam, and on oxidation with potassium permanganate yields *cyclopentanone* and a crystalline *glycol*, m. p. 61—63°. When heated with alcoholic sulphuric acid on the water-bath, the hydrocarbon I is transformed into II. This forms a crystalline *additive product*,  $C_8H_{14}NOCl$ , with nitrosyl chloride, which on conversion into the corresponding *oxime* and subsequent hydrolysis yields a *ketone*,  $\begin{array}{c} CH_2-CO \\ | \quad | \\ CH_2 \cdot CH_2 \end{array} > C \cdot CMe_2$  or  $\begin{array}{c} CH_2 \cdot CO \\ | \quad | \\ CH_2 \cdot CH \end{array} > C \cdot CHMe_2$ ; the *semicarbazone*, m. p. 183—185°.

The semicarbazone of *cyclopentanone*, m. p. 205—206° if heated slowly, but m. p. 212—213° if heated rapidly.

IV. *Compounds from 1-Methylcyclohexane-4-one*.—[With EDGAR EVANS.]—Since the crude 1-methylcyclohexeneacetic acid, formed from 1-methylcyclohexane-4-one (Abstr., 1906, i, 566), might be a mixture of the two acids I and II, it was examined successfully for Perkin and Pope's acid, m. p. 70—71° (Proc., 1906, 22, 107). On oxidation with

potassium permanganate, the crude acid yielded 1-methylcyclohexane-4-ol, whilst the acid, m. p. 42—43°, purified by distillation in a current of steam, yielded 1-methylcyclohexane-4-one. The acid, m. p. 42—43°, is considered to have the constitution II (compare Marckwald and Meth, Abstr., 1906, i, 360, 584, 663).



The following derivatives are prepared from the acid, m. p. 42—43°.

4-Chloro-1-methylcyclohexyl-4-acetic acid,  $\text{C}_9\text{H}_{15}\text{O}_2\text{Cl}$ , m. p. 88—89°. 4-Bromo-1-methylcyclohexyl-4-acetic acid, m. p. 85—86°, yields the acid, m. p. 41—42°, when heated with sodium methoxide solution. 3:4-Dibromo-1-methylcyclohexyl-4-acetic acid, m. p. 97—99°. 1-Methylcyclohexyl-4-acetamide,  $\text{C}_9\text{H}_{15}\text{ON}$ , m. p. 155—156°. The nitrile, b. p. 107°/15 mm.

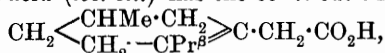
1-Methylcyclohexyl-4-acetic acid,  $\text{C}_6\text{H}_{10}\text{Me} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , formed in the same manner as cyclohexyl-1-acetic acid, separates from methyl alcohol in crystals, m. p. 63—65°; the amide,  $\text{C}_6\text{H}_{10}\text{Me} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 161—162°.

V. Compounds from Menthone.—[With EDUARD SCHELLACK.]—

Methyl mentholacetate,  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHPr}^\beta \end{array} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , prepared by condensation of menthone with methyl bromoacetate (compare Wallach and Thölke, Abstr., 1902, i, 799), readily forms crystals, m. p. 32—33°, b. p. 136—137°/10 mm.; the acid,

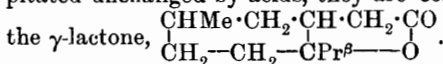
$\text{C}_6\text{H}_8\text{MePr}^\beta(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 82—83°, b. p. 193—197°/11 mm.

Mentheneacetic acid (*loc. cit.*) has the constitution



since on oxidation it yields only traces of menthone. When treated with hydrogen bromide in glacial acetic acid solution, it forms bromomenthaneacetic acid,  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHPr}^\beta \end{array} \text{CBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 126—130° when slowly, but 135—137° when rapidly, heated.

A levorotatory, liquid lactone,  $\text{C}_{12}\text{H}_{20}\text{O}_2$ , b. p. 300—305°,  $D_{20} 1.015$ ,  $n_D^{20} 1.4781$ , is obtained together with mentheneacetic acid by heating ethyl mentholacetate with potassium hydrogen sulphate and hydrolysing the resulting unsaturated ether. When boiled with hydrogen iodide and red phosphorus in glacial acetic acid solution, it is converted into a dextrorotatory, crystalline modification, m. p. 88.5—89.5°. As both substances dissolve when boiled with alkalis and are reprecipitated unchanged by acids, they are considered to be modifications of the  $\gamma$ -lactone,



Menthaneacetic acid,  $\text{C}_6\text{H}_9\text{MePr}^\beta \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , formed by reduction of ethyl bromomenthaneacetate, is an oil, b. p. 166—170°/11 mm.; the amide,  $\text{C}_{11}\text{H}_{21}\text{CO} \cdot \text{NH}_2$ , m. p. 148—150°. G. Y.

**Sulphonation in Presence of Mercury.** OTTO DIMROTH and WOLFGANG VON SCHMAEDEL (*Ber.*, 1907, 40, 2411—2415. Compare Abstr., 1899, i, 54, 428; 1901, i, 439; 1902, i, 656, 849; Iljinsky, Abstr., 1904, i, 176; Schmidt, *ibid.*, 256; Liebermann and Pleus, *ibid.*, 326; Farbenfabriken vorm. F. Bayer and Co., Abstr., 1906, i, 293).—This work was undertaken with the object of determining the nature of the influence of small amounts of mercury in the sulphonation of anthraquinone and in similar reactions. Contrary to the statement of Holdermann (Abstr., 1906, i, 439), it is found that whilst the sulphonation of benzoic acid in absence of mercury leads to the formation of the meta- and para-derivatives only, the reaction is accelerated and the ortho-derivative also is formed in small amount if mercuric sulphate is added to the reacting mixture. It is found further that *o*-hydroxymercuribenzoic anhydride yields *o*-sulphobenzoic acid, together with small amounts of the meta- and para-compounds, when treated at the ordinary temperature with sulphuric acid containing 18% of sulphur trioxide. It is concluded that in the sulphonation of benzoic acid by means of concentrated sulphuric acid in presence of mercury, the following reactions take place: (1) formation of *o*-carboxyphenylmercuric sulphate,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}\cdot\text{SO}_4\text{H}$ , which is limited by equilibrium with the reverse reaction; (2) formation of benzoic acid and mercuric sulphate; (3) conversion of *o*-carboxyphenylmercuric sulphate by sulphuric acid into *o*-sulphobenzoic acid and mercuric sulphate, and (4) direct sulphonation of benzoic acid in the meta- and para-positions. G. Y.

**Bimolecular Anhydrides of Anthranilic Acid.** GEORG SCHROETER (*Ber.*, 1907, 40, 2628—2630).—When the yellow anhydride of anthranoylanthranilic acid (this vol., i, 529) is warmed with benzenesulphonyl chloride, or benzenesulphonylanthranoylanthranilic acid with thionyl chloride, the anhydride of benzenesulphonylanthranoylanthranilic acid, m. p. 214—215°, is obtained, which yields the acid, m. p. 222°, by treatment with alkalis. These two compounds are identical with those prepared by Heller (Abstr., 1904, i, 160).

Pawlewski's *N*-phenylsulphoneanthranilic acid (Abstr., 1905, i, 437) is identical with the author's benzenesulphonylanthranilic acid (*loc. cit.*), the m. p. of which is 214° and not 223°. C. S.

**3-Nitro-4-dimethylaminobenzoic Acid.** FREDERIC REVERDIN (*Arch. Sci. phys. nat.*, 1907, [iv], 23, 458—466; *Ber.*, 1907, 40, 2442—2448).—The nitration of dimethylaminobenzoic acid with 30% nitric acid at 30° yields, in addition to 3-nitro-4-dimethylaminobenzoic acid and 2:4-dinitrodimethylaniline already described by Steiner, some 2:4-dinitromethylaniline. On nitrating the acid by means of a mixture of nitric and sulphuric acids, the author also obtained some *p*-nitrodimethylaniline, m. p. 161—162°. Nitration in glacial acetic acid solution yields a mixture of 2:4-dinitromethylaniline, 2:4:6-trinitrodimethylaniline, and two other substances melting at 179° and 164° respectively which were not identified; on a subsequent occasion, nitration under apparently similar conditions yielded a substance

which did not melt at  $240^{\circ}$  and appeared to be nitromethylaminobenzoic acid. The nitration of nitrodimethylaminobenzoic acid by means of nitric and sulphuric acids yields Romburgh's trinitrophenylmethylnitroamine (compare Abstr., 1885, 660), which, according to the present author, melts at  $129^{\circ}$  instead of  $127^{\circ}$ , and a substance melting at  $193^{\circ}$  which is probably trinitrodimethylaminobenzoic acid.

P. H.

**Triphenylamine and Triphenylamine-*o*-carboxylic Acid (Diphenylanthranilic Acid).** IRMA GOLDBERG and MARIE NIMEROVSKY [in part, R. MAAG] (*Ber.*, 1907, 40, 2448—2452).—Since phenylanthranilic acid is readily obtained by the interaction of anthranilic acid and bromobenzene in the presence of copper as a catalyst (Goldberg, Abstr., 1906, i, 426), attempts were made to replace the remaining imino-hydrogen atom by another phenyl group. This was found to be possible when iodobenzene was used instead of bromobenzene, *diphenylanthranilic acid*,  $\text{NPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , being obtained. This acid forms sulphur-yellow, feathery crystals, m. p.  $208^{\circ}$ ; when heated above its melting point, it is converted quantitatively into triphenylamine with the liberation of carbon dioxide. Triphenylamine may also be prepared from diphenylamine and iodobenzene by the use of copper as a catalyst.

10-*Phenylacridone*,  $\text{C}_{13}\text{H}_8\text{ONPh}$ , obtained by heating diphenylanthranilic acid with concentrated sulphuric acid at  $100^{\circ}$ , forms yellow crystals, m. p.  $276^{\circ}$  (corr.). Its solutions in amyl alcohol, benzene, and toluene are not fluorescent, whilst the acetic acid solution shows an intense blue fluorescence.

*Phenyl-p-tolylanthranilic acid*,  $\text{C}_7\text{H}_7 \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , a yellow powder, m. p.  $175^{\circ}$ , has also been prepared by the above method.

W. H. G.

**Calcium *p*-Hydroxybenzoate.** WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1907, 144, 1118—1119. Compare this vol., i, 532).—On treating anhydrous calcium *p*-hydroxybenzoate with a small quantity of water at  $15^{\circ}$ , the crystalline monohydrate is formed. When the anhydrous salt is shaken with excess of water, it slowly dissolves and at the moment before the dissolution of the last crystalline spangles the phenomenon of triboluminescence is observed.

The 3% solution at  $17^{\circ}$  when first prepared is turbid, but it afterwards becomes quite clear. Such a solution when kept in a closed vessel overnight (during which the temperature fell to  $5^{\circ}$  and then rose to  $14^{\circ}$ ) separated into two layers, of which the upper one remained clear and contained the monohydrate, whilst the lower one consisted of an emulsion of a perhydrated salt. After a time, dilute, clear solutions of calcium *p*-hydroxybenzoate deposit a salt of a spongy, flocculent appearance. This is quite insoluble and is a mixture of several hydrates of an allotropic salt, the trihydrate apparently predominating. The densities of solutions of calcium *p*-hydroxybenzoate in water are 0.5%  $D^{16} = 0.993$ , 0.8%  $D^{16} = 0.9973$ , 1%  $D^{18} = 1.0024$ , 1.5%  $D^{15} = 1.0065$ , 2%  $D^{18} = 1.0138$ , 2.5%  $D^{18} = 1.0156$ ; in ethyl alcohol (95%), 0.5%  $D^{16} = 0.8128$ , 1%  $D^{18.5} = 1.0147$ .

E. H.

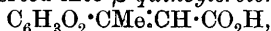
**6-Hydroxy-4-methylcoumarin and  $\beta$ -Quinoylcrotonic Acid.** WALTHER BORSCHKE (*Ber.*, 1907, 40, 2731—2736).—Pechmann (*Abstr.*, 1901, i, 285, 286) found that his method of synthesis of coumarin derivatives from the esters of  $\beta$ -ketonic acids and phenols failed in the case of quinol. This has been repeated, and under suitable conditions quinol and ethylacetoacetate react in presence of concentrated sulphuric acid forming 6-hydroxy-4-methylcoumarin, a faintly yellow, crystalline substance, m. p. 243°.

The acetate crystallises in long, colourless needles, m. p. 137—138°, whilst the 5:7-dibromo-derivative forms colourless needles, m. p. 202—203°.

7(1)-Nitro-6-hydroxy-4-methylcoumarin separates from alcohol in yellow, flat needles, m. p. 210° (decomp.), and forms a benzoate crystallising in colourless needles, m. p. 166—167; the 5:7-dinitro-compound forms orange-yellow needles, m. p. 219°.

Quinol reacts less readily with ethyl  $\alpha$ -methylacetoacetate and yields only small quantities of 3:4-dimethyl-6-hydroxycoumarin, which crystallises in colourless plates, m. p. 235—236°. Quinol does not react with ethylbenzoyl acetate.

6-Hydroxy-4-methylcoumarin is converted by the action of zinc dust and sodium hydroxide into 2:5-dihydroxy- $\beta$ -methylcinnamic acid,  $C_6H_3(OH)_2 \cdot CMe \cdot CH \cdot CO_2H$ , separating in faintly brown-coloured, round, crystalline aggregates, m. p. 155—156°. On oxidation with chromic acid it is converted into  $\beta$ -quinoylcrotonic acid,



crystallising in orange needles, m. p. 167—168°. The  $\beta$ -dianilino-derivative forms dark bluish-red, glistening needles, m. p. 232° (decomp.); the  $\beta$ -oximino-derivative crystallises in yellow needles, m. p. 179—180° (decomp.), and the phenylcarbamic acid hydrazone is a red, crystalline powder, m. p. 150° (decomp.). E. F. A.

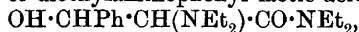
**Hydroxyamino-Acids.** ERNEST FOURNEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 549—558. Compare *Abstr.*, 1904, i, 377).—Dimethylamino-phenyl-lactic acid,  $OH \cdot CHPh \cdot CH(NMe_2) \cdot CO_2H$ , m. p. 145°, obtained by heating phenylchlorolactic acid with dimethylamine, dissolved in benzene, in a closed tube, crystallises in cubes, is insoluble in acetone and chloroform, and neutral to litmus. It decomposes at 150°, passing into a new substance, which itself decomposes at 205° (approx.). The sodium and copper salts are crystalline, but the second of these appears to have an abnormal constitution analogous to that of the copper derivative of isoserine described by Fischer (*Abstr.*, 1902, i, 269). The methyl ester hydrochloride, m. p. 175° (decomp.), prepared in the usual way, crystallises from alcohol in silky needles. The ethyl ester, b. p. 170—171°/24 mm., yields a hydrochloride, m. p. 197°, which crystallises in slender needles. The aurichloride, m. p. 162°, forms yellow spangles; the platinichloride decomposes at 203°; the benzoyl derivative, m. p. 172—173°, crystallises in silky needles. When methyl or ethyl phenylchlorolactate is heated with excess of dimethylamine, dissolved in benzene, in a closed tube, the dimethylamide of dimethylaminophenyl-lactic acid,  $OH \cdot CHPh \cdot CH(NMe_2) \cdot CO \cdot NMe_2$ , m. p. 148°, is produced. This is crystalline, readily soluble in alcohol or chloroform, slightly so



in ether or water, and is strongly basic. The *hydrochloride*, m. p. 210°, forms short, prismatic crystals. The *platinichloride*, m. p. 118°, forms slender, red needles, and the *aurichloride*, m. p. 81°, canary-yellow crystals. The *benzoyl* derivative, m. p. 156°, separates from acetone in tabular crystals; the *hydrochloride* of this forms silky tufts, m. p. 200° (decomp.), of acid reaction and bitter taste, and the *platinichloride*, m. p. 180°, bright red spangles.

When the amine is not used in excess, there are also formed some *dimethylamide* of phenylchlorolactic acid and some ethyl phenylglycidate. The former has m. p. 140°, separates from dilute alcohol in large leaflets, and is insoluble both in acids and bases. When warmed with a concentrated solution of potassium hydroxide, it decomposes, yielding dimethylamine, and, when heated in a closed tube at 130° with dimethylamine, passes into the dimethylamide of phenyl-dimethylaminolactic acid.

The *diethylamide* of diethylaminophenyl-lactic acid,



prepared similarly, has m. p. 92—93°, and separates from a mixture of ether and light petroleum in long, silky needles. The *diethylamide* of phenylchlorolactic acid, obtained when diethylamine is not used in excess, has m. p. 149°, and crystallises from a mixture of alcohol and ether in slender needles.

The *methylamide* of methylaminophenyl-lactic acid,



obtained by the action of methylamine dissolved in benzene on ethyl phenylchlorolactate, separates from acetone in slender, silky needles, m. p. 153°. The *hydrochloride*, m. p. 218° (decomp.), separates from alcohol in brilliant crystals. The *methiodide*, m. p. 205° (decomp.), crystallises in prisms. The *methylamide* of phenylchlorolactic acid, simultaneously produced, separates from boiling alcohol on addition of ether in needles, m. p. 141°.

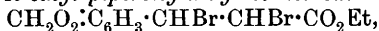
T. A. H.

**Action of a Mixture of Ethyl  $\alpha$ -Bromobutyrate and *p*-Tolaldehyde on Zinc. Synthesis of  $\beta$ -Hydroxy- $\beta$ -tolyl- $\alpha$  ethylpropionic Acid.** I. MAZUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 183—195. Compare Zeltner, *Abstr.*, 1907, i, 23).—*Ethyl  $\beta$ -hydroxy- $\beta$ -tolyl- $\alpha$ -ethylpropionate*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , b.p. 190.5—191°/28 mm., has been prepared by a similar process to that used by Zeltner in the formation of the isomeric  $\alpha$ -dimethyl compound, zinc being employed instead of magnesium. The yield can be augmented considerably by using impure aldehyde. On saponifying the ester with potassium hydroxide, the free acid,  $\text{C}_{12}\text{H}_{16}\text{O}_3$ , m. p. 134—135°, is obtained. The *potassium, sodium, ammonium, barium, strontium, tin, zinc, mercury, nickel, iron, and aluminium* salts are described. When the acid is heated at its melting point, it decomposes into water, carbon dioxide, and an unsaturated hydrocarbon, which is also formed on distillation in steam or when heated with 10% sulphuric acid. Possibly by reactions also occur which produce very small quantities of butyric and *p*-toluic acids. The *hydrocarbon*,  $\text{C}_8\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CHEt}$ , b. p. 218—218.5°/740 mm., unites with bromine, forming most probably the *dibromide*,  $\text{C}_{11}\text{H}_{14}\text{Br}_2$ .

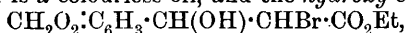
Z. K.

**Piperonylacrylic Acid Dibromide, and its Ethyl Ester.** PAUL HOERING (*Ber.*, 1907, 40, 2174—2182).—For the purpose of comparison with *isosafrole* dibromide, the dibromide of piperonylacrylic acid and its ethyl ester were prepared in order to examine what effect the replacement of the terminal methyl group by carboxyl or carbethoxyl groups exerts on the reactivity of the bromine atoms; the effect is intensified.

When ethyl piperonylacrylate is brominated in chloroform solution, the main product is *ethyl piperonylacrylate dibromide*,

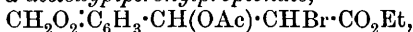


which separates in colourless crystals, m. p. 88°. An isomeric dibromide, m. p. 56—57°, is obtained from the mother liquors. The former dibromide was used for the subsequent preparations. When boiled with methyl alcohol, it forms *ethyl β-bromo-α-methoxypiperonylpropionate*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OMe})\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ , which separates from dilute alcohol in colourless needles, m. p. 54—55°; the corresponding *ethoxy*-compound is a colourless oil, and the *hydroxy*-compound,



obtained by heating the dibromide with aqueous acetone, separates from light petroleum in prismatic needles, m. p. 62°.

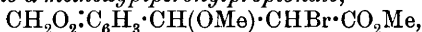
*Ethyl β-bromo-α-acetoxypiperonylpropionate*,



obtained by heating the dibromide with sodium acetate and glacial acetic acid, separates from light petroleum in needles, m. p. 80°.

*Ethyl α-ethoxypiperonylacrylate*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C}(\text{OEt})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , prepared by the action of sodium ethoxide on ethyl β-bromo-α-ethoxypiperonylpropionate, separates from light petroleum in crystals, m. p. 69°. An isomeride separates from the mother liquors in glistening needles, m. p. 55—56°.

*Methyl β-bromo-α-methoxypiperonylpropionate*,



prepared by heating piperonylacrylic dibromide with methyl alcohol, separates from a mixture of alcohol and light petroleum in prisms, m. p. 97—98°.

*β-Bromo-α-methoxypiperonylpropionic acid* separates from a mixture of benzene and light petroleum and has m. p. 150°.

*β-Bromo-α-hydroxypiperonylpropionic acid* is not formed by the action of aqueous acetone on the dibromide, but a compound, m. p. 228°, which, when dissolved in sodium carbonate and then acidified, gives piperonylacrylic acid.

Methylenedioxy-ω-bromostyrene,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CHBr}$ , is formed by heating piperonylacrylic dibromide with sodium acetate and glacial acetic acid; by the action of bromine it is converted into the *dibromide*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CHBr}\cdot\text{CHBr}_2$ , which is a yellow oil.

A. McK.

**Products of the Action of Acetic Anhydride on Phthalamide.** ARSÈNE BRAUN and JOSEPH TSCHERNIAC (*Ber.*, 1907, 40, 2709—2714).—By the action of boiling acetic anhydride on phthalamide, besides acetylphthalamide and phthalonitrile, the chief product formed is *o*-cyanobenzamide, m. p. 172—173°, which then solidifies and

melts again above  $200^{\circ}$ , and is identical with the supposed *o*-cyanobenzaldoxime obtained by Posner (Abstr., 1897, i, 472) from cyanobenzylidene chloride and hydroxylamine. The product formed by heating, or better by the action of alkali hydroxides or ammonia, is *iminophthalimide*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C(NH)} \\ \text{CO} \end{smallmatrix}\rangle\text{NH}$ , which crystallises in hard, colourless crystals, m. p.  $203^{\circ}$ . With formaldehyde, it forms *hydroxy-methyliminophthalimide*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C(NH)} \\ \text{CO} \end{smallmatrix}\rangle\text{N}\cdot\text{CH}_2\cdot\text{OH}$ , crystallising in colourless clusters, m. p.  $143\text{--}146^{\circ}$  (decomp.), whilst hypochlorites convert it into *iminophthalochloroimide*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C(NH)} \\ \text{CO} \end{smallmatrix}\rangle\text{NCl}$ , crystallising from glacial acetic acid in colourless, glistening needles, m. p.  $222\text{--}223^{\circ}$  (decomp.), which, when heated with alkaline hydroxides, undergoes the Hofmann rearrangement forming *o*-benzoylenecarbamide. Neutral hypochlorite converts *o*-cyanobenzamide into *o*-cyanobenzoic acid, which is not precipitated from its solution in alkali by acetic acid.

E. F. A.

**Synthetical Derivatives of Glycine and its Homologues.** SIEGMUND GABRIEL (*Ber.*, 1907, 40, 2647—2650).—It is found that phthalimino-derivatives of fatty acids are readily brominated by means of bromine and red phosphorus and these derivatives may be used in a variety of ways for the preparation of *isocystein*, &c.

*$\alpha$ -Bromo- $\beta$ -phthalylalanine*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{N}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ , prepared by heating the  $\beta$ -phthalylalanine, phosphorus and bromine at the temperature of the water-bath for four to five hours, crystallises from a mixture of water and alcohol in quadratic plates, m. p.  $169\text{--}170^{\circ}$ . On hydrolysis with hydrobromic acid,  *$\alpha$ -bromo- $\beta$ -amino-propionic acid hydrobromide* is obtained.

*Phthalylglycyl chloride*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{N}\cdot\text{CH}_2\cdot\text{COCl}$ , obtained from phthalylglycine and phosphorus pentachloride, crystallises in needles m. p.  $84\text{--}85^{\circ}$ .

W. R.

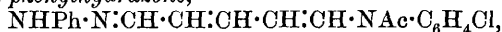
**Phenolphthalein.** HANS MEYER (*Ber.*, 1907, 40, 2430—2433).—A criticism of part of Green and King's investigation (Abstr., 1906, i, 670) and also of Meyer and Marx's recent work (this vol., i, 421). The colourless diethoxy- or dimethoxy-lactoid derivatives of tetrabromophenolphthalein are readily obtained by shaking a solution of this compound in excess of potassium hydroxide with the alkyl sulphate.

The *methoxy-lactoid derivative*,  $\text{C}_{20}\text{H}_8\text{O}_5\text{Br}_4(\text{OMe})_2$ , so prepared, forms brilliant, colourless crystals, m. p.  $205\text{--}206^{\circ}$ .

W. H. G.

**Dinitrophenylpyridinium Chloride and its Transformation Products.** V. **Action of Acetic Anhydride on Pyridine Dye Bases.** THEODOR ZINCKE and FR. SCHREYER (*Annalen*, 1907, 353, 380—385. Compare Abstr., 1904, i, 448, 921; 1905, i, 467, 923).—It is found now that the acetyl compound, formed together with

*p*-chloroacetanilide by the action of acetic anhydride on the base obtained from the di-*p*-chlorodianilide hydrochloride, m. p. 143°, has the constitution  $\text{CHO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{Ac}\cdot\text{C}_6\text{H}_4\text{Cl}$ , and not that ascribed to it previously (Abstr., 1904, i, 923). This aldehyde, m. p. 126°, and not 129° as given (*loc. cit.*), is decomposed readily by alcoholic hydrogen chloride forming *p*-chloroacetanilide, reacts with aniline in alcoholic solution in presence of hydrogen chloride forming the dianilide hydrochloride,  $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHPH}\cdot\text{HCl}$ , or with *p*-chloroaniline forming the di-*p*-chlorodianilide hydrochloride, and yields a *phenylhydrazone*,



crystallising in yellow leaflets, m. p. 175° (decomp.). When hydrolysed with sodium methoxide in acetone or methyl alcoholic solution, it yields the *aldehyde*,  $\text{CHO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , which crystallises in yellow leaflets or reddish-yellow needles, m. p. 109° (decomp.). This reacts with aniline forming the dianilide hydrochloride, and yields a *phenylhydrazone*,  $\text{N}_2\text{HPh}\cdot\text{C}_5\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , crystallising in yellow leaflets, m. p. 119° (decomp.). G. Y.

**Isomeric Forms of 3-Methylcyclohexenone.** PAUL RABE (*Ber.*, 1907, 40, 2482—2489. Compare Abstr., 1904, i, 509).—Methylcyclo- $\Delta^1$ -hexene-3-one, prepared by the methods given by Hagemann (Abstr., 1893, i, 393) and by the author (*loc. cit.*), mixes in all proportions with water, whilst the product of Knoevenagel's method of preparing this compound (Abstr., 1895, i, 51) is partly miscible with, and partly sparingly soluble in, water. The author finds that methylcyclo- $\Delta^1$ -hexene-3-one exists in two isomeric modifications, the one miscible with water being termed the  $\alpha$ - and the other the  $\beta$ -form. The investigations carried out with a view to ascertaining the nature of the isomerism have, up to the present, yielded the following results.

[With RICHARD EHRENSTEIN.]—The  $\alpha$ - and  $\beta$ -forms have the same molecular weight and both yield  $\gamma$ -acetylbutyric acid on oxidation with alkaline permanganate solution. The molecular refraction is the same in the two cases and agrees with the value calculated for an unsaturated alcohol of the formula  $\text{C}_7\text{H}_9\cdot\text{OH}$  containing two double linkings. The two modifications have the same boiling point, sp. gr., and refractive index, and exhibit the same chemical behaviour; the only differences observed lying in (1) the solubility in water and (2) the colour given with ferric chloride solution, the  $\alpha$ -compound yielding a faint red coloration, whilst the  $\beta$ -form gives a more intense reddish-violet solution. The *semicarbazone*,  $\text{C}_8\text{H}_{13}\text{ON}_3$ , prepared from either isomeride, crystallises from dilute alcohol in white needles, m. p. 199°. The action of sodium on ethereal solutions of the two ketones yields the sodium derivatives, both of which give the  $\alpha$ -ketone on treatment with sulphuric acid. Similarly, the sodium hydrogen sulphite compounds formed by the two isomerides both yield the  $\alpha$ -ketone when boiled with potassium carbonate.

The above observations are insufficient to permit of a definite decision concerning the nature of the isomerism between the  $\alpha$ - and  $\beta$ -modifications, but the author suggests that these may consist of allelotropic mixtures of desmotropic forms.

An alcoholic solution of the liquid 1 : 3-dimethylcyclohexene-5-one or of the solid 3-phenyl-1-methylcyclohexene-5-one gives a violet coloration on addition of ferric chloride, whilst with either of the stereoisomeric 1 : 2 : 3-triphenylcyclohexene-5-ones only an extremely faint wine-red colour is produced.

T. H. P.

**Action of Phosphorus Trisulphide on Menthone.** NICOLAS A. SPERANSKY (*J. Russ. Phys. Chem. Soc.* 1906, **38**, 1346—1350).—So far, the only thioketones known are such as have the sulphur atom attached to a carbon atom not in the ring, and even these are very few and difficult to obtain. By treating menthone with phosphorus trisulphide the following substances are obtained:

(1) *Thionmenthone*,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CS} \end{smallmatrix} \text{CH} \cdot \text{CHMe}_2$ , b. p. 217—220°/760 mm.,  $D_{15}^{20}$  0.9398, insoluble in water, but soluble in most organic solvents, decomposes when kept, and with an alcoholic solution of mercury chloride yields small, bright crystals, probably the mercury chloride salt of thiomenthone.

(2) *Thiomenthene*,  $\text{C}_{20}\text{H}_{34}\text{S}$ , the structural formula of which has not yet been elucidated, forms colourless crystals, m. p. 50.5°, b. p. 213°/28 mm. with slight decomposition.

(3) *Menthene*, b. p. 168—170°. Other cyclic ketones also yield sulphur derivatives with phosphorus trisulphide.

Z. K.

**Glycidic Synthesis of Hexahydroaromatic Ketones.** GEORGES DARZENS (*Compt. rend.*, 1907, **144**, 1123—1124. Compare Abstr., 1906, i, 430).—*cyclo*Hexanone and its *o*-, *m*-, and *p*-methyl derivatives condense with ethyl  $\alpha$ -chloropropionate giving good yields of the corresponding trisubstituted glycidic esters according to the general reaction previously described (Abstr., 1906, i, 62). *cyclo*Hexanone

gives the *glycidic ester*,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{O} \\ \text{CMe} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ , a colourless, oily liquid with a faint, fruity, rather disagreeable odour, b. p. 154—156°/40 mm. The ester is easily saponified, yielding an acid, which when distilled in a vacuum is decomposed with the formation of Bouveault's hexahydroacetophenone (Abstr., 1904, i, 62). Similarly, *o*-methylcyclohexanone gives a *glycidic ester*, b. p. 127—129°/15 mm., the acid from which decomposes into carbon dioxide and *o*-methylhexahydroacetophenone,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix} \text{CH} \cdot \text{COMe}$ , a liquid, b. p. 77—80°/18 mm., which forms a *semicarbazone*, m. p. 172—173°, and combines readily with sodium hydrogen sulphite. *m*-Methylcyclohexanone gives a *glycidic ester*, b. p. 143—144°/22 mm., of which the corresponding acid forms *m*-methylhexahydroacetophenone, b. p. 99—100°/38 mm. The latter forms a *semicarbazone*, m. p. 174—175°, but does not combine with sodium hydrogen sulphite. The corresponding *ester* from 1-methylcyclohexane-4-one has b. p. 129—130°/13 mm., and gives a *ketone* having b. p. 75—76°/14 mm. The latter forms a *semicarbazone*, m. p. 158—159°, and combines readily with sodium hydrogen sulphite. Menthone and pulegone do not give glycidic esters when similarly treated.

E. H.

**Action of Organo-magnesium Compounds on the Alkylidene Cyclic Ketones.** HENRI DE BÉVILLE (*Compt. rend.*, 1907, 144, 1221—1222. Compare Haller and Bauer, *Abstr.*, 1906, i, 441; Kohler, this vol., i, 535).—By the action of magnesium ethyl iodide on active benzylidenemethylcyclohexane-3-one there are produced (1) a solid,  $C_{16}H_{22}O$ , in white crystals, m. p.  $135^{\circ}$ , and (2) a colourless liquid having an agreeable odour, b. p.  $160$ — $162^{\circ}/10$  mm; this has not yet been obtained quite pure, but is probably the hydrocarbon  $C_{16}H_{20}$ . Similar products are obtained when magnesium *n*-propyl iodide is substituted for the ethyl compound. In this case, the solid,  $C_{17}H_{24}O$ , forms small, white needles, m. p.  $84^{\circ}$ , whilst the liquid (also slightly impure) has b. p.  $180$ — $184^{\circ}/14$  mm, and is probably the hydrocarbon  $C_{17}H_{22}$ . E. H.

**2:2'-Dinitrobenzoin.** JOAN POPOVICI (*Ber.*, 1907, 40, 2562—2563).—2:2'-Dinitrobenzoin,  $NO_2 \cdot C_6H_4 \cdot CO \cdot CH(OH) \cdot C_6H_4 \cdot NO_2$ , prepared by heating *o*-nitrobenzaldehyde in presence of potassium cyanide, alcohol, and water, crystallises from alcohol in long, pale yellow needles, m. p.  $155.5^{\circ}$ , and dissolves readily in glacial acetic acid or chloroform.

2:2-Dinitrobenzil, prepared by oxidising *o*-dinitrobenzoin by means of chromic acid in acetic acid solution, crystallises from alcohol in colourless rods, m. p.  $151^{\circ}$ , and is probably identical with the compound, m. p.  $147^{\circ}$ , described by Zagumenny (this Journal, 1873, 502).

T. H. P.

**Triketones. IV.** FRANZ SACHS and VICTOR HEROLD (*Ber.*, 1907, 40, 2714—2730).—The method of Ehrlich and Sachs of condensing aromatic nitroso-compounds with "acid" methylene derivatives in presence of an alkaline condensing agent and subsequent hydrolysis with mineral acids whereby the elements of water are taken up in such a way that oxygen replaces the hydrogen atoms of the methylene group, which led to the preparation of triketopentane (*Abstr.*, 1901, i, 670) and of phenyltriketobutane (*Abstr.*, 1902, i, 837), has been extended to other fatty aromatic triketones. Whereas the triketones previously described are reddish-yellow hygroscopic oils, *o*-methoxyphenyl and 2:4-dimethoxyphenyltriketobutane are yellow solids.

**I. *o*-Methoxyphenyltriketobutane.**—Salicylic acid can be directly methylated, with excellent yields, to the dimethyl ester by means of methyl sulphate. This is condensed with acetone under special precautions to *o*-methoxybenzoylacetone, m. p.  $37^{\circ}$ , of which the isonitroso-derivative,  $COMe \cdot C(N \cdot OH) \cdot CO \cdot C_6H_4 \cdot OMe$ , forms colourless plates, m. p.  $163.5^{\circ}$ , whilst the *p*-nitrobenzeneazo-derivative separates in reddish-yellow prisms, m. p.  $150^{\circ}$ .

When condensed with nitrosodimethylaniline, the ketone forms 4-dimethylaminophenyl-*o*-methoxybenzoylacetylazomethine,



crystallising in brilliant, red needles, m. p.  $125^{\circ}$  (sinters at  $120^{\circ}$ ). When hydrolysed with sulphuric acid and extracted with ether, this yields an oil, b. p.  $210$ — $225^{\circ}/25$  mm., which solidifies to yellow crystals of *o*-methoxyphenyltriketobutane,  $OMe \cdot C_6H_4 \cdot CO \cdot CO \cdot COMe$ , separating from ethyl acetate in straw-yellow cubes, m. p.  $78^{\circ}$  (decomp. at  $220^{\circ}$ ). The

triketone reduces copper solutions and gives a characteristic dark red ring if the benzene solution containing thiophen be allowed to run on to concentrated sulphuric acid.

It condenses with *o*-phenylenediamine to form *2-acetyl-3-o-methoxy-phenylquinoxaline*, separating in colourless needles, m. p. 136—137°, and forming a *phenylhydrazone* identical with that obtained by the action of phenylenediamine on methoxyphenyltriketobutane phenylhydrazone. The *monosemicarbazone* of the triketone forms colourless, matted needles, m. p. 188·5°, and the two remaining *o*-carbonyl groups react with phenylenediamine forming a compound,  $C_{18}H_{17}O_2N_5$ , crystallising in colourless plates, m. p. 247—248° (decomp.). The *monophenylhydrazone* of the triketone crystallises from methyl alcohol in reddish-yellow prisms, m. p. 146·5°, and reacts with phenylenediamine as already mentioned to form a compound,  $C_{23}H_{20}ON_4$ , crystallising in yellow needles, m. p. 131°, which dissolves in concentrated sulphuric acid with a blue coloration.

The triketone forms an additive compound with *p*-nitrophenyl-acetonitrile,  $OMe \cdot C_6H_4 \cdot CO \cdot CAc(OH) \cdot CH(CN) \cdot C_6H_4 \cdot NO_2$ , separating in colourless plates, m. p. 148°; this shows a violet coloration with alkali or ammonia and reduces copper sulphate to copper. Ammonia converts the triketone into *methysalicylamide*,  $OMe \cdot C_6H_4 \cdot CO \cdot NH_2$ , crystallising in colourless needles, m. p. 125°.

II. 2:4-*Dimethoxyphenyltriketobutane*.—The *oxime* of resacetophenone dimethyl ether forms colourless columns aggregated in bunches, m. p. 125°. The dimethyl ether condenses with ethyl acetate to form 2:4-*dimethoxybenzoyl acetone*, which separates in colourless, rhombic plates, m. p. 58·5°, and forms an *iso nitroso*-derivative, colourless plates, m. p. 144·5°, and a *p*-nitrobenzeneazo-compound which crystallises in yellowish-brown needles, m. p. 161°. When condensed with nitrosodimethylaniline, the ketone gives rise to 4-*dimethylaminophenyl-acetyl-2:4-dimethoxybenzoylazomethine*, which crystallises in splendid ruby-red prisms, m. p. 183°.

2:4-*Dimethoxyphenyltriketobutane*,  $C_6H_3(OMe)_2 \cdot CO \cdot CO \cdot COMe$ , separates in yellow, well-formed, prismatic plates, m. p. 97°, of deeper tone than the monomethoxy-triketone, but otherwise has similar properties; it forms 2-*acetyl-3-o-p-dimethoxyphenylquinoxaline*, yellow needles, m. p. 116°; a *monosemicarbazone*, colourless needles, m. p. 191°. It forms no hydrate, but the middle carbonyl can be acetalised and the product yields with *o*-phenylenediamine the *diethylacetal* of 2:4-*dimethoxyphenyltriketobutane-o-aminophenylimide*, separating in bright yellow plates, m. p. 181°.

III. 2:3:4-*Triketohexane*.—[With PAUL ALSLEBEN.]—Diketohexane was condensed with nitrosodimethylaniline and the azomethine formed immediately hydrolysed to 2:3:4-*triketohexane*, a mobile, ruby-red oil, b. p. 70°/18 mm., which acts as a powerful reducing agent and, like triketopentane, forms a *hydrate*. It dyes wool and silk yellow, but has no action on cotton. With *o*-phenylenediamine, either 2-*propionyl-3-methylquinoxaline* or 2-*acetyl-3-ethylquinoxaline* is formed, the product crystallising in bright yellow, rhombic plates, m. p. 56°.

The *bisphenylmethylhydrazone* of triketopentane separates from

alcohol in well-formed, yellow rhombs, m. p.  $126^{\circ}$  (decomp.), whereas the *bisbromophenylhydrazone* forms glistening, brownish-yellow, rhombohedral prisms, m. p.  $145^{\circ}$  (decomp.). E. F. A.

**Phenanthrene Series. XX. Constitution and Colour of Phenanthraquinone Derivatives.** JULIUS SCHMIDT and JULIUS SÖLL (*Ber.*, 1907, 40, 2454—2460).—Notwithstanding the fact that they possess a quinonoid structure, the dibenzoyl and dimethyl derivatives of phenanthraquinonedioxime, likewise the anhydride of the dioxime, have been obtained in a colourless form.

The use of barium carbonate for the liberation of free hydroxylamine from its hydrochloride is recommended in the preparation of phenanthraquinonedioxime and of oximes generally, a quantitative yield being readily obtained. *Phenanthraquinonedioxime dimethyl ether*,  $C_{14}H_8(NOMe)_2$ , prepared by the interaction of the dioxime with methyl sulphate in the presence of a large excess of sodium hydroxide, crystallises in colourless plates, m. p.  $145$ — $146^{\circ}$ . At the same time is obtained what appears to be the *monomethyl ether*,  $OH \cdot N : C_{14}H_8 \cdot N \cdot OMe$ , pale yellow needles, m. p.  $222$ — $223^{\circ}$ . The *dibenzoyl* derivative,  $C_{14}H_8(NO_2)_2$ , prepared by the Schotten-Baumann method, crystallises in white, silvery leaflets, m. p.  $209$ — $210^{\circ}$ . The anhydride of the dioxime,  $C_{14}H_8ON_2$ , described by Goldschmidt (*Abstr.*, 1884, 62) as a yellow substance, crystallises when pure in white needles, m. p.  $186$ — $187^{\circ}$ . W. H. G.

**Two New Terpenes.** OSSIAN ASCHAN (*Ber.*, 1907, 40, 2750—2755).—The mixture of liquid hydrochlorides, obtained on saturating crude American pinene with hydrogen chloride, when decomposed with bases yields a fraction, b. p.  $145$ — $148^{\circ}$ , of constant rotatory power. This  $C_{10}H_{16}$  terpene is termed *pinolene*, and has  $D_4^{20}$  0.8599  $[\alpha]_D + 1.63$ ,  $n_D$  1.45768. The hydrochloride,  $C_{10}H_{17}Cl$ , is a paraffin-like substance, m. p.  $38^{\circ}$ ,  $[\alpha]_D + 9.78^{\circ}$ . Pinolene takes up a molecule of bromine; it is not attacked by 20% oxalic acid or 10% sulphuric acid, but is oxidised by permanganate, forming as chief product a sparingly soluble, syrupy acid. On heating with a mixture of acetic and 50% sulphuric acids, an *alcohol*,  $C_{10}H_{17} \cdot OH$ , b. p.  $202$ — $203^{\circ}$ , is formed, which smells like menthol and fusel oil, and yields a liquid *ketone*,  $C_{10}H_{16}O$ , b. p.  $200^{\circ}$ , on oxidation, the *semicarbazone* of which crystallises in large, oblique, glass-glistening plates, m. p.  $224$ — $225^{\circ}$ .

Pinolene hydrochloride, when heated with aniline and distilled, yields an isomeric hydrocarbon, *isopinene*, b. p.  $154$ — $156^{\circ}$ ,  $D_4^{20}$  0.8648,  $[\alpha]_D^{20} + 6.0$ , mol. ref. 43.77, which is thus a dicyclic terpene with a double linking. It decomposes 1 mol. of bromine and forms a glistening, crystalline *hydrochloride*,  $C_{10}H_{17}Cl$ , m. p.  $36$ — $37^{\circ}$ ,  $[\alpha]_D^{22} + 9.18$ , which is probably identical with that obtained from pinolene. When heated with acetic and sulphuric acids, *isopinene* gives rise to an *alcohol*, b. p.  $200$ — $203^{\circ}$ , and a *ketone*, b. p.  $200^{\circ}$  (*semicarbazone*, m. p.  $221^{\circ}$ ), possibly identical with those obtained from pinolene. E. F. A.

**Essential Oil of the Pacific Arbor Vitæ.** WALTER C. BLASDALE (*J. Amer. Chem. Soc.*, 1907, 29, 539—541).—From 13.8 kilos. of leaves of the Pacific arbor vitæ (*Thuja plicata*), 400 c.c. of a dark



brown, volatile oil were obtained, which has a penetrating, terpene-like odour, b. p. 150—225°,  $D^{15}_D$  0.8997,  $n_D$  1.4575, and  $\alpha_D$  1°45' (100 mm.). distillation, the largest fraction collected at 198—200° and consisted of thujone (apparently a mixture of the two optically active modifications). The constituents of the other fractions were not identified.

The wood of the plant has a peculiar odour, which is due to the presence of a volatile substance,  $C_{10}H_{12}O_2$ , m. p. 80°, which forms white crystals. E. G.

**Barbaloin : its Existence in most Aloes. Composition and Formula.** EUGÈNE LÉGER (*J. Pharm. Chim.*, 1907, 25, [vi], 513—517. Compare this vol., i, 545).—Although it has now been established that barbaloin occurs in Barbados, Curaçoa, Cape, Socotra, Uganda, and Jafferabad aloes (*Bull. Soc. chim.*, 1902, [iii], 27, 1902; this vol., i, 545; compare Tschirch and Klaveness, *Abstr.*, 1901, i, 602), there is still a tendency to use specific names for the aloins, isolated from various aloes, and there is reason to believe that Aschan's "feroxaloin" (*Abstr.*, 1903, i, 772) is merely barbaloin, although the identity of zanaloin and barbaloin is still doubtful (compare Tschirch and Hoffbauer, *Abstr.*, 1905, i, 913). The various formulæ proposed for barbaloin,  $C_{17}H_{18}O_7$  (Stenhouse),  $C_{15}H_{16}O_7$  (Liebelt),  $C_{16}H_{18}O_7$  (Tilden),  $C_{17}H_{20}O_7$  (Treumann),  $C_{16}H_{16}O_7$  (Grønwald), are incompatible with the production from this substance, by the action of sodium peroxide or by the prolonged action of alcohol, of isohydroxymethylchrysasin and aloinose (methyl aldopentose), and, further, it is difficult to account for the optical activity of barbaloin by means of such formulæ. The ebullioscopic measurements made by Tschirch and Klaveness (*loc. cit.*) do not afford satisfactory evidence in favour of Grønwald's formula, as the changes in temperature obtained were small and variable, and this also applies to Aschan's observations (*Abstr.*, 1903, i, 772). The formula proposed by the author,  $C_{21}H_{20}O_9$  (*Abstr.*, 1902, i, 685; 1903, i, 356; 1904, i, 907), is, on the contrary, in accordance with the analytical data, cryoscopic measurements of the mol. weight of the chloroacetyl derivative, and the hydrolytic products of barbaloin. T. A. H.

**A New Crystalline Substance from Fresh Kola.** GORIS (*Compt. rend.*, 1907, 144, 1162—1164).—Kola nuts, sterilised by heating at 105° in an autoclave for ten minutes, are powdered and extracted with hot 80% alcohol, or better, lixiviated with cold alcohol. The alcoholic extract, when evaporated in a vacuum, gives a syrup which, after repeated washing with chloroform, gradually crystallises. The white crystals so obtained seem to be a loose combination of caffeine and a substance, *kolatin*, probably belonging to the group of tannins. The caffeine is removed by dissolving the crystals in water and extracting with chloroform. Kolatin is a phenolic compound,  $C_8H_{10}O_4$ , crystallising in prismatic needles, which under certain conditions oxidise to a red, insoluble powder and, similarly to sodium benzoate and salicylate, dissolve caffeine. Dried Kola nuts and their pharmaceutical extract do not contain kolatin, which disappears during drying. The sterilised nuts yield 15 grams of the kolatin-caffeine substance, or about half as much kolatin per kilogram. E. H.

### Synthesis of Unsymmetrical Substituted Thianthrenes.

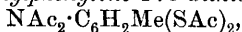
JAROSLAV FRÖHLICH (*Ber.*, 1907, **40**, 2489—2492. Compare Hillyer, *Abstr.*, 1902, **i**, 50; Mauthner, *Abstr.*, 1905, **i**, 461).—By the action of picryl chloride on 2-amino-1-methylphenylene-4:5-dithiol (Fröhlich and Fichter, *Verh. Naturf. Ges. Basel*, **19**, 44), an unsymmetrical dinitro-methylaminothianthrene (compare Krafft and Kaschau, *Abstr.*, 1896, **i**, 297) is obtained.

1:3-Dinitro-7-amino-6-methylthianthrene (? 1:3-dinitro-6-amino-7-methylthianthrene),  $C_{13}H_9O_4N_3S_2$ , crystallises from alcohol in red, coppery leaflets, m. p.  $203^\circ$ , and forms a diazo-derivative which yields a poppy-red dye with  $\beta$ -naphthol.

1:3:7-Triamino-6-methylthianthrene (? 1:3:6-triamino-7-methylthianthrene),  $C_{13}H_{13}N_3S_2$ , obtained by reducing the preceding compound, yields a hydrochloride,  $C_{13}H_{13}N_3S_2 \cdot 3HCl$ , crystallising in white needles.

1:3-Dinitro-7-diacetyl-amino-6-methylthianthrene (? 1:3-dinitro-6-diacetyl-amino-7-methylthianthrene),  $C_{17}H_{15}O_6N_3S_2$ , prepared by acetylating the dinitroamino-compound, separates from a mixture of benzene and light petroleum in microscopic, yellow crystals, m. p.  $168^\circ$ .

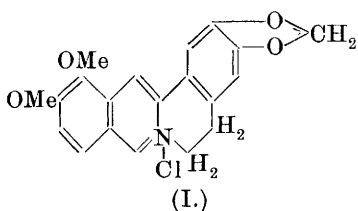
2-Diacetyl-amino-1-methylphenylene-4:5-dithiolacetate,



prepared by acetylating 2-amino-1-methylphenylene-4:5-dithiol, crystallises from alcohol in pale brown plates, m. p.  $112^\circ$ .

T. H. P.

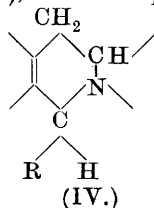
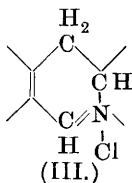
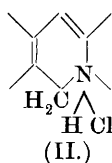
**Homologues of Berberine and Canadine.** MARTIN FREUND and FRITZ MAYER (*Ber.*, 1907, **40**, 2604—2614).—If Gadamer's modification (compare *Abstr.*, 1902, **i**, 555) of Perkin's formula for berberine (compare *Trans.*, 1894, **55**, 63; 1895, **57**, 991) be accepted,



the conversion of the hydrochloride (I) into *r*-canadine by the addition of four atoms of hydrogen should take place in two steps. The addition of the first pair of hydrogen atoms may occur as in (II), followed by elimination of hydrogen chloride, or as in (III).

The former compound has been obtained by Gadamer (*Chem. Zeit.*, **26**,

385) and its homologues by Freund and Beck (*Abstr.*, 1905, **i**, 151). These homologues of dihydroberberine contain one asymmetric carbon atom; by the addition of a second pair of hydrogen atoms, another carbon atom becomes asymmetric as in (IV), and consequently two



stereoisomeric racemic tetrahydro-bases ought to exist, a deduction which has been realised in the case of propyltetrahydroberberine, although neither of the racemic bases has as yet been resolved into its active constituents.

By the removal of two atoms of hydrogen from the alkyldihydroberberines, the corresponding homologues of berberine have been obtained in the form of salts, but the free bases have not been prepared in a pure state.

*α-Methyltetrahydroberberine hydrochloride*,  $C_{21}H_{23}O_4N \cdot HCl$ , m. p.  $264^\circ$ , crystallises in white needles, and is obtained by the addition of dilute hydrochloric acid to an alcoholic solution of *α*-methyltetrahydroberberine (Abstr., 1905, i, 657).

*α-Methylberberine hydriodide*,  $C_{21}H_{19}O_4N \cdot HI$ , forms golden-yellow needles, decomposes at  $255-260^\circ$ , and is most conveniently prepared by treating *α*-methyl-dihydroberberine hydriodide with bromine in hot glacial acetic acid and digesting the dark brown mass which separates with sulphurous acid. The *nitrate*,  $C_{21}H_{19}O_4N \cdot HNO_3$ , forms yellow needles and decomposes at  $240-260^\circ$ .

*α-Ethyl-dihydroberberine*,  $C_{22}H_{23}O_4N$ , m. p.  $164-165^\circ$ , is obtained in the form of the *hydriodide*, m. p.  $223^\circ$ , in a similar manner to the methyl compound (compare Freund and Beck, *loc. cit.*).

*α-Ethyltetrahydroberberine*,  $C_{22}H_{25}O_4N$ , m. p.  $151-152^\circ$ , is obtained in a similar manner to the methyl compound by the electrolytic reduction of *α*-ethyl-dihydroberberine (Abstr., 1905, i, 657); the *hydrochloride*,  $C_{22}H_{25}O_4N \cdot HCl$ , crystallises in white leaflets, softens at  $220^\circ$ , and has m. p.  $245^\circ$  (decomp.).

*α-Ethylberberine hydriodide*,  $C_{22}H_{21}O_4N \cdot HI$ , obtained in a similar manner to the methyl homologue, separates from dilute alcohol in slender, yellow needles, darkens at  $230^\circ$ , and decomposes at  $248^\circ$ ; the *nitrate* decomposes at  $240^\circ$ .

*α-Propyl-dihydroberberine*,  $C_{23}H_{25}O_4N$ , m. p.  $132^\circ$ , forms yellow leaflets; its *hydriodide* has m. p.  $207^\circ$ . The electrolytic reduction of the base leads to the formation of a basic mixture which, after conversion into the nitrates, is treated with a quantity of hot alcohol insufficient for complete solution. The filtrate contains *α-propyltetrahydroberberine nitrate*, m. p.  $203-212^\circ$  (decomp.), which forms white needles and is soluble in hot dilute alcohol; the free *base*,  $C_{23}H_{27}O_4N$ , m. p.  $111-114^\circ$ , crystallises in flat prisms, and exhibits a faint greenish-yellow fluorescence; the *hydrochloride* has m. p.  $230-240^\circ$  (decomp.). From the residual nitrate which has not dissolved in the alcohol, *ψ-α-propyltetrahydroberberine*, m. p.  $177-179^\circ$ , is obtained; it crystallises in flat plates, and forms a *nitrate*, m. p.  $200^\circ$  (decomp.), and a *hydrochloride*, m. p.  $245^\circ$  (decomp.), which are sparingly soluble in hot aqueous alcohol.

*α-Propylberberine hydriodide*,  $C_{23}H_{23}O_4N \cdot HI$ , m. p.  $246^\circ$  (decomp.), forms golden-yellow needles, and is prepared in a similar manner to the methyl homologue.

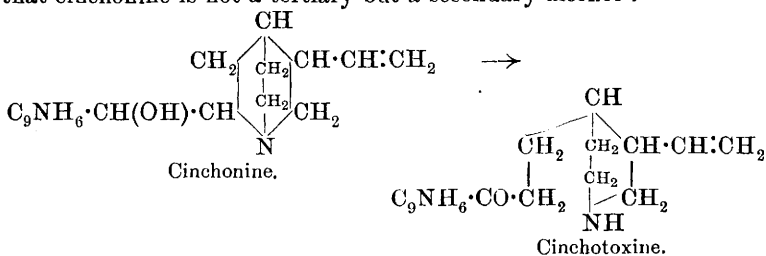
The physiological action of *α*-methyltetrahydroberberine hydrochloride is very slight; ethyl-dihydroberberine hydrochloride has a pronounced local effect.

C. S.

**Carnosine.** FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1907, 51, 545—548).—Polemical against Gulewitsch (compare this vol., i, 436). W. D. H.

**Quinine Alkaloids.** GEORG ROHDE and A. ANTONAZ (*Ber.*, 1907, 40, 2329—2338).—In the preparation of *isonitrosomethylquinotoxine* (Abstr., 1905, i, 228) by the action of sodium ethoxide and amyl nitrite on methylquinotoxine, a 10% yield of a by-product is obtained in the form of yellow, glistening needles. These consist of a sodium derivative which is not decomposed by carbon dioxide, and from which dilute mineral acids precipitate quinic acid. The formation of this acid is quantitative when a solution of methylquinotoxine in absolute alcohol is mixed with the requisite amount of sodium ethoxide and nitrobenzene (2 mols.) and kept overnight. Quinotoxine behaves in a similar manner, and cinchotoxine yields cinchoninic acid. The other decomposition product may be meroquinine, but so far all attempts to identify and isolate it have proved fruitless. Small amounts of aniline and of azoxybenzene have been isolated from the mixtures. Nitrosoquinotoxine and the sulphonamide of cinchotoxine are not decomposed by sodium ethoxide and nitrobenzene. The *sulphonamide*,  $C_{25}H_{26}O_3N_2S$ , is crystalline, has m. p. 108—109°, and is only sparingly soluble in cold alcohol or ether.

The fact that *isonitrosomethylquinotoxine* is not decomposed by the same method indicates that the carbinol group of the toxine bases (compare Rabe and Ritter, this vol., i, 78; Koenigs, this vol., i, 345) is adjacent to a carbon atom of the quinoline ring. It is suggested that cinchonine is not a tertiary but a secondary alcohol :



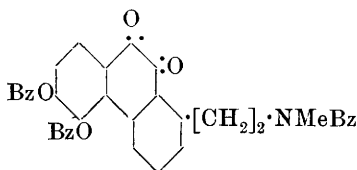
J. J. S.

**Solubility of Morphine in Ethyl Ether.** M. MARCHIONESCHI (*Boll. Chim. Farm.*, 1907, 46, 389—391).—The amount of morphine remaining in solution after heating the alkaloid with boiling ether during two hours and allowing the solution to cool at 5·5° during forty-eight hours was determined. The solubility under such conditions is greatest for anhydrous morphine in dry ether distilled from sodium, being 0·56 gram per litre. In the case of crystalline morphine ( $C_{17}H_{19}O_3N \cdot H_2O$ ) and dry ether distilled from sodium, the solubility is 0·23 gram per litre, whilst for the same substance in ordinary ether previously washed with aqueous sodium hydroxide and distilled it is about 0·05 gram per litre. W. A. D.

**Constitution of apoMorphine. Constitution of Morphine.** ROBERT PSCHORR (*Ber.*, 1907, 40, 1984—1995. Compare Abstr., 1903, i, 193).—*apoMorphine* contains two phenolic hydroxyl groups and as morphine contains only one of these groups, the formation of *apo*-morphine from morphine by concentrated hydrochloric acid must involve the conversion of the "ether-like" oxygen of the morphine into the second phenolic hydroxyl grouping. To further prove the constitution of *apomorphine*, tribenzoyl*apomorphine* (*loc. cit.*) was oxidised to a phenanthraquinone derivative containing all the original substituents (compare following abstract). This result excludes therefore the possibility of substitution having occurred in the medial ring of the phenanthrene nucleus. The 3:4-dimethoxyphenanthrene-carboxylic acid was converted into 3:4:8-trimethoxyphenanthrene by Curtius' method and this establishes the position of the carboxyl group; consequently the carbon chain of the side-ring must be united to position-8 of the phenanthrene nucleus. These considerations support the constitution formerly ascribed to *apomorphine* (*loc. cit.*).

W. R.

**Oxidation of Tribenzoyl*apomorphine*.** ROBERT PSCHORR and O. SPANGENBERG (*Ber.*, 1907, 40, 1995—1998).—*Tribenzoyl**apomorphine*



*phinequinone* (annexed formula), obtained by the action of chromic acid on an acetic acid solution of tribenzoyl-*apomorphine*, crystallises in yellowish-red rods from ethyl acetate; m. p. 178—179° (corr.). It gives the same colour reactions as diacetylmorphol. The *phenylhydrazone*,

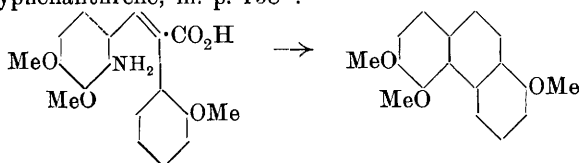
$C_{44}H_{33}O_6N_3$ , crystallises in glistening, red leaflets, m. p. 235—236° (corr.). The *azine* from *o*-phenylenediamine,  $C_{44}H_{31}O_5N_3$ , forms light yellow needles, m. p. 221—222° (corr.). On hydrolysis with sodium ethoxide, *N*-benzoyl*apomorphinequinone*,  $C_{24}H_{19}O_5N$ , is formed in red flakes, m. p. 218° (corr.); its *phenylhydrazone* has m. p. 228° (corr.).

W. R.

**Transformation of apoMorphine into 3:4:8-Trimethoxyphenanthrene.** ROBERT PSCHORR, HANS EINBECK, and O. SPANGENBERG (*Ber.*, 1907, 40, 1998—2001. Compare Abstr., 1906, i, 878; 1903, i, 193).—*Ethyl* 3:4-dimethoxyphenanthrene-9-carboxylate,  $C_{19}H_{18}O_4$ , forms yellow crystals, m. p. 81—83°, and on treatment with hydrazine hydrate at 100° for twenty hours yields the *hydrazide*,  $C_{17}H_{16}O_3N_2$ , crystallising in needles, m. p. 194—195°. This was converted into the *urethane*,  $C_{19}H_{19}O_4N$ , by means of amyl nitrite and hydrogen chloride in alcohol; it crystallises in glistening needles, m. p. 165°. On hydrolysis with alcoholic ammonia at 180° and subsequent acidification, 8-amino-3:4-dimethoxyphenanthrene hydrochloride is obtained in long needles, m. p. 290°. This, by diazotisation, is converted into 3:4-dimethoxy-8-phenanthrol, crystallising in prisms, m. p. 182—183°; by methylation, 3:4:8-trimethoxyphenanthrene,  $C_{17}H_{16}O_3$ , is obtained. The *picrate* has m. p. 129°.

W. R.

**Synthesis of 3:4:8-Trimethoxyphenanthrene.** ROBERT PSCHORR and HANS BUSCH (*Ber.*, 1907, 40, 2001—2003).—This communication describes the preparation of trimethoxyphenanthrene, identical in all respects with that obtained from *apomorphine*. Sodium *o*-methoxyphenylacetate on being heated at 120° with 1.5 mol. of *vic.*-*o*-nitrovanillin methyl ether, and acetic anhydride for forty-eight hours, yields *α*-*o*-methoxyphenyl-2-nitro-3:4-dimethoxycinnamic acid,  $C_{18}H_{17}O_7N$ , crystallising in prisms, m. p. 219—221° (corr.). This, on reduction with ammonia in the presence of ferrous sulphate, gives the corresponding amino-acid,  $C_{18}H_{19}O_5N$ , which forms yellow rhombohedra, m. p. 189—190° (corr.). The conversion into 3:4:8-trimethoxyphenanthrene-9-carboxylic acid, m. p. 250° (corr.), was accomplished by treatment of the diazo-compound from the amino-acid with copper powder, and this acid when heated with glacial acetic acid at 220—230° loses carbon dioxide and gives 3:4:8-trimethoxyphenanthrene, m. p. 138°:



W. R.

**Constitution of Morphothebaine.** ROBERT PSCHORR and W. L. HALLE (*Ber.*, 1907, 40, 2004—2006).—The similarity in properties as well as in its mode of preparation renders it probable that *apomorphine* and *morphothebaine* are allied in constitution. Tribenzoylmorphothebaine, m. p. 184° (corr.), when oxidised with chromic acid in acetic acid, yields a thick brown oil containing *tribenzoylmorphothebainequinone*, but from which the quinone could not be obtained in a crystalline form. It, however, forms with phenylhydrazine the *tribenzoylmorphothebainequinone phenylhydrazone*,

$C_{45}H_{35}O_7N_3$ , m. p. 227° (corr.), crystallising in red needles; with *o*-phenylenediamine it gives the *azine*,  $C_{45}H_{33}O_6N_3$ , of m. p. 201° (corr.), and crystallising in yellow prisms. *N*-Benzoylmorphothebainequinone,  $C_{25}H_{21}O_6N$ , is obtained from the uncrystallisable oil by hydrolysis with sodium ethoxide and forms light brown prisms, m. p. 267° (corr.). The *phenylhydrazone*,  $C_{31}H_{27}O_5N_3$ , forms reddish-brown needles, m. p. 271° (corr.), and the *azine*,  $C_{31}H_{25}O_4N_3$ , light brown prisms, m. p. 274—275°. Morphothebaine has therefore the annexed constitution.

W. R.

**Catalytic Actions of Finely-divided Metals on Nitrogen Compounds.** MAURICE PADOA (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 818—822).—In continuation of work previously published (*Abstr.*, 1906, i, 530, 765), the author has investigated the action of reduced nickel, in presence of hydrogen, on pyridine and piperidine.

When pyridine vapour and hydrogen are passed over reduced nickel

heated at 180—250°, the products obtained are traces of secondary bases (? piperidine) and a non-basic compound, which has the properties of the pyrroles, but could not be identified owing to the smallness of the yield.

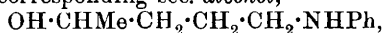
Since piperidine contains sufficient hydrogen to bring about the desired transformation, this compound was submitted to the action of reduced nickel alone, the temperatures employed varying between 180° and 250°. The products obtained consist of: (1) pyridine; (2) pyrrole compounds in larger proportion than in the case of pyridine, but still insufficient for identification; (3) a secondary base,  $C_{10}H_{21}N$  or  $C_5NH_{10} \cdot C_5H_{11}$ , b. p. 170—190°, which is obtained as a colourless oil having an odour like that of piperidine, gives Liebermann's reaction for nitroso-compounds, and yields a yellow, crystalline *picrate*,

$C_{10}H_{21}N, C_6H_3O_7N_3$ ,  
m. p. 125°; (4) a dense, oily base,  $C_{14}H_{28}N_2$  or  $C_5NH_{10} \cdot [CH_2]_4 \cdot C_5NH_{10}$ ,  
b. p. 175—180°/28 mm., which yields a *picrate*,  $C_{14}H_{28}N_2, 2C_6H_3O_7N_3$ ,  
m. p. 192—193°, an *aurichloride*, m. p. 176—177°, and a *platini-*  
*chloride*, m. p. 230° (decomp.); the base gives Liebermann's reaction,  
and has the normal molecular weight in freezing benzene. The  
constitution and characters of this base are similar to those of  
 $\alpha$ - $\delta$ -dipiperidylbutane (Töhl, Abstr., 1895, i, 681). T. H. P.

**Action of Aniline and *p*-Toluidine on Methyl  $\gamma$ -Bromopropyl Ketone. Synthesis of *N*-Phenylated Pyrrole and Pyrrolidine Derivatives.** JOSEPH MARKWALDER (*J. pr. Chem.*, 1907, [ii], 75, 329—368).—It was shown by Lipp (Abstr., 1887, 277) that methyl  $\gamma$ -bromopropyl ketone reacts with ammonia forming a pyrrole derivative, whilst Hielscher (Abstr., 1898, i, 338) found that derivatives of dihydropyrrole are formed by the action of ammonia and of methylamine on the bromo-ketone. The present work was undertaken to determine if this bromo-ketone reacts in the same manner with primary aromatic amines, since tetrahydropyridines are formed by the action of ammonia, or of primary aliphatic or aromatic amines on methyl  $\delta$ -bromobutyl ketone (Lipp, Abstr., 1892, 1243; 1896, i, 317); to compare the behaviour of the resulting *N*-phenylated dihydropyrroles with that of the corresponding *N*-phenylated tetrahydropyridines, and, in view of the interest attached to the 2-substituted pyrrolidines in their relation to hygrine and the alkaloids of the tropine group (Willstätter, Abstr., 1900, i, 405), to study the products obtained on reduction of the dihydropyrroles in question.

*Methyl  $\gamma$ -anilinopropyl ketone*,  $NHPh \cdot CH_2 \cdot CH_2 \cdot COMe$ , the primary product of the action of aniline on methyl  $\gamma$ -bromopropyl ketone, undergoes immediate condensation in the presence of the hydrogen bromide simultaneously formed, hence the product obtained is 1-phenyl-2-methyl-4:5-dihydropyrrole hydrobromide,  $\begin{matrix} CH:COMe \\ | \\ CH_2 \cdot CH_2 \end{matrix} > NPh, HBr$ ; on

liberation of the base, the pyrrole ring is resolved, the  *$\gamma$ -anilino-ketone* being formed (compare Freund, Abstr., 1893, i, 116). Whilst reduction of the anilino-ketone with sodium in alcoholic solution leads to the formation of the corresponding *sec.-alcohol*,



the reduction by means of tin and hydrochloric acid leads to that of 1-phenyl-2-methylpyrrolidine,  $\begin{matrix} \text{CH}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{matrix} > \text{NPh}$ , which is stable on liberation from its salts.

Similar compounds are obtained by the action of *p*-toluidine on methyl  $\gamma$ -bromopropyl ketone.

As Fischer has shown that pyrrolidine-2-carboxylic acid is formed by the hydrolysis of egg-albumin (Abstr., 1901, i, 745), some interest was attached to the oxidation of 1-phenyl-2-methylpyrrolidine to 1-phenylpyrrolidine-2-carboxylic acid; an attempt to accomplish this by means of potassium permanganate and sulphuric acid was unsuccessful.

1-Phenyl-2-methyl-4:5-dihydropyrrole hydrobromide is formed with development of heat by the action of aniline on methyl  $\gamma$ -bromopropyl ketone; the *hydrochloride*, formed by the action of hydrochloric acid on methyl  $\gamma$ -anilinopropyl ketone, and the *sulphate* are obtained as light brown, viscid oils; the *picrate*,  $\text{C}_{17}\text{H}_{16}\text{O}_7\text{N}_4$ , crystallises in yellow needles, m. p.  $132^\circ$ ; the orange, crystalline *platinichloride* is unstable.

*Methyl  $\gamma$ -anilinopropyl ketone* crystallises in microscopic leaflets, m. p.  $23-25^\circ$ , and when heated yields an oily *anhydride*,  $\text{C}_{22}\text{H}_{28}\text{ON}_2$ . The *oxime* of the anilino-ketone,  $\text{C}_{11}\text{H}_{16}\text{ON}_2$ , crystallises in leaflets, m. p.  $86-88^\circ$ ; the *phenylhydrazone* gives a dark red, almost violet, coloration with ferric chloride in concentrated sulphuric acid solution; the *semicarbazone*,  $\text{C}_{12}\text{H}_{18}\text{ON}_4$ , forms colourless leaflets, m. p.,  $142^\circ$ ; the *benzoyl* derivative was obtained as a viscid, light brown oil.

1-Phenyl-2-methylpyrrolidine (Schultz and Friemehlt, Abstr., 1899, i, 541), b. p.,  $127.5^\circ/13$  mm.; the *stannochloride*, m. p.,  $107-109$ ; the *platinichloride*, m. p.  $114^\circ$  (decomp.); the *picrate*, m. p.  $110^\circ$ .

*Methyl- $\gamma$ -anilinopropylcarbinol* is obtained as a viscid, brown oil, forms syrupy salts, and readily loses water; the *benzoyl* derivative is a light brown oil.

*Methyl  $\gamma$ -p-toluidinopropyl ketone*,  $\text{C}_{12}\text{H}_{17}\text{ON}$ , formed by the action of *p*-toluidine on methyl  $\gamma$ -bromopropyl ketone and treatment of the product with potassium hydroxide, crystallises in needles, m. p.  $73^\circ$  (decomp.); the *oxime hydrochloride* forms needles, m. p.  $154^\circ$ ; the *oxime* crystallises in needles or rhombic plates, m. p.  $131-132^\circ$ , and reduces ammoniacal silver and Fehling's solutions when heated.

1-*p*-Tolyl-2-methyl-4:5-dihydropyrrole hydrochloride and hydrobromide are deliquescent; the *picrate*,  $\text{C}_5\text{H}_8\text{N} \cdot \text{C}_7\text{H}_7 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in scales, m. p.  $132^\circ$ .

*Methyl- $\gamma$ -p-toluidinopropylcarbinol*,  $\text{C}_{12}\text{H}_{19}\text{ON}$ , formed by reduction of the ketone with sodium in alcoholic solution, crystallises in slightly brown leaflets, m. p.  $64^\circ$ ; the salts and *benzoyl* derivative cannot be crystallised. G. Y.

**10-Phenylacridinium Compounds.** FRITZ ULLMANN and RUDOLF MAAG (*Ber.*, 1907, 40, 2515-2524).—Reduction of 10-phenylacridone by means of sodium and ethyl or amyl alcohol gives a good yield of 10-phenyldihydroacridine, which, on oxidation with iodine, is converted into 10-phenylacridinium periodide. 10-Phenylacridone may also be transformed into compounds of the acridinium series



by the action of Grignard's reagent; thus, when magnesium phenyl bromide is used, 9:10-diphenylacridol is obtained, the reaction being analogous to that observed by Bünzly and Decker (Abstr., 1904, i, 344) in the case of methylacridone. Of the salts of the new acridinium compounds, the chlorides especially are readily soluble in water giving yellow solutions. When ammonia-solution is added to a solution of the diphenylacridinium chloride, the liquid becomes turbid after some time; the reaction which takes place is analogous to that occurring with the alkyl halogen derivatives of the acridine series investigated by Hantzsch and Kalb (Abstr., 1900, i, 113) and by Decker (Abstr., 1902, i, 691), the first product being an ammonium base, which becomes rapidly transformed into the insoluble acridol. 9:10-Diphenylacridol is very stable and yields the corresponding ether on boiling with alcohol. The analogous 10-phenylacridol could not be obtained pure, as it readily undergoes oxidation to 10-phenylacridone.

10-Phenyldihydroacridine,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{NPh} \end{smallmatrix} C_6H_4$ , prepared by the action of sodium on an amyl alcoholic solution of 10-phenylacridone, crystallises from glacial acetic acid in colourless needles or prisms, m. p.  $119^\circ$ .

10-Phenylacridinium periodide,  $C_6H_4 \begin{smallmatrix} \text{CH} \\ \text{NPhI}_3 \end{smallmatrix} C_6H_4$ , crystallises from alcohol in feather-like aggregates of thick, brownish-red needles.

10-Phenylacridinium iodide,  $C_6H_4 \begin{smallmatrix} \text{CH} \\ \text{NPhI} \end{smallmatrix} C_6H_4$ , prepared by the action of dilute sulphuric acid on the periodide, separates in long, cinnabar-red needles, m. p.  $233^\circ$  (decomp.).

On treating 10-phenylacridinium iodide with benzene and dilute sodium hydroxide solution and passing hydrogen chloride into the dried benzene solution of the 10-phenylacridol thus obtained, 10-phenylacridinium chloride separates in oily drops changing to star-shaped aggregates of needles; the yellow alcoholic solution of 10-phenylacridinium chloride, which exhibits an intense green fluorescence, is decolorised by ammonia and then shows a blue fluorescence. 10-Phenylacridinium chloride may also be obtained by passing chlorine into a benzene solution of 10-phenyldihydroacridine.

10-Phenylacridinium chloride forms double salts with ferric chloride,  $C_{19}H_{14}NCl, FeCl_3$ , and platinum chloride,  $(C_{19}H_{14}NCl)_2, PtCl_4$ .

5:10-Diphenylacridol,  $C_6H_4 \begin{smallmatrix} \text{CPh(OH)} \\ \text{NPh} \end{smallmatrix} C_6H_4$ , crystallises from light petroleum in colourless, glassy prisms, m. p.  $178^\circ$ . The addition of potassium iodide to its solution in dilute acetic acid gives the iodide,  $C_{25}H_{18}NI$ , which crystallises in purple needles. 5:10-Diphenylacridol forms a platinichloride,  $(C_{25}H_{18}NCl)_2PtCl_4$ , which separates in yellow needles.

The methyl ether of 5:10-diphenylacridol,  $C_6H_4 \begin{smallmatrix} \text{CPh(OMe)} \\ \text{NPh} \end{smallmatrix} C_6H_4$ , separates from methyl alcohol in shining, colourless crystals, m. p.  $184^\circ$ .

The conversion of acridone into dihydroacridine is also easily accomplished by reduction with sodium in either ethyl or amyl alcohol.

**4-Aminoacridine**,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ | \\ \text{N} \end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{NH}_2$ , prepared by reducing 1-aminoacridone with sodium in amyl alcohol, separates in yellowish-brown needles.

**Dihydroquinacridine**,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{N} \end{smallmatrix}\rangle\text{C}_6\text{H}_2\langle\begin{smallmatrix}\text{N} \\ | \\ \text{CH} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ , prepared by reducing an alcoholic solution of quinaacridone (compare Ullmann and Maag, Abstr., 1906, i, 459) by means of sodium or, in small quantity, by distilling quinaacridone with zinc dust, crystallises from alcohol in red needles, m. p.  $243^\circ$ ; its *hydrochloride*,  $\text{C}_{20}\text{H}_{14}\text{N}_2\cdot\text{HCl}$ , separates in steel-blue crystals.

**Quinaacridine**,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ | \\ \text{N} \end{smallmatrix}\rangle\text{C}_6\text{H}_2\langle\begin{smallmatrix}\text{N} \\ | \\ \text{CH} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ , prepared by the action of glacial acetic acid and a little nitric acid on dihydroquinacridine, crystallises from alcohol in slender, faintly yellow needles, m. p.  $245^\circ$ . T. H. P.

**Condensation of Oxalic Esters with *tert.*-Aromatic Amines.** ALFRED GUYOT (*Compt. rend.*, 1907, 144, 1051–1053. Compare Haller and Guyot, this vol., i, 565).—The oxalic esters react with *tert.*-aromatic amines in presence of a small quantity of aluminium chloride at low temperatures forming dialkylaminophenylglyoxalic esters of the type  $\text{NR}'_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{R}$ . At higher temperatures or in the presence of more aluminium chloride, the principal products are tetra-alkyldiaminophenylglycollic esters of the type  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NR}'_2)_2\cdot\text{CO}_2\text{R}$ . At still higher temperatures and in presence of a large excess of aluminium chloride, the substituted glycollic esters are replaced by hexa-alkyltriaminotriphenylacetic esters,  $\text{CO}_2\text{R}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NR}'_2)_3$ .

All these products are obtained in yields of 50–75% of the theoretical, except in the case of methyl oxalate. The three types of products formed, when treated with sulphuric acid, decompose quantitatively, evolving carbon monoxide, and giving respectively dialkylaminobenzoic acids,  $\text{NR}'_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , tetra-alkyldiaminobenzophenones,

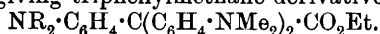
$\text{CO}(\text{C}_6\text{H}_4\cdot\text{NR}'_2)_2$ , and hexa-alkyltriaminotriphenylcarbinols,  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NR}'_2)_3$ .

Apart from its industrial interest as affording a means of preparing dyes, at present made by the use of carbonyl chloride, this reaction affords an explanation of the formation of such substances as rosolic and pararosolic acids and diphenylamine-blue, since it may be assumed that in the ordinary methods of preparing these substances reactions similar to those described take place, the intermediate products formed being under the conditions of the reaction decomposed with the evolution of carbon monoxide and carbon dioxide giving rise to the dyes. T. A. H.

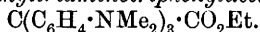
**Products of Condensation of Ethyl Oxalate with Dimethylaniline in Presence of Aluminium Chloride.** ALFRED GUYOT (*Compt. rend.*, 1907, 144, 1120–1123. Compare preceding abstract).—When a solution of ethyl oxalate and dimethylaniline in anhydrous

ether is added to a solution of aluminium chloride in dry ether, a 60% (of theory) yield of Michler and Hanhardt's ethyl *p*-dimethylanilino-glyoxylate,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$  (Abstr., 1878, 421), is obtained together with a small quantity of *ethyl tetramethyldiaminodiphenylglycollate*,  $\text{OH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{CO}_2\text{Et}$ . The latter compound becomes almost the sole product if the amount of dimethylaniline is increased, and the ethereal solution of aluminium chloride more dilute.

Ethyl tetramethyldiaminodiphenylglycollate forms transparent, colourless prisms, m. p.  $112^\circ$ , which in the light very rapidly become yellow. It dissolves in acetic acid with an intense indigo-blue coloration, and condenses with tertiary aromatic amines in neutral or acid aqueous solution giving triphenylmethane derivatives,



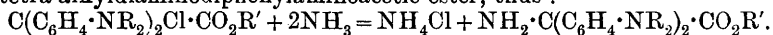
It dissolves in concentrated sulphuric acid with an intense yellow colour, and the solution when heated at  $140^\circ$  evolves carbon monoxide and gives a quantitative yield of tetramethyldiaminobenzophenone. If a solution of aluminium chloride in anhydrous ether be rapidly added to a mixture of ethyl oxalate and dimethylaniline, the chief product is *ethyl hexamethyltriaminotriphenylacetate*,



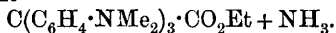
It forms colourless crystals, m. p.  $176^\circ$ , and dissolves without coloration in concentrated sulphuric; the solution on heating at  $140^\circ$  suddenly becomes orange-yellow, evolves carbon monoxide, and gives an almost theoretical yield of crystal-violet. Ethyl hexamethyltriaminotriphenylacetate is also formed by the condensation of the above glyoxylate or glycollate or of ethyl aminotetramethyldiaminodiphenylacetate with dimethylaniline, and together with ethyl dimethylanilino-glyoxylate, by the action of ethyl oxalylchloride on dimethylaniline, but not by the action of this base on ethyl trichloroacetate. E. H.

### Synthesis of the Auramines by Means of the Oxalic Esters.

ALFRED GUYOT (*Compt. rend.*, 1907, 144, 1219—1220).—The indigo-blue aqueous solutions of the neutral salts of the tetra-alkyldiaminodiphenylglycollic esters (preceding abstracts) with acids, when treated with ammonia, give, not the corresponding hydroxy-compound, but a tetra-alkyldiaminodiphenylaminoacetic ester, thus:



The new compounds are leucoauraminecarboxylic esters, and exhibit the properties of the leucoauramines. They dissolve in glacial acetic acid to intensely blue solutions, and in neutral or acid solution they condense with tertiary aromatic amines giving triphenylmethane derivatives; thus a theoretical yield of ethyl hexamethyltriaminotriphenylacetate is obtained by warming a molecular mixture of dimethylaniline and ethyl aminotetramethyldiaminodiphenylacetate,  $\text{C}_6\text{H}_5 \cdot \text{NMe}_2 + \text{NH}_2 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{CO}_2\text{Et} =$



They are oxidised by potassium ferricyanide to the auramines  $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NR}_2)_2 \cdot \text{NH}$ , which are precipitated in a pure condition. E. H.

**Quinonoid Compounds. XII. Aniline-black. I.** RICHARD WILLSTÄTTER and CHARLES WATSON MOORE (*Ber.*, 1907, 40, 2665—2689. Compare Nover, this vol., i, 262).—Caro (*Chem. Zeit.*, 1896, 21, 840)

obtained by the oxidation of aniline in aqueous alkaline solution a yellow substance, which he showed to be a quinonoid derivative of *p*-aminodiphenylamine. He drew the conclusion that the substance was benzoquinonephenyldi-imine, but a re-examination of the substance (m. p. 73—77°) shows it to be a mixture of this di-imine and the benzoquinonephenylmonoimine, which crystallise together in long, yellow needles; they may, however, be separated by using hexane as solvent, and on reduction the substance gives nearly equal amounts of *p*-hydroxy- and *p*-amino-diphenylamines.

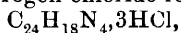
*p*-Benzoquinonemonomethyldi-imine,  $\text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ , best prepared by the oxidation of phenylenemethyldiamine by dry lead peroxide in boiling light petroleum (b. p. 35—40°), crystallises in colourless prisms, m. p. 64—67°. In one hour it changes into a brown-tarry mass. The sulphate is precipitated in long, colourless prisms from a petroleum solution of the imine on addition of an ethereal solution of the monohydrate; on warming the aqueous solution of the sulphate, *p*-benzoquinone is formed. An ethereal solution of hydrogen chloride gives a green precipitate which is not hydrolysed to benzoquinone by water. *p*-Benzoquinonemonophenyldi-imine,  $\text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ , is obtained from an ethereal solution of *p*-aminodiphenylamine and dry silver oxide, and crystallises in light-yellow prisms, m. p. 88—90°; the substitution of the phenyl group for methyl results in a deepening of the colour. Its properties are similar to the other imines described; hot dilute sulphuric acid gives benzoquinone; hydroxylamine hydrochloride yields *p*-nitrosodiphenylamine.

The aqueous solution of benzoquinonephenyldi-imine, after a time, slowly deposits Bandrowski's quinonephenylmonoimine, m. p. 100—101° (Abstr., 1888, 943: m. p. 97°).

The hydrochloride of quinonephenyldi-imine,  $\text{C}_{12}\text{H}_{10}\text{N}_2 \cdot \text{HCl}$ , is brown, and in the course of one day polymerises to a mixture of green insoluble salts, the separation of which is accomplished by taking advantage of their different basicities. It is, however, easier to oxidise *p*-aminodiphenylamine by ferric chloride (Nietzki, *Ber.*, 1879, 12, 1402), or, better still, by hydrogen peroxide in the presence of a small quantity of ferrous sulphate.

The emeraldine base, *azurine*,  $\text{C}_{24}\text{H}_{20}\text{N}_4$ , obtained in a well crystallised condition by first precipitating the crude base from its benzene solution by light petroleum, then reducing it to the leuco-base, and subsequent reoxidation, crystallises from hexane in deep blue, microscopic prisms, m. p. about 165°. It is strongly basic; the hydrochloride is bluish-green. A molecular weight determination by the freezing point method shows it to be a  $\text{C}_{24}$  derivative. The leuco-base,  $\text{C}_{24}\text{H}_{22}\text{N}_4$ , results along with black oxidation substances by heating with water in a sealed tube at 150—170° for five hours, or by reduction with stannous chloride or phenylhydrazine. It crystallises in microscopic prisms, m. p. 185°.

On oxidation of the azurine in cold benzene solution by dry lead peroxide, a dark red imine,  $\text{C}_{24}\text{H}_{18}\text{N}_4$ , is obtained in leaflets. It is further purified by shaking quickly with very dilute acid and then liberating the base from the acid solution by ammonia; m. p. 195—196° with polymerisation. Hydrogen chloride forms the compound,



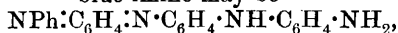
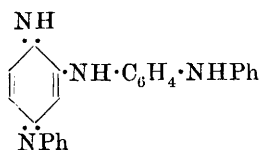
which is not, however, a true trihydrochloride, some of the chlorine being contained in the aromatic nucleus. This red imine, when heated with water at 150—170°, polymerises to a black, glistening mass,  $(C_{24}H_{13}N_4)_x$ . A table is given comparing aniline-black and this "polymerisation-black" which show them to be very similar, but not identical. The polymerisation-black yields a *hydrochloride*, the aniline-black does not give a simple hydrochloride. An *acetyl* derivative is obtained from this new black. The conclusion is drawn that the molecular formula of aniline-black must be at least  $C_{48}H_{36}N_8$ .

Accompanying the red imine, obtained by oxidising the emeraldine base, there is 8—10% of a weaker base containing oxygen. This *red imine*,  $C_{24}H_{17}ON_3$ , does not form salts with *N*/10 acids, and crystallises in microscopic needles, m. p. 216—217°. It polymerises to an insoluble black substance when heated with water at 150—170°. The *leuco-base*,  $C_{24}H_{21}ON_3$ , obtained on reduction of the imine with phenylhydrazine, is colourless, m. p. 194—195°, and oxidises easily with atmospheric oxygen to a semi-quinonoid imine; with silver oxide it is further oxidised.

A second series of oxygen derivatives of emeraldine is obtained from the oxidation of mixture of *p*-hydroxy- and *p*-aminodiphenylamine with 3% hydrogen peroxide and a little ferrous sulphate. The operation is finished in five minutes. The *blue imine*,  $C_{24}H_{19}ON_3$ , is purified through its sulphate, and crystallises from a mixture of benzene and petroleum in rosettes of needles, m. p. 148—149°. It behaves towards water at 150—170° like emeraldine, partly giving rise to a leuco-base and partly to a black substance. Another *red imine* of composition  $C_{24}H_{17}ON_3$  is obtained by oxidising the blue imine with lead peroxide; it is light red and has m. p. 222—223°. The *leuco-base*,  $C_{24}H_{21}ON_3$ , has m. p. 198—200°.

The paper concludes with a table giving the various colour changes which these imines undergo in alcohol, benzene, and sulphuric acid.

The constitution of the emeraldine bases cannot be of the nature of aminoazo-dyes. Although such condensations have been recognised in the case of the oxidation of *o*-phenylenediamine and benzidine (Abstr., 1905, i, 723; 1906, i, 996), the emeraldine bases do not contain the azo-group, as reduction of the leuco-bases cannot be effected under circumstances where the azo-bond would be broken. The blue imine may be

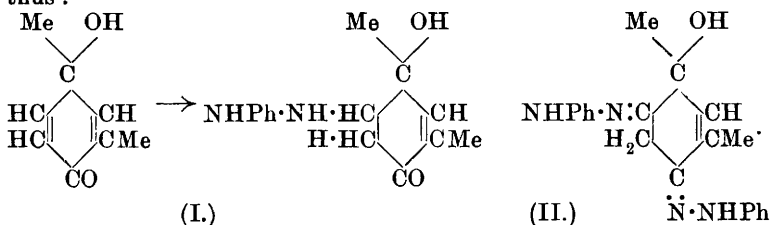


the red,  $\text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ ; the annexed formula has been rejected as such a compound might be expected to yield an azine.

W. R.

**Action of Phenylhydrazine on Ketonic 2 : 4-Dimethylquinol.**  
EUGEN BAMBERGER and EMIL REBER (*Ber.*, 1907, 40, 2253—2274. Compare this vol., i, 606).—The action of phenylhydrazine on ketonic xyloquinol differs according as hydroxyl ions are present or not. In the presence of hydroxyl ions, addition of the  $\text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  group

and the H atom takes place in positions 5 and 6 respectively, thus :

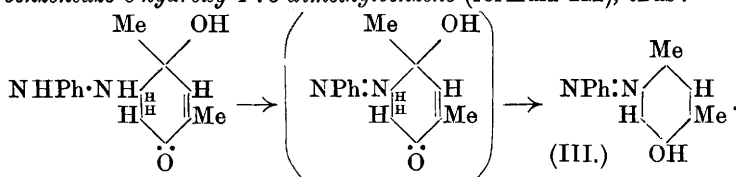


The resulting hydroxyketophenylhydrazinodimethyltetrahydrobenzene (I) has the reactions typical of hydrazo-compounds.

When the action of phenylhydrazine on xyloquinol is conducted in neutral (etheral) solution, the main product of the action is the bisphenylhydrazone of a hydroxydiketodimethyltetrahydrobenzene (II).

*Hydroxyketophenylhydrazinodimethyltetrahydrobenzene* (formula I) forms silky needles, m. p. 213—213·5° (decomp.). It is readily soluble in mineral acids and is reprecipitated on the addition of alkali; it reduces Fehling's solution in the cold. Its *picrate*,

$\text{C}_{20}\text{H}_{21}\text{O}_5\text{H}_5$ , has m. p. 177° (decomp.). Its *oxalate*,  $(\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2)_2 \cdot \text{C}_2\text{H}_2\text{O}_4$ , has m. p. 180° (decomp.). When oxidised by ferric chloride in dilute hydrochloric acid solution, the hydrazinoquinol is converted into *4-benzeneazo-6-hydroxy-1:3-dimethylbenzene* (formula III), thus :



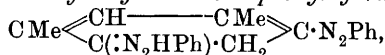
The latter forms orange-yellow, glistening needles, m. p. 113·5—114°. Its solution in concentrated sulphuric acid is red. It forms a *benzoyl* derivative, crystallising in orange-coloured, glistening needles or leaflets, m. p. 115—116°. The benzeneazoxylenol itself is reduced by aluminium amalgam to form *6-amino-4-hydroxy-1:3-dimethylbenzene*,  $\text{CMe} \leq \begin{array}{c} \text{C}(\text{NH}_2) : \text{CH} \\ \text{CH} - \text{CMe} \end{array} \geq \text{C} \cdot \text{OH}$ , which forms glistening needles or nacreous scales, m. p. 166·5—167°. In order to confirm the constitution assigned to the preceding compound, it was synthesised from *nitro-as-m-xylidine*,  $\text{CMe} \leq \begin{array}{c} \text{C}(\text{NO}_2) : \text{CH} \\ \text{CH} - \text{CMe} \end{array} \geq \text{C} \cdot \text{NH}_2$ , the amino-group being replaced by a hydroxy-group in the usual manner, and the resulting *6-nitro-4-hydroxy-1:3-dimethylbenzene* then reduced by stannous chloride.

When ketonic xyloquinol is heated with phenylhydrazine for thirty-five to forty hours in the presence of ether, one of the products of the action is *1-benzeneazo-2:4-dimethylbenzene*, which was identified by reducing it by zinc dust to the corresponding hydrazo-compound, m. p. 99·5—100°. The main product is, however, *hydroxydiketodimethyltetrahydrobenzene bisphenylhydrazone* (formula II), which separates

from benzene, alcohol, or light petroleum in silky, orange-coloured needles, m. p. 168·5—169·5°. Its alcoholic solution does not reduce either Fehling's solution or silver oxide, but reduces silver nitrate slowly at the ordinary temperature. When oxidised by ferric chloride, it is converted into 4:6-bisbenzenazo-1:3-dimethylbenzene,  $\text{CMe} \begin{smallmatrix} \text{CH} \\ \text{C}(\text{N}_2\text{Ph}) \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CMe} \begin{smallmatrix} \text{---} \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{N}_2\text{Ph}$ , which forms glistening, orange-red scales, m. p. 171—171·5°.

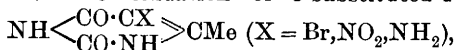
The latter compound, on reduction with aluminium amalgam, forms 1:3-xylylene-4:6-diamine.

*Benzeneazoketodimethyldihydrobenzene phenylhydrazone*,



may be obtained by adding a little hydrochloric acid to a concentrated solution of hydroxydiketodimethyltetrahydrobenzene bisphenylhydrazone in acetone as orange-coloured needles, m. p. 152·5—153·5°, the operation being conducted in an atmosphere of coal-gas. This compound is very readily oxidised to form the azo-compound with m. p. 171—171·5°, already described. A. McK.

**Oxidation of Uracil Derivatives.** GUSTAV OFFE (*Annalen*, 1907, 353, 267—283. Compare Behrend and Dietrich, *Abstr.*, 1900, i, 120; Behrend and Thurm, *Abstr.*, 1902, i, 832; Behrend and Fricke, *Abstr.*, 1903, i, 739; Behrend and Hufschmidt, *Abstr.*, 1906, i, 310; Hoebel, this vol., i, 557).—It has been shown previously that when oxidised with potassium permanganate equivalent to three atoms of oxygen in the cold, 4-methyluracil yields chiefly acetylcarbamide and oxalic acid, the hydrolysis products of acetyloxaluric acid, whereas if the reaction mixture is heated, the principal product is oxaluric acid, the hydrolysis product of parabanic acid, which is formed together with acetic acid. The oxidation of 5-substituted-4-methyluracils,



has been studied now in the same manner. The products obtained are those formed from 4-methyluracil, but their relative amounts are found to depend largely on the nature of the substituting group. 5-Bromo- and 5-nitro-4-methyluracils yield acetylcarbamide together with little oxaluric acid, the proportion between the amounts of the products being almost the same if the oxidation takes place in cold or in boiling solution. 5-Amino-4-methyluracil, on the other hand, resembles 4-methyluracil, yielding acetylcarbamide together with smaller amounts of oxaluric acid when oxidised in the cold, but oxaluric acid as the chief product when oxidised in boiling solution. This difference in behaviour is ascribed to the pronounced acid nature of the bromo- and nitro-methyluracils, in consequence of which the formation of free alkali and therefore the conversion of the immediately formed methylsodialuric acid, or the corresponding bromo- and nitro-derivatives, into acetyllallanturic acid is prevented. In agreement with this, acetyloxaluric acid,  $\text{NHAc} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , is obtained from 5-bromo-, 5-nitro, and 5-amino-methyluracils if the formation of free alkali during the oxidation is prevented entirely.

It is shown that when hydrolysed with alkalis or when boiled in neutral or slightly acid solution, acetyloxaluric acid yields acetylcarbamide and oxalic acid, but that oxaluric acid is not formed. This is of importance as showing that the oxaluric acid, obtained on oxidation of 4-methyluracil, must be derived wholly from intermediately formed parabanic acid,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ , this five atom-ring being formed by oxidation of the six atom pyrimidine ring of the uracil.

Derivatives of uracil undergo oxidation in a manner similar to those of 4-methyluracil; the intermediate product is *formyloxaluric acid*,  $\text{CHO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , which differs from acetyloxaluric acid in that on hydrolysis it yields formic acid and oxaluric acid. Formyloxaluric acid has been isolated from the oxidation products of *isobarbituric acid*, 5-nitrouracil, and 5-aminouracil hydrochloride; only the final product, oxaluric acid, was obtained from 5-carbamidouracil (hydroxyxanthine).

*Potassium formyloxalurate*,  $\text{C}_4\text{H}_3\text{O}_5\text{N}_2\text{K}$ , crystallises from water in small needles containing about  $\frac{1}{2}\text{H}_2\text{O}$ , which is lost at  $120^\circ$ ; the anhydrous salt decomposes at  $208.5^\circ$ . G. Y.

**Transformation of Pyrroles into Derivatives of Pyrazole.** VICENZO CASTELLANA (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 767—775. Compare Abstr., 1905, i, 941).—The author gives details of the work previously published (*loc. cit.*), and describes the means adopted to establish the constitutions of the products obtained.

When the ketone, m. p.  $90^\circ$ , is treated with potassium permanganate in presence of alkali, one of the following two compounds is obtained according to the conditions of the reaction. (1) 1-Phenyl-5-methylpyrazole-3-carboxylic acid (compare Claisen and Roosen, Abstr., 1891, 1106); (2) 1-phenylpyrazole-3:5-dicarboxylic acid (compare Balbiano, Abstr., 1890, 1164). The ketone hence has the constitution previously suggested for it (*loc. cit.*).

When treated with amyl nitrite (1 mol.) in presence of sodium ethoxide, the ketone (1 mol.) yields an *isomitoso*-derivative,  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}_3$ , which crystallises from benzene in small, almost white, hard needles, m. p.  $172^\circ$ , whilst the use of double the above proportion of amyl nitrite leads to the formation of the *anhydride* of the *diisonitoso*-derivative (annexed formula), which crystallises from benzene in minute needles, m. p.  $175^\circ$ , and is soluble in alkalis, from which it is reprecipitated by carbon dioxide. T. H. P.

**Diphenylglyoxaline and  $\psi$ -Chlorodiphenylglyoxaline.** HEINRICH BILTZ (*Ber.*, 1907, 40, 2630—2636).—A new method of preparing diphenylglyoxaline (compare Pinner, Abstr., 1905, i, 476). Although 4:5-diphenyliminazolone (Abstr., 1905, i, 674) cannot be directly reduced by phosphorus and hydriodic acid, the reduction to the glyoxaline may be accomplished almost quantitatively in two stages.

2-Chloro-4:5-diphenylglyoxaline,  $\begin{smallmatrix} \text{NH} - \text{CCl} \\ \diagup \quad \diagdown \\ \text{CPh} : \text{CPh} \end{smallmatrix} \text{>N}$ , prepared by heating phosphoryl chloride and diphenyliminazolone in a sealed tube at  $140^\circ$



for four hours, crystallises in colourless, slender needles, m. p.  $217.5^{\circ}$ , and is easily reduced to diphenylglyoxaline by zinc and hydrochloric acid. Diphenyliminazolone cannot be regenerated from the chloro-compound by heating with hydrochloric acid or by silver oxide. Heating with 10% nitric acid results in its hydrolysis to benzil and carbamide.

2-Chloro-4:5-diphenylglyoxaline does not form salts with weak acids like oxalic and picric acid; the *hydrochloride* has m. p.  $167-168^{\circ}$ ; the *hydrogen sulphate*, m. p.  $123-124^{\circ}$  (decomp.). 2-Chloro-3-acetyl-4:5-diphenylglyoxaline,  $C_{17}H_{18}ON_2Cl$ , m. p.  $185^{\circ}$ , is easily hydrolysed by water or alcohol.

The following salts of diphenylglyoxaline are described: the hydrochloride has no m. p. as it loses hydrogen chloride at  $140^{\circ}$  (Pinner, Abstr., 1903, i, 123, gives m. p.  $202^{\circ}$ ); the *sulphate*, *nitrate*, decomposes explosively at  $164^{\circ}$ , *oxalate*, decomp. at  $244^{\circ}$ , and *picrate* has m. p.  $135^{\circ}$ . 3-Acetyl-4:5-diphenylglyoxaline,  $C_{17}H_{14}ON_2$ , crystallises in colourless needles, m. p.  $149.5^{\circ}$ . It is more stable than the 2-chloro-compound, but slowly decomposes in water into the acetate.

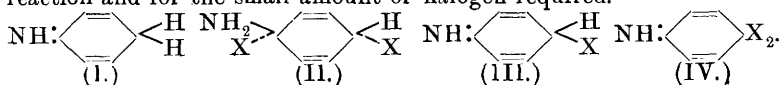
Oxidation of diphenylglyoxaline with potassium permanganate in acid solution yields dibenzoylcarbamide.

An additive compound of diphenylglyoxaline and hydroxydiphenyltriazine is formed by mixing their ethylacetate solutions, and crystallises in light yellow needles, m. p.  $184-185^{\circ}$ . The chloro-compound does not yield an additive product.

W. R.

**Explanation of the Formation of Quinoneimine Dyes from Amines by Oxidising and Halogen Fusions.** ADRIANO OSTROGOVICH and T. SILBERMANN (*Chem. Zentr.*, 1907, i, 1194; from *Bul. Soc. Sci. Bucuresci*, 15, 281-302).—It having been found that indulines are formed if anilines are heated with halogens or substances which yield free halogens, as ethylene iodide, it was sought to form rosaniline and chrysaniline dyes in the same manner, since whilst oxidation of aniline leads to the formation of induline, rosaniline dyes are formed if *p*-toluidines are present. Although chlorine, bromine, and iodine give similar results in the induline formation, only iodine is capable of forming rosaniline from a mixture of aniline with *o*- and *p*-toluidines, whilst chlorine converts the aniline into induline and the *p*-toluidine into chrysaniline.

Any explanation of the formation of induline by oxidation or by the action of halogens must include that of the intermediate product, benzoquinoneimine. The halogens cannot act as oxidising agents, as the reaction takes place with a quarter of the halogen necessary for oxidation of the hydrogen atoms; moreover, the halogens are oxidising agents only in presence of water or alkalis. It is assumed that the aniline acts in the quinone form I, giving with halogens the hypothetical intermediate substances II, III, and IV. Benzoquinoneimino-phenylimine is then formed by the action of aniline on IV, or possibly on III, which would account for the liberation of hydrogen during the reaction and for the small amount of halogen required.

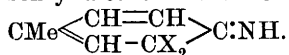


Benzoquinonediphenylimine is formed by the action of aniline on the quinoneimidephenylimine.

It is shown that the formation of indulines from *p*-halogenoanilines and aniline hydrochlorides takes place, not directly, but in consequence of the liberation of the halogen by decomposition of the halogeno-aniline.

The formation of rosaniline from aniline and *p*-toluidine is explained usually as resulting from oxidation of the toluidine to *p*-aminobenzaldehyde and condensation of this with the aniline; it is argued, contrary to this view, that the first products of the reaction are benzoquinoneimine and *p*-aminobenzyl alcohol, which condense with unchanged aniline. In the action of iodine on a mixture of aniline and *p*-toluidine, the intermediate products are analogously di-iodobenzoquinoneimine and *p*-aminobenzyl alcohol. Brunner and Brandenburg's formation of methyl violet from *p*-bromodimethylaniline is explained in the same manner (Abstr., 1878, 314).

Chrysaniline must be formed by condensation of aniline with *p*-aminobenzyl alcohol and an *o*-benzoquinoneimine derived from *p*-toluidine,



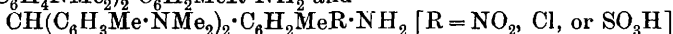
Induline dyes are formed by heating aniline with iodine or with chlorine at 180°, or by heating aniline at 180° with aniline hydrochloride which has been oxidised with air, lead dioxide, persulphate, &c. G. Y.

**Preparation of Magenta and Ortho- and Meta-halogen Magentas by Means of Iodine.** T. SILBERMANN and ADRIANO OSTROGOVICH (*Chem. Zentr.*, 1907, i, 1197; from *Bul. Soc. Sci. Bucuresti*, 15, 303—307. Compare preceding abstract).—Paramagenta is prepared by adding 60 grams of iodine to a solution of 22 of *p*-toluidine in 38 of aniline, gradually raising the temperature to 180° and maintaining it at this point until the mass becomes solid. Magenta is prepared in a similar way, using 19 grams of aniline, 22 of toluidine, and 60 of iodine. When *p*-bromoaniline is heated with *p*-toluidine, induline, chrysaniline, and chrysotoluidine are formed, but if a trace of iodine is added, magenta is practically the only product. Nitroaniline yields only chrysaniline. Ortho- and meta-halogen derivatives of magenta have been prepared from the corresponding substituted anilines. All the halogen derivatives are very sparingly soluble in water. *o*-Dichloroparamagenta does not crystallise, but has all the properties of a magenta derivative; *o*-dibromoparamagenta resembles the corresponding, chloro-derivative. In the preparation of *m*-dichloro- and *m*-dibromo-paramagenta, rather large quantities of chrysaniline are formed and can be isolated by extracting with ether.

E. W. W.

**Relations between the Constitution, Colour, and Absorption Spectra of the Triphenylmethane Dyes.** FRITZ REITZENSTEIN and WALTHER SCHWERDT (*J. pr. Chem.*, 1907, [ii], 75, 369—415. Compare Abstr., 1905, i, 300; 1906, i, 316).—In continuation of the investigation into the influence of substituting groups on the shade of

dyes of the triphenylmethane series (*loc. cit.*), a number of leuco-bases,  $\text{CH}(\text{C}_6\text{H}_4\text{NMe}_2)_2 \cdot \text{C}_6\text{H}_2\text{MeR} \cdot \text{NH}_2$  and



have been prepared by condensation of chloro-, nitro-, and sulpho-toluidines with tetramethyldiaminobenzhydrol and tetramethyldiaminoditolylhydrol, and converted into products of the types  $\text{CH}(\text{C}_6\text{H}_4\text{NMe}_2)_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} : \text{CH} : \text{CH} : \text{CH} : \text{CH} : \text{CH} \cdot \text{NH}_2\text{Cl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}(\text{C}_6\text{H}_4\text{NMe}_2)_2$  by the action of dinitrophenylpyridinium chloride (Abstr., 1906, i, 316), and  $\text{CH}(\text{C}_6\text{H}_4\text{NMe}_2)_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} : \text{CH} : \text{CH} : \text{CH} : \text{NHCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}(\text{C}_6\text{H}_4\text{NMe}_2)_2$  by the action of propionaldehyde diethylacetal (compare Claisen, Abstr., 1904, i, 14). Compounds of the former type could not be obtained from the leuco-bases derived from the nitrotoluidines. The corresponding dyes are obtained by oxidation of the leuco-bases by chloranil in alcoholic-acetic acid solution. The examination of the absorption spectra of the dyes by Formánek's method shows that, in agreement with Noetting's rule, the condensation of tetramethyldiaminobenzhydrol with substituted toluidines leads, in general, to the formation of isomeric leuco bases, the constitution of the product depending on whether the condensation takes place in hydrochloric or sulphuric acid solution, but that the products obtained from *p*-chloro-*o*-toluidine and tetramethyldiaminobenzhydrol by the two methods of condensation are identical, having identical absorption spectra, as have also the dianilides obtained from them by the action of dinitrophenylpyridinium chloride; nevertheless, the substances have different melting points.

It is found that the shade of the simple triphenylmethane dyes, derived from tetramethyldiaminobenzhydrol, is weakened by a nitro-group in the ortho-, but, contrary to Reitzenstein and Runge's statement (Abstr., 1905, i, 300), is intensified by a nitro-group in the meta-position. The colour of the dye becomes pure and more intense on introduction of a chlorine atom into the ortho-, is intensified if the chlorine atom assumes the meta-, and becomes deeper and clearer if the chlorine is introduced into the para-position. The introduction of the sulpho-group into the ortho-position results in a weakening of the shade which changes towards the green; into the meta-position, in weakening of the shade which becomes less clear; and into the para-position, in intensification of the colour.

The dyes obtained from tetramethyltriaminoditolylhydrol have weaker colours; in consequence of their feeble dyeing properties, the influence of the position of the nitro-, chloro-, and sulpho-groups cannot be observed.

The dyes in which two tetramethyltriaminotriphenylmethane groups are united by a five carbon atom-chain have stronger shades than the simple dyes; the colour is further intensified by the introduction of a chlorine atom. The union of two molecules of a simple dye by a three carbon atom-chain results in a change from blue to light green.

The wave-lengths given in the following description are those of the bands in the absorption spectra of the leuco-bases.

The following leuco-bases are derived from tetramethyldiaminobenzhydrol by condensation with the substituted toluidines mentioned, in sulphuric or hydrochloric acid as stated; the substituted groups,

the positions of which are given, are those in the phenyl nucleus derived from the toluidine. The hydrochlorides are the products of the action of dinitrophenylpyridinium chloride on the simple leucobases.

*m*-Nitro-*p*-toluidine (sulphuric acid)  $[\text{NO}_2:\text{NH}_2:\text{Me}=2:3:6]$ : green powder, m. p.  $208^\circ$ ,  $\lambda=617\cdot50$ , yields a green dye. *m*-Nitro-*p*-toluidine (hydrochloric acid)  $[\text{NO}_2:\text{NH}_2:\text{Me}=3:2:5]$ : yellow precipitate,  $\lambda=595\cdot38$ , yields a blue dye. *p*-Nitro-*m*-toluidine (sulphuric acid)  $[\text{NO}_2:\text{NH}_2:\text{Me}=2:3:5]$ : whitish-grey powder,  $\lambda=661\cdot36$ , yields a green dye. *p*-Nitro-*m*-toluidine (hydrochloric acid)  $[\text{NO}_2:\text{NH}_2:\text{Me}=5:4:2]$ : dull-green powder,  $\lambda=602\cdot14$ , yields a dye which dyes tannin-mordanted cotton blue. *o*-Chloro-*p*-toluidine (sulphuric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=5:3:6]$ : brown powder,  $\lambda=632\cdot15$ , yields a dye which dyes tannin-mordanted cotton green; the *hydrochloride* forms a red, crystalline powder; the *base*,  $\text{C}_{53}\text{H}_{60}\text{ON}_6\text{Cl}_2$ , is soluble in carbon disulphide,  $\lambda=639\cdot50$ , yields a dye which dyes tannin-mordanted cotton a dark green. *o*-Chloro-*p*-toluidine (hydrochloric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=4:2:5]$ : grey powder, m. p. about  $100^\circ$ ,  $\lambda=613\cdot4$ , yields a dye which dyes tannin-mordanted cotton dark blue; the *hydrochloride*,  $\text{C}_{53}\text{H}_{59}\text{N}_6\text{Cl}_3$ , forms orange crystals,  $\lambda=655\cdot60$ , yields a dye which dyes tannin-mordanted cotton a dark blue. *p*-Chloro-*m*-toluidine (sulphuric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=2:3:5]$ : light grey,  $\lambda=614\cdot50$ , after oxidation dyes tannin-mordanted cotton blue; the *hydrochloride* yields a *base*, which is obtained as an orange-red powder, m. p.  $110^\circ$ ,  $\lambda=620\cdot70$ , and after oxidation dyes mordanted cotton dark blue. *p*-Chloro-*m*-toluidine (hydrochloric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=5:4:2]$ : greyish-blue, crystalline powder, m. p.  $177^\circ$ ,  $\lambda=611\cdot50$ , yields a blue dye; the *base*, obtained from the *hydrochloride*, m. p. about  $105^\circ$ ,  $\lambda=612\cdot10$ , after oxidation dyes tannin-mordanted cotton dark blue. *m*-Chloro-*p*-toluidine (sulphuric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=4:3:6]$ : bluish-grey powder, m. p.  $170^\circ$ ,  $\lambda=620\cdot38$ , yields a bluish-green dye which dyes mordanted cotton green; the *hydrochloride* forms yellow, flocculent crystals, m. p.  $175^\circ$ ; the *base*,  $\lambda=640\cdot20$ , after oxidation dyes mordanted cotton dark green. *m*-Chloro-*p*-toluidine (hydrochloric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=3:2:5]$ : m. p.  $105^\circ$ ,  $\lambda=594\cdot60$ , yields a blue dye; the *base*, derived from the *hydrochloride*,  $\lambda=605\cdot50$ , after oxidation dyes mordanted cotton blue. *p*-Chloro-*o*-toluidine (sulphuric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=5:3:2]$ : blue powder, m. p.  $154^\circ$ ,  $\lambda=617\cdot64$ , yields a blue dye; the *base*, m. p.  $105^\circ$ ,  $\lambda=514\cdot20$ , derived from the *hydrochloride*, yields a blue dye. *p*-Chloro-*o*-toluidine (hydrochloric acid)  $[\text{Cl}:\text{NH}_2:\text{Me}=2:4:5]$ : m. p.  $210^\circ$ ,  $\lambda=617\cdot50$ , after oxidation dyes mordanted cotton reddish-blue; the *hydrochloride* is red, and yields a *base*, m. p.  $184^\circ$ ,  $\lambda=514\cdot20$ , which after oxidation dyes mordanted cotton dark blue. *p*-Sulpho-*o*-toluidine (sulphuric acid)  $[\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=5:3:2]$ : m. p.  $70^\circ$ ,  $\lambda=632\cdot50$ , yields a green dye. *p*-Sulpho-*o*-toluidine (hydrochloric acid)  $[\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=2:4:5]$ : m. p.  $210^\circ$ ,  $\lambda=617\cdot20$ , yields a bluish-green dye. *o*-Sulpho-*p*-toluidine (sulphuric acid)  $[\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=5:3:6]$ :  $\lambda=632\cdot15$ , yields a green dye. *o*-Sulpho-*p*-toluidine (hydrochloric acid)  $[\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=4:2:5]$ : sinters at  $130^\circ$ ,  $\lambda=590\cdot75$ , after oxidation dyes mordanted cotton blue.

The following similar substances are prepared from tetramethyldiaminoditolylhydrol by condensation with substituted toluidines; the positions of the substituting groups in the toluidine nucleus are given.

*m*-Nitro-*p*-toluidine (sulphuric acid) [ $\text{NO}_2:\text{NH}_2:\text{Me}=2:3:6$ ]: brown powder, yields a green *dye*. *m*-Nitro-*p*-toluidine (hydrochloric acid) [ $\text{NO}_2:\text{NH}_2:\text{Me}=3:2:5$ ]: yellow powder, resinifies and becomes green on exposure to air, after oxidation dyes mordanted cotton blue. *p*-Nitro-*m*-toluidine (sulphuric acid) [ $\text{NO}_2:\text{NH}_2:\text{Me}=2:3:5$ ]: brown precipitate, after oxidation dyes mordanted cotton a weak light green. *p*-Nitro-*m*-toluidine (hydrochloric acid) [ $\text{NO}_2:\text{NH}_2:\text{Me}=5:4:2$ ]: brown powder, yields a green *dye*. *o*-Chloro-*p*-toluidine (sulphuric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=5:3:6$ ]: brown precipitate, after oxidation dyes mordanted cotton dull green; the *hydrochloride* dissolves in carbon disulphide, and yields a free base,  $\text{C}_{55}\text{H}_{64}\text{ON}_6\text{Cl}_2$ , which is orange, and after oxidation dyes mordanted cotton green. *o*-Chloro-*p*-toluidine (hydrochloric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=4:2:5$ ], brown mass, yields a dull green *dye*; the *hydrochloride* yields a blue *dye*. *p*-Chloro-*m*-toluidine (sulphuric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=2:3:5$ ]: grey becoming black, after oxidation dyes mordanted cotton brown; a dianilide hydrochloride could not be obtained. *p*-Chloro-*m*-toluidine (hydrochloric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=5:2:4$ ]: yields a dull green *dye*; the *hydrochloride* forms a reddish-brown powder, sinters at  $85^\circ$ , yields a weak green *dye*. *m*-Chloro-*p*-toluidine (sulphuric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=4:3:6$ ]: on oxidation yields a brown solution; the hydrochloride is brown, and yields a weak green *dye*. *m*-Chloro-*p*-toluidine (hydrochloric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=3:2:5$ ]: brownish-yellow, yields a weak blue *dye*; the *hydrochloride*,  $\text{C}_{57}\text{H}_{67}\text{N}_6\text{Cl}_3$ , yellowish-red substance, m. p.  $95^\circ$ , yields a blue *dye*. *p*-Chloro-*o*-toluidine (sulphuric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=5:3:2$ ]: brown powder, yields a weak green *dye*; the base, from the *hydrochloride*, is obtained as a brownish-yellow powder, and yields a weak green *dye*. *p*-Chloro-*o*-toluidine (hydrochloric acid) [ $\text{Cl}:\text{NH}_2:\text{Me}=2:4:5$ ]: brown, crystalline powder, yields a dull green *dye*; the *hydrochloride* is obtained as a reddish-brown powder, after oxidation dyes mordanted cotton a weak blue. *p*-Sulpho-*o*-toluidine (sulphuric acid) [ $\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=5:3:2$ ]: light brown powder. *p*-Sulpho-*o*-toluidine (hydrochloric acid) [ $\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=2:4:5$ ]: grey precipitate. *o*-Sulpho-*p*-toluidine (sulphuric acid) [ $\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=5:3:6$ ]: brown powder, m. p. about  $140^\circ$ , on oxidation yields a green solution. *o*-Sulpho-*p*-toluidine (hydrochloric acid) [ $\text{SO}_3\text{H}:\text{NH}_2:\text{Me}=4:2:5$ ]: light grey, crystalline powder, m. p. above  $220^\circ$ .

When heated on the water-bath with propionaldehyde diethylacetal in 38% aqueous hydrochloric acid, the leuco-base, obtained by condensation of tetramethyldiaminobenzhydrol and *p*-toluidine in sulphuric acid solution, yields a yellowish-green *hydrochloride*, from which the base,  $\text{C}_{51}\text{H}_{59}\text{N}_6\cdot\text{OH}$ , m. p.  $170^\circ$ ,  $\lambda=625\cdot18$ , is liberated by ammonia. After oxidation, it dyes cotton mordanted with tannin and tartar emetic, a grass-green. G. Y.

1:2-Naphthaquinone-4-sulphonic Acid. III. FRANZ SACHS and ERICH BERTHOLD (*Zeit. Farb. Ind.*, 1907, 6, 141—143. Compare this vol., i, 426).—The readiness with which 1:2-naphthaquinone-

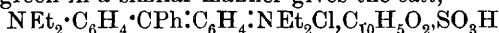
4-sulphonic acid condenses with substances containing a primary amino-group has been utilised as a means of ascertaining the structure of the following compounds.

Auramine is shown to be  $C(C_6H_4 \cdot NMe_2)_2 \cdot NH, HCl$  by its combining with the sulphonic acid to form the salt

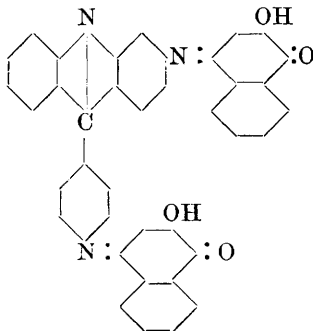


instead of condensing with the quinone as would happen if it had the structure  $NMe_2Cl : C_6H_4 : C(C_6H_4 \cdot NMe_2) \cdot NH_2$ ; the salt obtained crystallises from alcohol in bluish-black needles, m. p.  $200^\circ$ .

Brilliant-green in a similar manner gives the salt,



(m. p.  $118-120^\circ$ ), and crystal-violet the



salt  $C(C_6H_4 \cdot NMe_2)_2$   
 $C_6H_4 : NMe_2Cl, C_{10}H_5O_2 \cdot SO_3H$

Chrysaniline, however, condenses with 2 mols. of the naphthaquinonesulphonic acid giving the annexed compound, which separates from nitrobenzene in the form of a crimson, crystalline powder.

In the case of *p*-rosaniline, only two of the three amino-groups condense with 1 : 2-naphthaquinone-4-sulphonic acid even in presence of an excess of the latter.  
 W. A. D.

**Synthesis of Polypeptides. XX. Derivatives of Tryptophan.** EMIL ABDERHALDEN and MARTIN KEMPE (*Ber.*, 1907, 40, 2737—2750).—The methods described previously have been extended to the preparation of polypeptides from tryptophan. The tryptophan used was prepared by Hopkins and Cole's method (*Abstr.*, 1902, i, 193) from casein and had  $[\alpha]_D^{20} + 6.06^\circ$  in water and  $+1.31^\circ$  in normal hydrochloric acid.

Tryptophan was converted into the *chloride* by Fischer's method; this at once coupled with glycine ethyl ester, and the dipeptide separated by means of the mercury sulphate double salt. *Tryptophylglycine*,  $C_6H_4 \cdot \begin{smallmatrix} \text{---} \\ | \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{---} C \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , crystallises

in colourless, microscopic needles, m. p.  $180^\circ$  (corr.),  $[\alpha]_D^{20} + 78.7^\circ$ .

*Chloroacetyl-d-tryptophan*, prepared by the condensation of tryptophan with chloroacetyl chloride in presence of sodium hydroxide, forms glistening platelets, m. p.  $159^\circ$  (corr.),  $[\alpha]_D^{20} - 32.9^\circ$ . *Glycyl-d-tryptophan*,  $C_6H_4 \cdot \begin{smallmatrix} \text{---} \\ | \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{---} C \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CH_2 \cdot NH_2$ , separates in

small, equilateral, triangular plates, m. p.  $302^\circ$  (corr.),  $[\alpha]_D^{20} + 21.45^\circ$ , and has a bitter taste.

As crystalline products could not be obtained from tryptophan with *dl*-leucine or *dl*-alanine, it was condensed with *d*- $\alpha$ -bromopropionyl chloride to *d*- $\alpha$ -bromopropionyl-*d*-tryptophan, which softens at  $65^\circ$  and melts at  $72^\circ$ . *d*-Alanyl-*d*-tryptophan is very soluble in water, has a

bitter taste, decomposes at about  $150^{\circ}$  (corr.),  $[\alpha]_D^{20} + 18.65^{\circ}$ , and forms a well-crystallised, copper salt. *d*-*a*-Bromoisohexoyl-*d*-tryptophan crystallises in needles, m. p.  $118^{\circ}$  (corr.),  $[\alpha]_D^{20} + 27.1^{\circ}$ . 1-Leucyl-*d*-tryptophan forms colourless, microscopic, hair-like, matted needles, which sinter at  $130^{\circ}$ , m. p.  $148^{\circ}$  (corr., decomp.), and taste bitter with a sweet after-taste; they have  $[\alpha]_D^{20} + 4.48^{\circ}$ .

*d*-*a*-Bromoisohexylglycyl-*d*-tryptophan, prepared by condensing glycyltryptophan in the usual manner, sinters at  $60^{\circ}$ , m. p.  $90-98^{\circ}$ ,  $[\alpha]_D^{20} + 54.47^{\circ}$ . The tripeptide, 1-leucylglycyl-*d*-tryptophan, forms a colourless, amorphous, sparingly soluble mass (decomp.  $234^{\circ}$ , corr.),  $[\alpha]_D^{20} + 32.30^{\circ}$ . E. F. A

**Phenyltriazene (Diazobenzeneamide).** OTTO DIMROTH (*Ber.*, 1907, 40, 2376—2389. Compare Abstr., 1903, i, 450; 1905, i, 311, 618; this vol., i, 21).—*Phenyltriazene*, the preparation of which is described in this paper, is of great interest as the first monosubstituted triazene. Although it is formed probably as the first product of the action of diazobenzene salts on ammonia, which leads finally to the formation of bisdiazobenzeneamide, all attempts to isolate it from the reacting mixture have been unsuccessful. It has been obtained, however, by reduction of phenylazoimide (compare Griess, *Annalen*, 1866, 137, 77; Curtius, Abstr., 1896, i, 34; 1900, ii, 474) by means of stannous chloride and hydrogen chloride in ethereal solution at  $-20^{\circ}$ . The resulting *stannichloride* is stable only in contact with ether at low temperatures, decomposes on evaporation of the ether or, with evolution of nitrogen, on treatment with water or alcohol, and yields the free base when stirred with 20% sodium hydroxide and ether at  $-18^{\circ}$ .

*Phenyltriazene*,  $N_3H_2Ph$ , purified by conversion into its stable copper derivative and liberation by means of potassium cyanide below  $-18^{\circ}$ , crystallises from a mixture of ether and light petroleum in colourless, pointed leaflets, m. p.  $50^{\circ}$  (decomp.), is stable in solution only below  $-15^{\circ}$ , and decomposes when solid at the ordinary temperature, or when treated with solvents at the ordinary temperature, or with acids at low temperatures, developing heat and forming aniline and nitrogen. When spread in a thin layer on a porous plate, the leaflets change in five to ten minutes into small, indistinct crystals, m. p.  $40^{\circ}$  (decomp. evolving gas); this second *modification* is more stable, and when dissolved in ether at  $-18^{\circ}$  and precipitated with light petroleum is retransformed into the modification crystallising in leaflets. The nature of the modifications is discussed and it is concluded that they are stereoisomerides,  $\begin{smallmatrix} NPh \\ | \\ N \cdot NH_2 \end{smallmatrix}$  and  $\begin{smallmatrix} Ph \cdot N \\ | \\ N \cdot NH \end{smallmatrix}$ , or

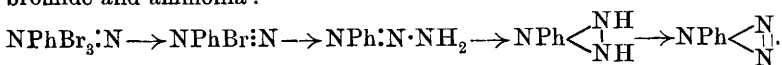
more probably, the desmotropic forms,  $NPh:N \cdot NH_2$  and  $NPh \begin{smallmatrix} < NH \\ NH \end{smallmatrix}$ .

The *copper* derivative,  $C_6H_5N_3Cu$ , formed by shaking phenyltriazene with cuprous chloride in ethereal solution at  $-15^{\circ}$ , crystallises from much boiling benzene or chloroform in yellow prisms with strong electrical properties, decomposes without melting at high temperatures, is stable at the ordinary temperature when pure, and is decomposed by concentrated sulphuric acid, hot ammonia, or pyridine. The *silver*

derivative forms unstable, pale yellow needles, decomposes when dried, and yields an odour of phenylazoimide on treatment with ammonia or sodium hydroxide.

The action of phenylcarbimide on phenyltriazene in ethereal solution leads to the formation of a *carbamide*, which on treatment with methyl iodide and sodium methoxide yields *s*-phenylmethylcarbamidoazobenzene (Abstr., 1905, i, 311).

*Phenylcarbamidoazobenzene*,  $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{NPh}$ , crystallises in needles having strong electrical properties, m. p.  $141^\circ$ , has pronounced acid properties, and is decomposed by hot dilute hydrochloric acid yielding an odour of phenylcarbimide. The *sodium*, *potassium*, and *silver*,  $\text{C}_{13}\text{H}_{11}\text{ON}_4\text{Ag}$ , salts are described. Phenyltriazene is oxidised readily and quantitatively to phenylazoimide by means of sodium hypobromide or alkaline silver solutions; this action is employed to explain the formation of phenylazoimide from diazobenzene perbromide and ammonia:



Small amounts of phenylazoimide are recognised best by conversion into 5-amino-1:4-diphenyl-1:2:3-triazole, m. p.  $179^\circ$  ( $169^\circ$ : Abstr., 1903, i, 129). When oxidised by potassium permanganate at  $-15^\circ$ , phenyltriazene yields a strong odour of *isonitrile*, but not phenylazoimide.

The action of benzaldehyde on phenyltriazene in ethereal solution at  $-15^\circ$  leads to the formation of benzylideneaniline and nitrogen. With  $\beta$ -naphthol, phenyltriazene evolves nitrogen and does not form benzenazo- $\beta$ -naphthol. G. Y.

### Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXIV. *N*-Aminotriazole (*s*-Dihydrotetrazine).

ROBERT STOLLÉ (*J. pr. Chem.*, 1907, [ii], 75, 416—432. Compare this vol., i, 359).—It is found now that the substance formed together with 1:3:6-triphenyl-1:2-dihydro-1:2:4:5-tetrazine by the action of phenylhydrazine on dibenzoylhydrazide dichloride and previously assumed to be 1:3:6-triphenyl-1:4-dihydro-1:2:4:5-tetrazine (Abstr., 1906, i, 462), yields an acetyl derivative which is identical with the condensation product of *as*-acetylphenylhydrazide and dibenzoylhydrazide dichloride, and must be therefore 1-acetylanilino-

2:5-diphenyl-1:3:4-triazole,  $\begin{smallmatrix} \text{N}\cdot\text{CPh} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{CPh} \end{smallmatrix} > \text{N}\cdot\text{NPhAc}$ . This result supports

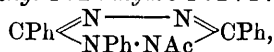
Bülow's view that the supposed *s*-dihydrotetrazines are *N*-amino-1:3:4-triazoles (Abstr., 1906, i, 905; this vol., i, 99). The feeble basic character of these substances (Pinner, Abstr., 1898, i, 94) is ascribed to the *as-sec*-hydrazide grouping:  $\text{NH}_2\cdot\text{N}(\text{CR}')_2$ , it being well known that the basic properties of hydrazine are greatly diminished already in the primary hydrazides. It was proposed to bring further evidence as to the constitution of the *N*-aminotriazoles by, on the one hand, elimination of the methyl group from 1-methylanilino-2:5-di-*p*-bromophenyl-1:3:4-triazole formed by the action of *as*-phenylmethylhydrazine on di-*p*-bromobenzoylhydrazide dichloride, and, on the



other, by the methylation of 1-anilino-2:5-diphenyl-1:3:4-triazole. This, however, could not be accomplished, since attempts in the first direction resulted in the elimination of the group  $\cdot\text{NPhMe}$  with formation of 2:5-di-*p*-bromophenyl-1:3:4-triazole, and in the second, in the formation of only the methiodide,  $\begin{matrix} \text{N}:\text{CPh} \\ \text{N}:\text{CPh} \end{matrix} > \text{N}\cdot\text{NPh,MeI}$ .

1-Acetylanilino-2:5-diphenyl-1:3:4-triazole,  $\text{C}_{22}\text{H}_{18}\text{ON}_4$ , crystallises in colourless prisms, m. p.  $180^\circ$ , and when boiled with aqueous sodium carbonate solution is hydrolysed, forming 1-anilino-2:5-diphenyl-1:3:4-triazole. In connexion with the formation of the acetyl compound, it is shown that *as*-acetylphenylhydrazine remains unchanged when heated with benzene in a sealed tube at  $140^\circ$ .

2-Acetyl-1:3:6-triphenyl-1:2-dihydro-1:2:4:5-tetrazine,



formed from triphenyl-1:2-dihydrotetrazine, crystallises in prisms, m. p.  $186^\circ$ . Only triphenyltriazole and diphenyloxadiazole could be isolated from the product of the action of *s*-acetylphenylhydrazine on dibenzoylhydrazide dichloride.

1-Methylanilino-2:5-di-*p*-bromophenyl-1:3:4-triazole,  $\text{C}_{21}\text{H}_{16}\text{N}_4\text{Br}_2$ , forms small prisms, m. p.  $251^\circ$ .

1-Anilino-2:5-diphenyl-1:3:4-triazole methiodide,  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{,MeI}$ , crystallises in leaflets, m. p.  $188^\circ$ .

1-Methylanilino-2:5-diphenyl-1:3:4-triazole,  $\text{C}_{21}\text{H}_{18}\text{N}_4$ , prepared by heating dibenzoylhydrazide dichloride with *as*-phenylmethylhydrazine in benzene solution at  $115^\circ$ , forms small, stout crystals, m. p.  $174^\circ$ .

The author now adopts Busch's formula (Abstr., 1901, i, 488; compare 1906, i, 315) for the benzylidene derivative of Curtius and Heidenreich's dicarbamide (Abstr., 1895, i, 12), as the action of iodine on its silver derivative leads to the formation of the intensely coloured

azo-compound  $\begin{matrix} \text{N}:\text{CO} \\ \text{N}:\text{CO} \end{matrix} > \text{N}\cdot\text{N}:\text{CHPh}$ . Similarly, methenylcarbohydrazide (Curtius and Heidenreich, *loc. cit.*; Busch, *loc. cit.*) must be 1-amino-2-hydroxy-1:3:4-triazole, since it yields a *benzylidene* derivative,  $\begin{matrix} \text{N}=\text{CH} \\ \text{N}:\text{C}(\text{OH}) \end{matrix} > \text{N}\cdot\text{N}:\text{CHPh}$ , crystallising in needles, m. p.  $178^\circ$ .

Purgotti and Viganò's dibenzophenone- and diacetophenone-*p*-urazines (Abstr., 1902, i, 322) are shown to be identical with diphenylketazine (Curtius and Rauterberg, Abstr., 1891, 1359) and bisphenylmethylazimethylene (Curtius and Thun, Abstr., 1891, 1355) respectively.

G. Y.

**Condensation of Acetoguanamine with Aromatic Aldehydes.** V. HUMNICKI (*Bull. Acad. Sci. Cracow*, 1907, 16–24).—Formoguanamine (diaminocyanuric dihydride) and its homologues were first prepared by von Nencki (Abstr., 1874, 1089; 1875, 754, 1201; 1876, 188, 191, 509; 1877, i, 299) by the destructive distillation of the corresponding guanidine salt, and the formulæ now assigned to the group are due to Claus (*Ber.*, 1876, 9, 722) and Bamberger and Dieckmann (Abstr., 1892, 736; compare Diels, Abstr., 1899, i, 406).

When acetoguanamine,  $\text{N} \begin{smallmatrix} \text{CMe} \text{---} \text{N} \\ \text{C}(\text{NH}_2) \text{:N} \end{smallmatrix} \text{C} \cdot \text{NH}_2$ , is condensed with benzaldehyde in presence of sulphuric acid, *benzylideneacetoguanamine sulphate*,  $\text{N} \begin{smallmatrix} \text{C}(\text{CH} \text{:} \text{CHPh}) \text{---} \text{N} \\ \text{C}(\text{NH}_2) \text{=====N} \end{smallmatrix} \text{C} \cdot \text{NH}_2, \text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ , m. p.  $286^\circ$  (decomp.), is formed. It crystallises from dilute methyl alcohol in long needles, and on treatment with sodium hydroxide solution yields the *free base*, m. p.  $260^\circ$  (approx.), in small needles. The *hydrochloride*,  $\text{C}_{11}\text{H}_{11}\text{N}_5, \text{HCl}, \text{H}_2\text{O}$ , is crystalline, as are also the *chromate* and *picrate*. The *dibenzoyl* derivative, m. p.  $146^\circ$ , obtained by heating the base with benzoic anhydride at  $130^\circ$ , crystallises from a mixture of alcohol and benzene, and yields with bromine in chloroform a *bromo-derivative* containing 23.7% of bromine in place of 27.5% as required by the formula  $\text{C}_{25}\text{H}_{19}\text{O}_2\text{N}_5\text{Br}_2$ . Benzylideneacetoguanamine is not produced when guanidine cinnamate is submitted to destructive distillation (compare Elzanowski, *Inaug. Diss. Freiburg*, 1898). Formoguanamine does not condense with benzaldehyde in presence of sulphuric acid; acetoguanamine, on the contrary, condenses with a number of aldehydes, but not with acetophenone or benzophenone. With formaldehyde it furnishes a *base* which gives amorphous salts with mineral acids. The *product* contained with *o*-hydroxybenzaldehyde is also amorphous, but that prepared by condensation with *p*-hydroxybenzaldehyde yields a crystalline, yellow *sulphate*. The condensation *product* obtained with *o*-nitrobenzaldehyde also gives a crystalline *sulphate*, but the *substances* obtained from anisole and vanillin are amorphous. The greater reactivity of acetoguanamine appears to be due to the presence of the methyl group, since 2-methylpyridine and 2-methylquinoline show a similar readiness to condense with aldehydes.

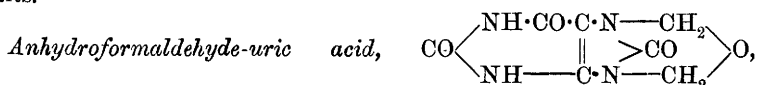
*Dibenzoylaceto-guanamine*, m. p.  $153\text{--}154^\circ$ , obtained by heating acetoguanamine with benzoic anhydride, crystallises from alcohol or benzene in needles. *Dibenzoylformoguanamine*, m. p.  $207\text{--}208^\circ$ , similarly prepared, crystallises in broad needles from the same solvents.  
T. A. H.

**Xanthine Bases.** ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1907, 4, 244--247).--Polemical. Certain statements in Steudel's recent historical article on the subject (*Biochem. Zentr.*, 6, 125) are objected to.  
W. D. H.

**Compounds of Uric Acid with Formaldehyde.** ARTHUR NICOLAÏER (*Chem. Zentr.*, 1907, i, 949; from *Arch. klin. Med.*, 89, 168--185. Compare *Abstr.*, 1905, ii, 188).--The solvent action of formaldehyde on uric acid results from the formation of *additive* compounds which have been found in urotropin urine.

Diformaldehyde-uric acid (Weber, Pott, and Tollens, *Abstr.*, 1898, i, 66; Weber and Tollens, *ibid.*, 300) is decomposed by alkalis, but is stable towards acids, gives the murexide reaction, reduces silver nitrate in alkaline solution, and forms a *compound* with 2 mols. of urotropin. His statement that diformaldehyde-uric acid may be separated from uric acid by means of concentrated sulphuric acid could not be confirmed.

*Formaldehyde-uric acid* (oxymethylene-uric acid),  $C_5H_4O_8N_4 \cdot CH_2O$ , crystallises in needles or prisms, decomposes slowly at  $37^\circ$ , rapidly above  $320^\circ$  or when treated with alkalis, and gives reactions similar to those of the diformaldehyde-uric acid; it forms crystalline *alkali* salts.



formed by pouring diformaldehyde-uric acid dissolved in concentrated sulphuric acid into ice-water, or by the action of trioxymethylene on uric acid in sulphuric acid solution, decomposes at 125° or on prolonged boiling with water, is soluble in alkalis, reduces silver nitrate, and gives an orange coloration when evaporated with nitric acid and treated with ammonia. It is not found in urine, being decomposed in the body.

The author considers that the formation of the additive compounds prevents the total decomposition of uric acid in the human body.

G. Y.

**Indigotin-like Groups of Blue Colouring Matters from Isatin.** CARL LIEBERMANN and RUDOLPH KRAUSS (*Ber.*, 1907, 40, 2492—2515).—The authors have prepared, in the pure state, a number of members of the pyrrole-blue group (compare Liebermann and Häse, *Abstr.*, 1905, i, 841), and have also extended Schotten's isatin-blue group (*Abstr.*, 1891, 928, 1491). Attempts to obtain useful variants of these colouring matters by modifying the basic portion of the molecule have been successful in only one instance, in which piperazine was introduced in place of the piperidine.

In the pyrrole-blue group the authors have prepared several new derivatives. To the two pyrrole-blues, A and B, the new formulæ,  $C_{24}H_{16}O_3N_4$  and  $C_{24}H_{16}O_2N_4$  respectively, are ascribed (compare Liebermann and Häse, *loc. cit.*). The A-compound is formed by the action of the oxygen of the air on the B-derivative, which passes into the other the more readily as the conditions of its preparation are rendered more unfavourable. The formation of compounds of the B-type, such as dichloropyrrole-blue B, is regarded as taking place according to the equation:  $2C_8H_4O_2NCl + 2C_4H_5N = 2H_2O + C_{24}H_{14}O_2N_4Cl_2$ , and the conclusion is drawn that compounds of the pyrrole-blue group have the same structure as those of the indophenines (compare Baeyer and Lazarus, *Abstr.*, 1886, 154; Oster, *Abstr.*, 1904, i, 914).

*Dichloropyrrole-blue* B,



obtained from chloroisatin and pyrrole, is a blue powder with metallic lustre and closely resembles pyrrole-blue B. The *chloroisatin*,

$$\text{C}_8\text{H}_4\text{O}_2\text{NCl},$$

here used is obtained by passing chlorine into water containing finely-divided isatin in suspension, and separates from alcohol in crystals, m. p. 246°.

Tetrachloropyrrole-blue, prepared from dichloroisatin, was not analysed.

*Dibromopyrrole-blue* A,  $C_{24}H_{14}O_3N_4Br_2$ , obtained from bromoisatin and pyrrole, separates from alcohol in crystals, m. p.  $255^\circ$ .

*Tetrabromopyrrole-blue* A or B,  $C_{24}H_{12}O_3N_4Br_4$  or  $C_{24}H_{12}O_2N_4Br_4$ , prepared from dibromoisatin, forms a blue powder with slight metallic lustre.

*Dinitrpyrrole-blue* A,  $C_{24}H_{14}O_3N_4(NO_2)_2$ , obtained from nitroisatin and pyrrole, exhibits metallic lustre. The *nitroisatin*,  $C_8H_4O_4N_2$ , employed crystallises from alcohol in yellow needles, m. p.  $245^\circ$  (decomp.).

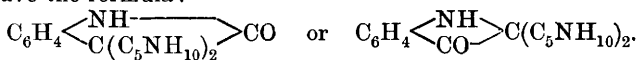
Acetyl- $\psi$ -isatin and pyrrole yield pyrrole-blue B, the acetyl group being removed during the reaction.

*Dibenzoylpyrrole-blue* A,  $C_{24}H_{14}O_3N_4Bz_2$ , and B,  $C_{24}H_{14}O_2N_4Bz_2$ , prepared from benzoyl- $\psi$ -isatin, form blue powders, the B-compound being less soluble than the A and exhibiting metallic lustre. The B-compound dissolves in cold concentrated sulphuric acid without change, but after some time the solution is found to contain benzoic and *pyrrole-blue-disulphonic acids*,  $C_{24}H_{14}O_2N_4(SO_3H)_2$ .

Benzoylisatin exhibits the indophenine reaction, *dibenzoylisatinindophenine*,  $C_6H_4 \begin{smallmatrix} \text{NBz} \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_4\text{SH}_2 \\ \text{C}_4\text{SH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{NBz} \\ \text{CO} \end{smallmatrix} C_6H_4$ , being obtained as an insoluble, blue powder.

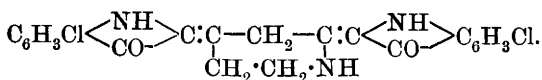
If indole or acetonilpyrrole is used in place of pyrrole, steric relations prevent the formation of compounds analogous with pyrrole-blue.

The authors confirm the formulæ given by Schotten (*loc. cit.*) for the colourless dipiperides prepared from isatin and bromoisatin, and also the provisional formula,  $C_{21}H_{17}O_2N_3$ , given by him to isatin-blue. Substituted isatins vary in their capability of yielding monopiperides, which are readily obtained when the acid character of the isatin is reinforced by the introduction of a halogen or acid group. All the six monopiperides prepared (*vide infra*) resemble one another closely in external appearance, dissolve readily in alcohol, and form measurable, honey-yellow prisms. Whether formulæ analogous to that chosen by Schotten (*loc. cit.*) for the dibromoisatin derivative are to be ascribed to them, or whether they are to be regarded as salts of normal isatin, for example,  $C_6H_3Br \begin{smallmatrix} \text{N} \\ \text{CO} \end{smallmatrix} \text{C} \cdot O \cdot NH_2 \cdot C_5H_{10}$ , is uncertain. In the cold, acids decompose them into their components far more slowly than is the case with true salts, but this may result from the peculiar character of normal isatin salts. The dipiperides form white leaflets sparingly soluble in alcohol, and yield insoluble blue colouring matters when treated with dehydrating agents such as acetic anhydride. They are, like the monopiperides, unstable compounds, being rapidly resolved into their components by cold mineral acids, and have the formula:



Isatin-blue may be readily purified by dissolving in fuming hydro-

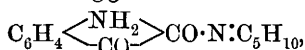
chloric acid, diluting with water, filtering, and treating with ammonia.



The annexed structure given to isatindipiperide - blue, indicates that the

two isatin residues are united by a double linking, just as in indigo, except that in the present instance the union takes place by way of the piperidine residue.

*Isatinmonopiperide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C} \cdot \text{O} \cdot \text{NH}_2 \cdot \text{C}_5\text{H}_{10}$ , or



crystallises from alcohol in yellow, monoclinic prisms [A. FOCK.  $a:b:c = 1.1027 : 1 : 0.5044$ ;  $\beta = 93^\circ 51'$ ], m. p.  $135^\circ$ , yields no colour when heated with acetic anhydride, and is quantitatively decomposed into its constituents by fuming hydrochloric acid. *Bromoisatinmonopiperide*,  $\text{C}_8\text{H}_4\text{O}_2\text{NBr} \cdot \text{C}_5\text{H}_{11}\text{N}$ , separates in yellow prisms, m. p.  $208^\circ$ . *Dibromoisatinmonopiperide* (compare Schotten, *loc. cit.*) forms monoclinic crystals [A. FOCK.  $a:b:c = 1.2349 : 1 : 0.7575$ ;  $\beta = 99^\circ 2'$ ]. *Chloroisatinmonopiperide*,  $\text{C}_8\text{H}_4\text{O}_2\text{NCl} \cdot \text{C}_5\text{H}_{11}\text{N}$ , has m. p.  $185^\circ$ . *Nitroisatinmonopiperide*,  $\text{C}_8\text{H}_4\text{O}_2\text{N} \cdot \text{NO}_2 \cdot \text{C}_5\text{H}_{11}\text{N}$ , separates in pale yellow leaflets, m. p.  $198^\circ$ . *Benzoylisatinmonopiperide*,  $\text{C}_8\text{H}_4\text{O}_2\text{NBz} \cdot \text{C}_5\text{H}_{11}\text{N}$ , crystallises from light petroleum in leaflets, m. p.  $138-140^\circ$ .

*Isatinpiperazide*,  $\text{C}_{24}\text{H}_{28}\text{O}_3\text{N}_6$ , decomposes at about  $196^\circ$ , and appears to be a compound intermediate between the mono- and di-piperides. It gives a small proportion of a blue colouring matter on treatment with acetic anhydride.

*Dibromoisatinpiperazide*,  $\text{C}_4\text{H}_8(\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Br}_2 \cdot \text{NO}_2)_2$ , or *bis-dibromoisatinic piperazide*,  $\text{C}_4\text{H}_8(\text{N} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Br}_2 \cdot \text{NH}_2)_2$ , prepared from dibromoisatin and piperazine, is a yellow compound decomposing at  $245^\circ$ .

The isatinpiperide-blues described below were prepared by the action of acetic anhydride on the corresponding dipiperides suspended in boiling toluene.

Isatinpiperide-blue and dibromoisatinpiperide-blue were obtained purer than the preparations of Schotten (*loc. cit.*). Isatinpiperide-blue hydrochloride and *dichloroisatinpiperide-blue*,  $\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_3\text{Cl}_2$ , were also prepared.

T. H. P.

**Synthesis of Tetrazoles from Phenylazoimide.** OTTO DIMROTH and SIEGFRIED MERZBACHER (*Ber.*, 1907, 40, 2402—2404. Compare Abstr., 1905, i, 98; this vol., i, 97).—When heated in alcoholic sodium ethoxide solution in a sealed tube in the water bath, phenylazoimide and benzylidenephénylhydrazone react forming aniline and 1:4-diphenyltetrazole. Since under similar conditions, phenylazoimide and benzylidene-*p*-bromophénylhydrazone form aniline and 4-phenyl-1-*p*-bromophényltetrazole, the group NPh appearing as aniline must be that of the phenylazoimide.

1:4-Diphenyltetrazole has m. p.  $101.5-102^\circ$ , at which temperature Wedekind's preparation (m. p.  $106-107^\circ$ ; Abstr., 1896, i, 630) is now found to melt.

4-Phenyl-1-p-bromophenyltetrazole,  $C_6H_4Br \begin{smallmatrix} N:N \\ | \\ N:CPH \end{smallmatrix}$ , crystallises in slightly yellow prisms, m. p. 122°. G. Y.

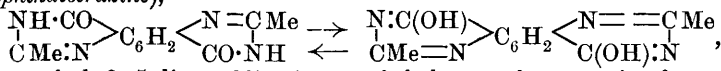
**Quinazolines. XIX. Synthesis of 1:3:6:8-Naphthatetrazines from p-Diaminoterephthalic Acid and from Certain of its Derivatives.** MARSTON T. BOGERT and JOHN MAURICE NELSON (*J. Amer. Chem. Soc.*, 1907, 29, 729—739).—Naphthatetrazines have been prepared by Bogert and Dox (Abstr., 1905, i, 841, 949) by the condensation of ethyl succinylsuccinate with guanidine and with acetamidine. Similar compounds have now been obtained by heating ethyl *p*-diaminoterephthalate with formamide, by heating its diacetyl derivative with primary amines, by the action of primary amines on the dilactam of *s*-2:5-diacetylaminoterephthalic acid, and by heating ethyl diphenylcarbaminoterephthalate with aniline. With the exception of 4:9-diketo-2:7-dimethyl-3:8-diisoamyltetrahydro-1:3:6:8-naphthatetrazine, all the naphthatetrazines thus prepared either have very high m. p.'s or are infusible, and are insoluble or nearly so in the usual organic solvents. Those compounds which contain the group  $\cdot CO \cdot NH \cdot \rightleftharpoons C(OH) : N \cdot$  dissolve readily in dilute alkali hydroxides and are reprecipitated by dilute acids.

*Ethyl 2:5-diphenylcarbaminoterephthalate*,  $C_6H_5(NH \cdot CO \cdot NHPh)_2(CO_2Et)_2$ , m. p. 262° (decomp.), obtained by treating ethyl *p*-diaminoterephthalate with phenylcarbimide, forms light yellow crystals. When this substance is heated with hydrazine hydrate in a sealed tube at 130°, a yellow, amorphous substance is produced which does not melt below 320°. *Ethyl 2:5-tetra-acetyldiaminoterephthalate*,  $C_6H_2(NAc)_2(CO_2Et)_2$ , m. p. 207—208° (corr.), from the action of acetic anhydride on ethyl diphenylcarbaminoterephthalate, forms colourless crystals. *Ethyl s-2:5-diacetyldiaminoterephthalate*,  $C_6H_2(NHAc)_2(CO_2Et)_2$ , m. p. 219° (corr.), forms yellowish-white crystals with a green fluorescence, and when heated with propylenediamine at 150° in a sealed tube yields a substance which separates in large yellow crystals. *Ethyl 2:5-diphthaliminoterephthalate*,  $C_6H_2 \left( N \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_4 \right)_2 (CO_2Et)_2$ , m. p. 326° (corr.), obtained by fusing ethyl *p*-diaminoterephthalate with phthalic anhydride, forms cream-coloured crystals. When this substance is treated with ammonia at 150° in a sealed tube, a product is obtained which on heating yields a white, crystalline sublimate, m. p. 228° (uncorr.). If an alcoholic solution of ethyl 2:5-diacetyldiaminoterephthalate is treated with sodium amalgam, a product is obtained which on boiling with acetic anhydride yields the dilactam,  $\begin{smallmatrix} CO- \\ | \\ NAc \end{smallmatrix} C_6H_2 \begin{smallmatrix} NAc \\ | \\ CO \end{smallmatrix}$ , which separates as white, infusible flakes. Bogert and Dox (Abstr., 1905, i, 841) have stated that *p*-diaminoterephthalic acid is not changed by boiling acetic anhydride, but it is now found that the above dilactam is produced.

4:9-Diketotetrahydro-1:3:6:8-naphthatetrazine (4:9-dihydroxy-1:3:6:8-naphthatetrazine),

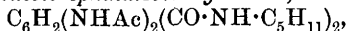
$$\begin{array}{ccc} NH \cdot CO \cdot \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot C \cdot N = CH & \rightleftharpoons & N : C(OH) \cdot \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot C \cdot N = CH \\ \begin{smallmatrix} | \\ CH \end{smallmatrix} : N - \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot C \cdot CO \cdot NH & \leftarrow & \begin{smallmatrix} | \\ CH \end{smallmatrix} : N - \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot \begin{smallmatrix} | \\ CH \end{smallmatrix} \cdot C \cdot C(OH) : N \end{array}$$

is obtained from ethyl *p*-diaminoterephthalate and formamide as a pale yellow, amorphous powder. 4:9-Diketo-2:7-dimethyltetrahydro-1:3:6:8-naphthattetrazine (4:9-dihydroxy-2:7-dimethyl-1:3:6:8-naphthattetrazine),

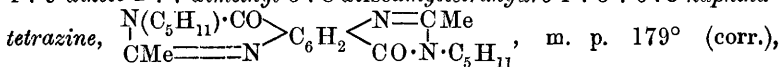


from ethyl 2:5-diacetyldiaminoterephthalate and ammonia, forms a pale yellow, amorphous powder.

2:5-Diacetyldiaminoterephthalisoamylamide,



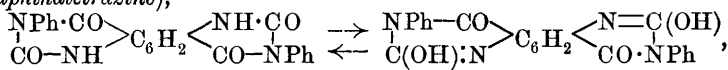
m. p. 255° (corr.), obtained by heating ethyl 2:5-diacetyldiaminoterephthalate or the dilactam with isoamylamine, forms long, silky needles, and when boiled with dilute potassium hydroxide is converted into 4:9-diketo-2:7-dimethyl-3:8-diisoamyltetrahydro-1:3:6:8-naphthattetrazine,



which crystallises in yellowish-white needles with a green fluorescence, and yields a yellowish-white, crystalline bromo-derivative, m. p. about 290°.

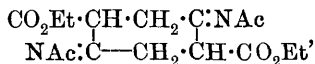
4:9-Diketo-3:8-diphenyl-2:7-dimethyltetrahydro-1:3:6:8-naphthattetrazine, from the dilactam of 2:5-diacetyldiaminoterephthalic acid and aniline, crystallises in pale, greenish-yellow leaflets.

2:4:7:9-Tetraketo-3:8-diphenyloctahydro-1:3:6:8-naphthattetrazine (2:7-dihydroxy-4:9-diketo-3:8-diphenyltetrahydro-1:3:6:8-naphthattetrazine),



from ethyl 2:5-diphenylcarbaminoterephthalate and aniline, forms bright yellow crystals.

Ethyl diacetylminosuccinylsuccinate,



m. p. 215—216° (corr.), obtained by the action of acetic anhydride on ethyl di-iminosuccinylsuccinate, forms white crystals with a green fluorescence; the free acid is very unstable. Ethyl dibenzoyliminosuccinylsuccinate, m. p. 255° (uncorr.), forms yellow, feathery needles, and when heated with a solution of bromine in acetic anhydride is converted into a substance, m. p. 264° (uncorr.), which is probably ethyl dibenzoylaminoterephthalate. E. G.

### Action of Nitrites and Nitrosyl Chloride on Aldazines.

HARTWIG FRANZEN and F. ZIMMERMANN (*Ber.*, 1907, 40, 2009—2012).—Benzylideneazine may be boiled with amyl nitrite without action occurring; if, however, a drop or two of acetyl chloride is added to an ethereal solution of the azine and nitrite, a reaction at once takes place, gas is evolved, consisting of nitrogen and nitrous oxide in equal volumes, and benzaldehyde and benzylidene diisoamyl ether are formed. The corresponding diethyl compound is obtained when ethyl nitrite is employed. This reaction also occurs when substituted benzylideneazines are used, thus cuminaldehyde and isopropylbenzylidenediisoamyl ether,

$C_{20}H_{84}O_2$ , are obtained from isopropylbenzylideneazaine. Experiments, however, with salicyldazine and *o*-methoxybenzylideneazaine were without result.

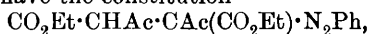
Nitrosyl chloride (2 mols.) and benzylideneazaine (1 mol.) in ether give benzylidene chloride (1 mol.), benzaldehyde (1 mol.), nitrogen (1 mol.), and nitrous oxide (1 mol.).

This result is used to explain the action of the acetyl chloride in the above experiments. The nitrosyl chloride, resulting from the interaction of nitrite and chloride, gives benzylidene chloride, which, in its turn, reacts with free amyl alcohol to produce the acetal compound and hydrogen chloride. The trace of hydrogen chloride regenerates nitrosyl chloride with the nitrite, and so the cycle of changes is repeated until the action is completed. W. R.

**Behaviour of Diazo-compounds with Keto-enolic Desmotropic Compounds.** OTTO DIMROTH (*Ber.*, 1907, 40, 2404—2411).—5-Hydroxy-1-phenyl-1:2:3-triazole couples with diazobenzene chloride forming two isomeric products (Dimroth and Eberhardt, *Abstr.*, 1905, i, 100), of which the scarlet isomeride must be an azo-derivative. With the object of throwing light on the constitution of the colourless isomeride, the action of diazobenzene chloride and of nitrous acid on the desmotropic compounds, 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylic acid and 1-phenyl-1:2:3-triazole-5-one-4-carboxylic acid, has been investigated. It is found that whilst the enolic acid loses carbon dioxide and forms the scarlet azo-compound and 4-isonitroso-1-phenyl-5-triazolone (this vol., i, 96) respectively, the keto-acid does not react with either reagent. These results led the author to study the action of diazo-compounds on the enolic and keto-forms of other desmotropic compounds.

The manner in which the coupling of enolic and keto-compounds with diazo-compounds may take place is discussed, and a number of experiments described, the compounds selected for study being such as permit of the isolation of both forms, the intramolecular transformation taking place in solution only slowly. To avoid this transformation during the reaction, the coupling was carried out with *p*-nitroantidiazobenzene hydrate in alcoholic solution at temperatures below 0°. It is found that the reaction takes place readily with the enolic compounds, but that in no case does the keto-form couple (compare Hantzsch and Kissel, *Abstr.*, 1900, i, 89; Hantzsch, *ibid.*, 618). Also the keto-form of tribenzoylmethane, the enolic modification of which is unstable in alcoholic solution, does not react with *p*-nitroantidiazobenzene hydrate.

Contrary to Bülow and Schlesinger's view (*Abstr.*, 1900, i, 56), ethyl benzeneazodiacetylsuccinate must be formed by the action of diazobenzene chloride on the enolic form of the ester, resulting from transformation of the diketo-modification in presence of sodium acetate, and must have the constitution



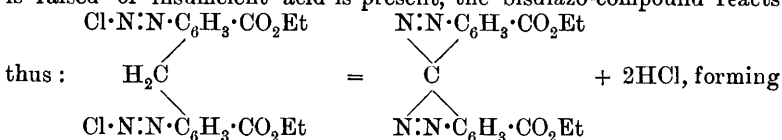
since, if an enolic compound as considered by these authors, it must couple with a second molecule of diazobenzene chloride.



*Ethyl p-nitrobenzeneazomesityloxidoxalate*,  $C_{16}H_{17}O_6N_3$ , crystallises from alcohol in orange prisms, m. p.  $134^\circ$ . *p-Nitrobenzeneazoacetyldibenzoylmethane*,  $C_{23}H_{17}O_5N_3$ , crystallises in orange needles, m. p.  $110.5^\circ$ , and when crystallised from boiling alcohol is converted into a colourless *isomeride*, m. p.  $201^\circ$ ; both isomerides are hydrolysed by sodium ethoxide or ammonia, forming *p-nitrobenzeneazodibenzoylmethane*,  $C_{21}H_{15}O_4N_3$ , which crystallises in yellow leaflets, m. p.  $173^\circ$ .

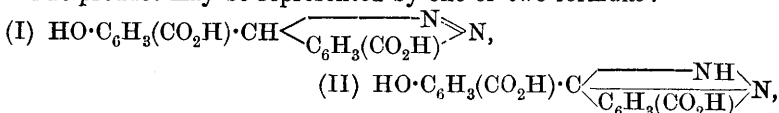
*Ethyl p-nitrobenzeneazodiacetylsuccinate*,  $C_{18}H_{21}O_8N_3$ , forms yellow crystals, m. p.  $153^\circ$ . G. Y.

**A New Type of Bisazo-compounds.** HENRI DUVAL (*Compt. rend.*, 1907, 144, 1222—1224).—When ethyl diaminodiphenylmethanedicarboxylate is diazotised in strongly acid solution at a low temperature, it undergoes the normal reaction, but if the temperature is raised or insufficient acid is present, the bisdiazo-compound reacts



a mixed bisazo-compound, of which the constitution is determined by its method of preparation, properties, and analysis. By heating with sulphuric acid, one of the azo-groups is replaced by hydroxyl, whilst the other is unattacked.

The product may be represented by one of two formulæ:



as (I) an azo-derivative; (II) an indazyl derivative. Of these, the former is probably correct, since the compound is insoluble in acids, forms only a monosubstituted *O*-acetyl derivative, is not attacked by ethyl iodide, and is reduced by sodium amalgam to a hydrazo-compound, which is reoxidised by mercuric oxide to the original substance.

*Ethyl bisazodiphenylmethanedicarboxylate* forms yellow needles, m. p.  $280^\circ$  (decomp.), which are reduced by stannous chloride to a colourless hydrazo-compound, the latter being reoxidised by mercuric oxide in alkaline solution to the original substance. *Hydroxyazodiphenylmethanedicarboxylic acid* (I above) forms clear yellow needles which are easily esterified by ethyl alcohol and hydrochloric acid. The *ethyl ester* crystallises in needles, m. p.  $204^\circ$ , which give a blue coloration with ferric chloride, and which dissolve in alkali hydroxides, but are reprecipitated by carbon dioxide. This ester, when treated with acetic anhydride, gives an *acetyl* derivative, m. p.  $218^\circ$ , which gives no coloration with ferric chloride. *Ethyl chloroazodiphenylmethanedicarboxylate*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH}\langle\text{C}_6\text{H}_3(\text{CO}_2\text{H})\rangle\text{N}\rangle\text{N}$ , m. p.  $151^\circ$ , is formed by heating ethyl bisazodiphenylmethanedicarboxylate with hydrochloric acid in a sealed tube at  $150^\circ$ . E. H.

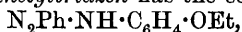
**Phenol-2 : 4 : 6-trisazobenzene.** EUGÈNE GRANDMOUGIN and H. FREIMANN (*Ber.*, 1907, 40, 2662—2664).—Phenol-2 : 4 : 6-trisazobenzene,  $C_6H_2(N:NPh)_3 \cdot OH$ , is formed when 3 mols. of diazobenzene chloride react with phenol in alkaline solution. It is freed from the accompanying bisazobenzene by extraction with alcohol, and crystallises from nitrobenzene in slender, orange needles, m. p. 215°. It dissolves in sodium ethoxide solution with a red coloration, and with sulphuric acid, it gives a deep reddish-violet colour. On reduction it yields 2 : 4 : 6-triaminophenol; this result fixes the position of the azo-groupings. The *acetate* forms yellow crystals, m. p. 165°.

W. R.

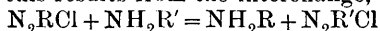
**Tautomerism of Diazoamino-compounds.** OTTO DIMROTH, M. EBLE, and W. GRUHL (*Ber.*, 1907, 40, 2390—2401. Compare Abstr., 1905, i, 311).—The behaviour of phenylmethyltriazene, on the one hand, with phenylcarbimide and, on the other, with acids, led to the assumption that the substance exists in the tautomeric forms: (I)  $NPh:N \cdot NHMe$  and (II)  $NHPh \cdot N:NMe$ . As a proof of (II) by the action of acids was indirect, it seemed desirable to seek for a reaction leading to the formation of derivatives of the type  $NPhR \cdot N:NMe$ . With this object, the formation of bisdiazoamino-compounds has been investigated.

Phenylmethyltriazene couples with diazobenzene salts forming bisbenzeneazomethylamine, prepared previously by Goldschmidt and Badl (Abstr., 1889, 774) and considered by these authors to have the constitution  $NMe(N_2Ph)_2$ , since when boiled with dilute sulphuric acid it yields methylamine, aniline, methyl alcohol, phenol, and aminoazobenzene. It having been found now that the action of alcoholic sulphuric or hydrochloric acid on the bisdiazoamino-compound at temperatures below 0° leads to the formation of 1 mol. of nitrogen and 1 mol. of the diazobenzene salt, isolated in the form of benzeneazo- $\beta$ -naphthol, it seemed probable that the bisdiazoamino-compound has the unsymmetrical constitution:  $N_2Ph \cdot NPh \cdot N_2Me$ . Were this the case, the product obtained by coupling phenylmethyltriazene with p-diazotoluene chloride must be isomeric with that obtained from p-tolylmethyltriazene and diazobenzene chloride. It is shown that, on the contrary, the products of every such pair of reactions investigated are identical in all respects, hence the bisdiazoamino-compounds must have the constitution  $N_2R \cdot NR' \cdot N_2R''$ . It is argued that the decomposition of the bisdiazoamino-compounds must take place in two stages, the products of the first stage being the arylmethyltriazene and the diazo-chloride, and that phenylmethyltriazene exists only in the form (I), and is not tautomeric. The decomposition of arylmethyltriazene by acids is discussed, and the formation of intermediate additive products,  $NHR \cdot NCl \cdot NHMe$  or  $NHR \cdot N:NHMeCl$ , postulated.

Attempts to prepare isomeric triazenes by the action of magnesium p-tolyl bromide on phenylazoimide and by that of magnesium phenyl bromide on p-tolylazoimide were unsuccessful, the products of the two reactions being identical, as were also those of other similar pairs of reactions. *Phenyl-p-phenetyltriazene* has the constitution



since with phenylcarbimide it forms a *phenylcarbamido*-derivative, which on hydrolysis yields diazobenzene chloride and *phenyl-p-phenetylcarbamide*. For similar reasons, *phenyl-α-naphthyltriazen* must have the constitution  $C_{10}H_7 \cdot N_2 \cdot NHPh$ . In agreement with these constitutions, the triazens when decomposed by means of cold dilute hydrochloric acid, yield diazobenzene chloride and *p*-phenetidine, and *α*-diazonaphthalene chloride and aniline respectively. On the other hand, the decomposition by means of boiling dilute hydrochloric acid is more complicated, *phenyl-α-naphthyltriazen* yielding aniline, *α*-naphthylamine, phenol, *α*-naphthol, and benzeneazobenzene. It is considered that this results from the interchange,



(compare Griess, Abstr., 1883, 56; Schraube and Fritsch, Abstr., 1896, i, 221; Hantzsch and Perkin, Abstr., 1897, i, 465), which takes place in acid solution slowly at the ordinary temperature and therefore presumably more rapidly in the boiling acid. To this interchange must be ascribed also the complicated decomposition of diazoamino-compounds observed by Noetting and Binder (Abstr., 1888, 271).

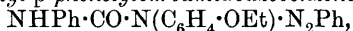
The following arylmethyltriazens,  $N_2R \cdot NHMe$ , are formed by the action of magnesium methyl iodide on the corresponding diazo-imides.

$R = C_7H_7(p)$ : crystallises from light petroleum in colourless plates, m. p.  $81.5^\circ$ ; the *silver* derivative was analysed.  $R = C_6H_4Br(p)$ : crystals, m. p.  $86-86.5^\circ$ .  $R = C_6H_4 \cdot OEt(p)$ : m. p.  $73^\circ$ .

The bisarylazomethylamines,  $N_2R \cdot NMe \cdot N_2R'$ , were hydrolysed with cold alcoholic hydrogen chloride.

$R = Ph$ ,  $R' = C_7H_7(p)$ : yellow needles, m. p.  $84.5$  or, in one preparation, m. p.  $76^\circ$ , yields *p*-diazotoluene chloride and aniline.  $R = Ph$ ,  $R' = C_6H_4Br(p)$ : brownish-yellow needles, m. p.  $119^\circ$ , yields diazobenzene chloride and *p*-bromoaniline.  $R = Ph$ ,  $R' = C_6H_4 \cdot OEt(p)$ : brownish-yellow prisms, m. p.  $71.5^\circ$ , yields diazobenzene chloride and *p*-phenetidine. The diazo-chlorides were isolated by coupling with  $\beta$ -naphthol, the amines by conversion into the acetyl derivatives.

*Phenyl-p-phenetyltriazen*,  $C_{14}H_{15}ON_3$ , crystallises in yellow leaflets, m. p.  $113^\circ$ . *s-Phenyl-p-phenetylcarbamidoozobenzene*,



forms yellowish-white needles, m. p.  $115^\circ$ . *s-Phenyl-p-phenetylcarbamide*,  $NHPh \cdot CO \cdot NH \cdot C_6H_4 \cdot OEt$ , m. p.  $187^\circ$ , crystallises from alcohol.

*Phenyl-α-naphthyltriazen* crystallises in reddish-brown needles, m. p.  $84^\circ$ . *s-Diphenylcarbamidoozonaphthalene*,



crystallises in yellow needles, m. p.  $110^\circ$ .

G. Y.

**Synthesis of Protein by Trypsin.** ALONZO E. TAYLOR (*J. Biol. Chem.*, 1907, 3, 87-94).—The amino-acids resulting from the hydrolysis of protamine (derived from *Roccus lineatus*) by trypsin, were placed in concentrated form either as the free acids or their carbonates in contact with a very resistant trypsin prepared from the mollusc, *Schizothærus nuttallii*, for five months at room temperature. At the end of this time, 1.8 grams of protamine were obtained, 400

grams of protamine sulphate having been originally employed for the hydrolysis. A blank experiment in which the trypsin solution had been boiled gave negative results. The term synthesis through ferment action is in the direct sense a misnomer. The ferment simply accelerates the reaction of synthesis, but even in the presence of the ferment the velocity is slow.

W. D. H.

**Synthesis of Protein by Pepsin.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1907, 3, 95—99).—Paranuclein, which is derived from caseinogen by incomplete digestion with pepsin, is probably a mixture of two substances differing in their percentage of phosphorus. Paranuclein containing 4.175% of phosphoric acid digested with lime-water at 40° for twelve hours yields a small quantity of paranuclein A, which contains only 1.5% of phosphoric acid. By acting at 40° on an acid concentrated solution of the products of the peptic digestion of caseinogen, containing no caseinogen or paranuclein, a substance is precipitated which is identical with paranuclein A. Appropriate control experiments gave negative results.

W. D. H.

**Hydrolysis of Excelsin.** THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, 19, 53—60).—Excelsin (the globulin of Brazil nuts) was obtained in crystalline form: hexagonal plates belonging to the regular system. On acid-hydrolysis it yielded in parts per cent.: glycine, 0.6; alanine, 2.33; aminovaleric acid, 1.51; leucine, 8.7; proline, 3.65; phenylalanine, 3.55; aspartic acid, 3.85; glutamic acid, 12.94; serine, 0; cystine, 0; oxyproline, 0; tyrosine, 3.03; arginine, 16.02; histidine, 1.47; lysine, 1.64; ammonia, 1.8. The large proportion of arginine is unusual; tryptophan was present.

W. D. H.

**Hydrolysis of Hordein.** THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, 19, 117—124).—The composition of hordein, the alcohol-soluble protein of barley, is, C, 54.29; H, 6.80; N, 17.21; S, 0.83, and O, 20.87%. On acid-hydrolysis it yields: glycine, 0; alanine, 0.43; valine, 0.13; leucine, 5.67; proline, 13.73; phenylalanine, 5.03; glutamic acid, 36.35; tyrosine, 1.67; arginine, 2.16; histidine, 1.18; lysine, 0; ammonia, 4.87. Aspartic acid and serine were not isolated; cystine and oxyproline were not determined, and tryptophan was found to be present. Like other proteins soluble in alcohol, it yields no lysine, little histidine and arginine, and much ammonia. The proportion of glutamic acid is the same as in gliadin. Proline, however, is twice as abundant as in gliadin, and greatly exceeds that obtained so far from any protein.

W. D. H.

**The Existence in Wool of Sulphur united with Oxygen.** PAUL N. RAIKOW (*Chem. Zeit.*, 1907, 31, 539—540. Compare Abstr., 1905, i, 725).—Polemical. A reply to Grandmougin (*Chem. Zeit.*, 1907, 31, 174).

P. H.

**The Lecithin of Bone-Marrow.** S. W. OTOLSKI (*Biochem. Zeitsch.*, 1907, 4, 124—153).—The lecithin found in bone-marrow yields on decomposition: choline, glycerophosphoric acid, and unsaturated fatty-

acids. It is best prepared by extraction with warm 96% alcohol; this is treated with ether and the precipitated substance separated by decantation; the ether-alcohol solution is then evaporated to dryness, the residue dissolved in ether, and the lecithin precipitated from the ethereal solution by acetone. Bergell's method is not advisable. The lecithin is best estimated by cadmium determinations in the cadmium lecithinate. W. D. H.

**The Solubility of Albumoses and Ferments with Reference to their Relationships to Lecithin and Mastic.** LEONOR MICHAELIS and PETER RÓNA (*Biochem. Zeitsch.*, 1907, 4, 11—20).—The authors' researches bear on the question of the nature of toxin-lecithide and the chemistry of toxin action. Attention is called to the great biological significance of the discovery that certain protein colloidal substances, although themselves soluble in water only, dissolve in such organic solvents as chloroform if lecithin is dissolved therein at the same time. The question at once arises as to whether these phenomena are due to the specific chemical nature of lecithin, or whether they represent the mutual adsorption of two colloidal substances. The experiments described support the latter view. Mastic, a substance in no way connected with lecithin in its chemical nature, shows a marked similarity to it in its physical properties. The authors find also that its solubility-relationships with reference to albumoses and ferments are almost a strict counterpart of those of lecithin.

*The Behaviour of Albumoses.*—When a suspension of mastic is precipitated by acidification in the presence of Riedel's peptone, the percentage of the total nitrogen which comes down is independent of the original concentration of the peptone and probably represents that portion of the peptone which is of a colloidal nature. When the precipitate, washed with water until no further biuret reaction is given, is dried, it may be dissolved almost completely in chloroform or alcohol. On adding ether, a precipitation occurs. This precipitate is also a peptone-mastic combination. It differs, however, from the former one in that the proportion of mastic is smaller, and that, when treated with water, the peptone tends to dissolve out. With lecithin, almost precisely similar phenomena were observed. The following conclusions were arrived at from further experiments on these lines: the difference of solubility in various solvents do not appear to be so well marked with lecithin as with mastic-peptone compounds; the solubility relationships of a combination of this order depend on the proportions in which its components are mutually adsorbed; the greater the proportion of peptone present in such combinations the more easily is the peptone washed out of them by water; mastic-serum-albumin is insoluble in alcohol chloroform.

*The Behaviour of Ferments.*—An important résumé of already known lecithin-ferment combinations is given. A mastic-suspension mixed with a filtered solution of rennet was faintly acidified. The whole of the enzyme was contained in the resulting precipitate. By extracting this precipitate by various solvents and precipitating in various ways, a number of mastic-rennet combinations were obtained and the

relationship was found to hold that the lower the mastic content the more readily was the rennet removed. It was further established experimentally that lecithin-rennet behaves in an analogous manner to mastic-rennet.

The precipitation reactions of mastic-trypsin, although analogous, differ considerably from those of mastic-rennet. G. S. W.

**Action of Salts on the Fermenting Power of Different Diastatic Ferments.** L. PRETI (*Biochem. Zeitsch.*, 1907, 4, 1—5).—Solutions of pancreatin, urine, and blood-serum, after dialysis, have no diastatic action on starch. Activity is restored by the addition of any one of a number of electrolytes. Takadiastase and maltin solutions cannot be rendered inactive by dialysis. G. S. W.

**Chemistry of Silicon.** ALBERT LADENBURG (*Ber.*, 1907, 40, 2274—2279).—*Triphenylbromosilicane*,  $\text{SiPh}_3\text{Br}$ , is formed when tetraphenylsilicane (Polis, Abstr., 1885, 973; 1886, 618) is heated with bromine, first at  $100^\circ$  and afterwards in tubes at  $150^\circ$ . It forms colourless, crystalline needles, m. p.  $118\text{--}120^\circ$ , fumes slightly in contact with the air, and is decomposed by water or alcohol.

Triphenylsilicol, obtained by heating the bromide with dilute potassium carbonate solution at  $120^\circ$ , separates from ether or acetone in small, transparent crystals, m. p.  $148\text{--}150^\circ$  (Polis, 139— $140^\circ$ ). Its *acetyl* derivative melts at  $96\text{--}97^\circ$ . The silicol dissolves in fuming sulphuric acid yielding a *trisulphonic acid*,  $\text{OH}\cdot\text{Si}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_3$ , the *barium* salt of which crystallises from water in compact prisms. A *trinitro*-derivative of the barium salt,  $\text{C}_{36}\text{H}_{20}\text{O}_{32}\text{N}_6\text{S}_6\text{Ba}_3\text{Si}$ , has been obtained as a yellow, crystalline crust.

*Diphenyldibromosilicane*,  $\text{SiPh}_2\text{Br}_2$ , obtained by heating the monobromo-derivative with bromine at  $150^\circ$ , has b. p.  $175\text{--}183^\circ/12\text{ mm.}$ , and with zinc ethyl yields *diphenyldiethylsilicane*,  $\text{SiEt}_2\text{Ph}_2$ , b. p.  $305\text{--}320^\circ$ .

Triphenylbromosilicane and zinc ethyl at  $120^\circ$  yield either *triphenylsilicane*,  $\text{SiHPh}_3$ , which crystallises from acetone in plates, m. p.  $200\text{--}203^\circ$ , or *triphenylethylsilicane*,  $\text{SiEtPh}_3$ , m. p.  $72\text{--}74^\circ$ .

J. J. S

**Combination of Mixed Organo-magnesium Compounds with the Pyridine and Quinoline Bases.** BERNARDO ODDO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 413—418. Compare Abstr., 1904, i, 920; Sachs and Sachs, Abstr., 1904, i, 925).—In addition to the additive compounds of quinoline and magnesium phenyl bromide already obtained (*loc. cit.*), the author has prepared the *compound*,  $(\text{C}_9\text{H}_7\text{N})_3\text{MgPhBr}$ , in the form of an unstable yellow powder insoluble in all the neutral solvents.

Similar additive compounds containing four or more mols. of quinoline for 1 mol. of magnesium phenyl bromide are still more unstable than the above and could not be isolated.

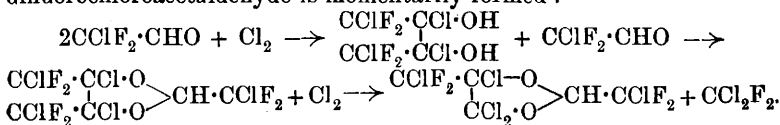
The simultaneous action of pyridine (1 mol.) and quinoline (1 mol.) on magnesium phenyl bromide also yields an unstable compound which is decomposed by water, giving pyridine and 2-phenylquinoline.

T. H. P.

## Organic Chemistry.

**Decomposition of Gaseous Hydrocarbons by Heating with Finely-divided Aluminium.** M. I. KUSNETZOFF (*Ber.*, 1907, 40, 2871—2873).—It is found that aluminium at temperatures near its melting point, like red-hot magnesium (Lidoff and Kusnetzoff, *Abstr.*, 1906, ii, 201), decomposes methane, ethane, ethylene, and acetylene completely into their elements. The hydrogen and part of the carbon are obtained in the free state, whilst the remainder of the carbon combines with the aluminium, forming aluminium carbide. W. H. G.

**Chlorination of Difluoroethyl Alcohol.** FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1907, 339—358).—Under the influence of sunlight, chlorine attacks difluoroethyl alcohol fairly rapidly at first, but more slowly afterwards, and the action is not complete after several weeks. The products of an experiment lasting twenty-six days consisted of (1) *difluorochloroacetyl chloride*,  $\text{CClF}_2\cdot\text{COCl}$ , a colourless, very mobile liquid having an irritating odour, b. p.  $34^\circ$ , and fuming strongly in air. It reacts violently with water and alcohol to form the corresponding acid (*Abstr.*, 1906, i, 478) and ester. (2) Difluorochloroacetic acid, formed from the chloride by the action of water vapour, the presence of which cannot be avoided in an experiment of such long duration. (3) A *polymeride* of difluorochloroacetyl chloride, a liquid, b. p.  $134^\circ$ , which is slowly attacked by water and rapidly by alcohol, giving the (non-polymerised) acid and ester. It is partially depolymerised on distillation. Vapour density determinations give it a polymerisation coefficient of 1.82 at  $100^\circ/161$ — $163.1$  mm., 1.75 at  $137.5^\circ/176.6$  mm., and 1.59 at  $208^\circ/149$  mm., but the depolymerisation is not reversible by lowering the temperature. Cryoscopic determinations give a polymerisation coefficient slightly above 2, unaltered by dilution. The formula  $\text{COCl}\cdot\text{CCl}\begin{smallmatrix} \text{F}\cdot\text{F} \\ \text{F}\cdot\text{F} \end{smallmatrix} \text{CCl}\cdot\text{COCl}$  is suggested for the polymeride. When treated in benzene solution with gaseous ammonia, it gives *difluorochloroacetamide*,  $\text{CClF}_2\cdot\text{CO}\cdot\text{NH}_2$ , in the form of tabular crystals, m. p.  $78.5^\circ$ , identical with the product from ethyl difluorochloroacetate. (4) *Carbon difluorodichloride*,  $\text{CCl}_2\text{F}_2$ , a gas, b. p.  $-25^\circ$ . (5) A small quantity of a substance, b. p.  $170^\circ$ , smelling like chloralide. The author suggests the following scheme in explanation of the formation of the last two substances, supposing that difluorochloroacetaldehyde is momentarily formed :

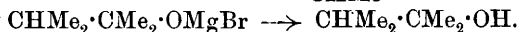
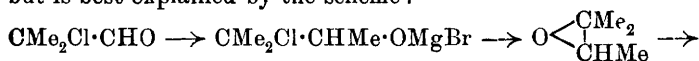


Since about 80% of the difluoroethyl alcohol is converted into difluorochloroacetyl chloride and the corresponding acid, the author

considers that the principal reaction is that represented by the equation  $\text{CHF}_2 \cdot \text{CH}_2 \cdot \text{OH} + 3\text{Cl}_2 = \text{CClF}_2 \cdot \text{COCl} + 4\text{HCl}$ .

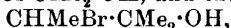
In an incomplete chlorination, difluoroacetyl chloride and what is probably a polymeride of the latter are also formed. E. H.

**Various Syntheses with Compounds Containing the Group  $\text{CMe}_2\text{Cl} \cdot \text{Cl}$ .** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 162—189).—In the esters of carboxylic acids containing the radicles  $\cdot\text{CH}_2\text{Cl}$  or  $\cdot\text{CHMe} \cdot \text{Cl}$ , only the carboxylic group is attacked by magnesium methyl bromide, whilst in esters containing the group  $\cdot\text{CMe}_2\text{Cl}$ , both the chlorine and the alkyloxy-group are replaced by methyl. Thus ethyl chloroacetate gives chloro*tert.*butyl alcohol, whilst ethyl chloro*isobutyrate* gives pentamethylethanol (Abstr., 1906, i, 782). But chloro*isobutaldehyde* in ethereal solution when added to an ethereal solution of magnesium methyl bromide, instead of giving the expected pinacolyl alcohol, gives the isomeric  $\alpha\beta$ -trimethylpropyl alcohol,  $\text{CHMe}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ . The formation of the latter cannot be due to the intramolecular change of the pinacolyl alcohol first formed, since changes of this kind are only known with the corresponding halides, but is best explained by the scheme :



This is supported by (1) production of  $\alpha\beta$ -trimethylpropyl alcohol by the action of magnesium methyl bromide on trimethylethylene oxide ; (2) the different course followed by the reaction when oxide-formation is impossible owing to the absence of the  $\text{CH} \cdot \text{O} \cdot \text{MgBr}$  group ; thus when an ethereal solution of magnesium methyl bromide (1 mol.) is added to an ethereal solution of  $\alpha\beta$ -dichloro- $\beta$ -methylpropyl *isobutyl ether*,  $\text{CMe}_2\text{Cl} \cdot \text{CHCl} \cdot \text{OC}_4\text{H}_9(\text{iso})$ ,  $\beta$ -chloro- $\alpha\beta$ -dimethylpropyl *isobutyl ether*,  $\text{CMe}_2\text{Cl} \cdot \text{CHMe} \cdot \text{OC}_4\text{H}_9(\text{iso})$ , is formed as a strongly smelling, highly refractive, colourless liquid, b. p. 178—179°/774 mm.,  $D^{20}_D$  0.9048,  $n_D$  1.42711, whilst by adding the solution of the ether to that of magnesium methyl bromide (2 mols.),  $\beta$ -*isobutyl*- $\beta$ -*isoamyl ether*,  $\text{CMe}_2 \cdot \text{CMe} \cdot \text{OC}_4\text{H}_9(\text{iso})$ , is produced, a colourless liquid, b. p. 160—161°,  $D^{20}_D$  0.7952,  $n_D$  1.41692, which has a powerful smell and combines readily with bromine (compare Vitoria, *Bull. Acad. roy. Belg.*, 1901, 1087).

When the ethereal solution of magnesium methyl bromide is added to that of chloro*isobutaldehyde*, besides  $\alpha\beta$ -trimethylpropyl alcohol, the chlorohydrin,  $\text{CHMeCl} \cdot \text{CMe}_2 \cdot \text{OH}$ , and the bromohydrin,



are formed, probably from the action of magnesium methyl bromide on trimethylethylene oxide (compare Grignard, Abstr., 1903, i, 552).

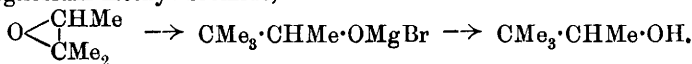
Rizza's preparation of  $\alpha\beta$ -trimethylpropyl alcohol by the action of excess of zinc-methyl on chloral (Abstr., 1882, 491) can be explained by a scheme similar to the above.

$\alpha\beta$ -Trimethylpropyl alcohol is also formed by the action of magnesium methyl bromide on  $\beta$ -*isoamylene chlorohydrin*,

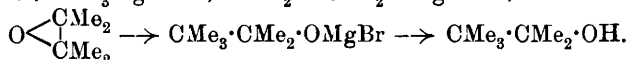
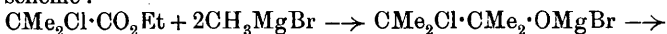




and whichever way it is prepared it always reacts with bromine, probably owing to the presence of a trace of Friedel's pinacolyl alcohol, formed by the alternative reaction of trimethylethylene oxide with magnesium methyl bromide,



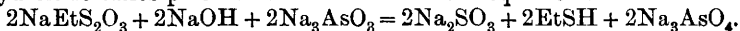
From these results, the author considers that the formation of pentamethylethanol from ethyl chloroisobutyrate is explained by the scheme:



Pentamethylethanol is also produced by the action of magnesium methyl bromide on Friedel's pinacolin,  $\text{CMe}_3 \cdot \text{COMe}$ , on tetramethylethylene oxide, or on  $\beta$ -chloro- $\alpha\alpha\beta$ -trimethylpropyl alcohol,  $\text{CMe}_2\text{Cl} \cdot \text{CMe}_2 \cdot \text{OH}$ , a liquid, b. p. 151–152°, which reacts with potash, giving tetramethylethylene oxide. E. H.

**Velocity of Addition of Iodine to Allyl Alcohol.** WALTER HERZ and BRUNO MYLIUS (*Ber.*, 1907, 40, 2898–2904).—The reaction  $\text{C}_3\text{H}_5 \cdot \text{OH} + \text{I}_2 \rightleftharpoons \text{C}_3\text{H}_5\text{I}_2 \cdot \text{OH}$  proceeds almost to completion (compare Bauer and Moser, this vol., i, 307). The constant  $K$ , calculated for a bimolecular reaction, varies largely with the nature of the solvent. In carbon tetrachloride or chloroform at 25° it is fairly steady and independent of the initial concentrations, provided that the concentration of the alcohol is much greater than that of the iodine. In carbon disulphide the value of  $K$  is dependent on the initial concentration of the alcohol (compare Burke and Donnan, *Trans.*, 1904, 85, 553). The constant has been determined in mixtures of these solvents, and the results are expressed graphically. If the concentration of the alcohol is regarded as a constant, the value of  $K$ , calculated for a unimolecular reaction, varies with the initial concentration of the alcohol, and the reaction is pseudo-unimolecular. C. S.

**Action of Sodium Arsenite on Sodium Ethyl Thiosulphate.** AUGUST GUTMANN (*Ber.*, 1907, 40, 2818–2822).—The action of sodium arsenite on sodium ethyl thiosulphate in the presence of sodium hydroxide takes place in accordance with the equation:



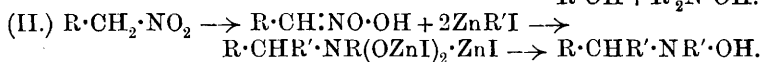
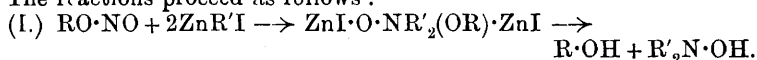
The amounts of sodium sulphite and arsenate and of mercaptan formed were estimated.

Sodium ethyl thiosulphate does not interact with  $N/10$  iodine solution, it does not dissolve silver haloids, does not decolorise a blue solution of a cupric salt, and does not form potassium thiocyanate with potassium cyanide. A. McK.

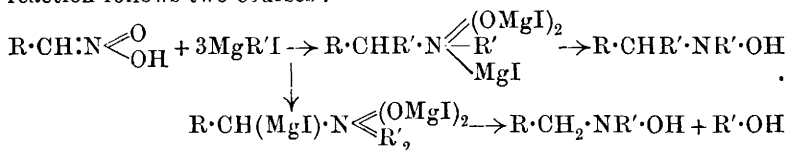
**Action of Magnesium or Zinc Alkyl Iodides on Esters of Nitrous Acid and on Nitroparaffins.** IWAN BEWAD (*Ber.*, 1907, 40, 3065–3083).—In the preparation of  $\beta$ -dialkylhydroxylamines the

zinc alkyl usually employed can be replaced advantageously by zinc alkyl iodides or magnesium alkyl iodides when esters of nitrous acid are used, but not in the case of nitroparaffins. The reactions have been examined between zinc *isopropyl* iodide and *isoamyl* nitrite, zinc *isopropyl* iodide and nitroethane, zinc ethyl iodide and *isoamyl* nitrite, zinc ethyl iodide and nitroethane, magnesium propyl iodide and *isopropyl* nitrite, magnesium propyl iodide and nitroethane, magnesium ethyl iodide and nitropropane, and magnesium ethyl iodide and nitroethane. Ethereal solutions of the reacting substances are mixed slowly at 0°; where zinc compounds are employed, the mixture is kept for three to seven weeks before being decomposed with cold water. The products have been described (Bewad, *Abstr.*, 1900, i, 629; *J. pr. Chem.*, 1901, 63, 94, 193; Mouren, *Abstr.*, 1901, i, 317).

The reactions proceed as follows:



Magnesium alkyl iodides react with esters of nitrous acid in a similar manner to the zinc compounds; with nitroparaffins the reaction follows two courses:



C. S.

**The Phosphorus of Lecithin Prepared from Certain Seeds.** ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1907, 52, 54—61).—Previous estimations of phosphorus in vegetable lecithins have given varying figures. Thus, that from the seeds of *Vicia sativa* and *Lupinus luteus* contain 3.68%, a number which lies near to the values calculated for di-oleyl-lecithin (3.68) and distearyl-lecithin (3.84), and lower than that calculated for dipalmityl-lecithin (4.12). A lower percentage (about 2) was obtained for the lecithin prepared from cereals. In view of the fact that such preparations were not pure and probably were contaminated with carbohydrates, it was considered desirable to make further analyses. The present paper relates to the lecithin prepared from *Lupinus luteus*, *Vicia sativa*, and *Pinus Cembra*; the percentages of phosphorus in these were respectively 3.46—3.76, 3.51—3.62, and 3.60.

W. D. H.

**Phosphorus Percentage of various Samples of Protagon.** A. C. LOCHHEAD and WILHELM CRAMER (*Bio Chem. J.*, 1907, 2, 350—356).—The agreement between the phosphorus percentage of various samples of protagon prepared by different methods is regarded as evidence in favour of the view that protagon is a well-defined chemical substance. The figures given vary from 0.96% to 1.34%.

W. D. H.

**Stannous Formate and its Decomposition Products.** MARTIN GOLDSCHMIDT (*Chem. Zeit.*, 1907, 31, 608).—The solution obtained by dissolving freshly precipitated stannous hydroxide in 30–40% formic acid yields on evaporation in a vacuum white, monoclinic crystals of anhydrous stannous formate. The salt decomposes into stannous oxide and formic acid when its solution in water, acidified with formic acid, is boiled. The dry salt is completely decomposed at temperatures slightly above 100°, the products of decomposition being stannous oxide, carbon dioxide, formaldehyde (chiefly as paraformaldehyde), and methyl formate,  $3(\text{HCO}_2)_2\text{Sn} \rightarrow 3\text{CO}_2 + 3\text{SnO} + \text{H}\cdot\text{CHO} + \text{H}\cdot\text{CO}_2\text{Me}$ .

W. H. G.

**Glucinum Acetates.** HERMANN STEINMETZ (*Zeitsch. anorg. Chem.*, 1907, 54, 217–222).—Basic glucinum acetate,  $\text{Be}_4\text{Ac}_6\text{O}$ , first prepared by Urbain and Lacombe (*Abstr.*, 1902, i, 132, 418), crystallises from organic solvents in well formed, octahedral crystals which, on sublimation, change to doubly-refracting prisms and leaflets; the latter modifications are unstable at the ordinary temperature. From a solution of the basic acetate in cold pyridine, a double compound of the formula  $\text{Be}_4\text{Ac}_6\text{O}\cdot 3\text{C}_5\text{H}_5\text{N}$  was obtained; the pyridine is very loosely combined.

*Normal glucinum acetate*,  $\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$ , not previously known, was obtained by heating a mixture of equal parts of the basic acetate and glacial acetic acid with five to six parts of acetic anhydride for two hours at 140° in a sealed tube. It occurs in doubly-refracting, microscopic leaflets, which are insoluble in water as well as in alcohol, ether, and other organic solvents; on continued boiling with water it goes into solution and simultaneously suffers partial hydrolysis. It melts with decomposition above 300°, the basic acetate subliming.

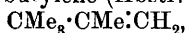
The author considers that these results support the formula for the basic acetate advanced by Glassman (this vol., i, 109). G. S.

**Modified Nickel Acetate, a New Type of Excitant of Oxidation for Quinols.** ANDRÉ JOB (*Compt. rend.*, 1907, 144, 1266–1267).—Examination of the acetates of manganese and cobalt according to the very sensitive method previously described (*Abstr.*, 1903, ii, 214; 1906, ii, 531) shows that the rapidity of oxidation by these salts is greater at first, and diminishes much more quickly in the first two than in the succeeding minutes. When pure nickel acetate is heated for a long time at 100°, it loses acetic acid, but remains soluble in cold water. The activity of the product in oxidising quinol exceeds that of manganese acetate. The activity of both manganese acetate and heated nickel acetate is diminished either by decreasing the amount present or by adding acetic acid. But whilst the first method renders the activity of manganese acetate less persistent and the second method renders it more stable, with nickel acetate both methods effect a rapid diminution in the rate of oxidation. Thus heated nickel acetate forms a new type of oxydase for quinol, its activity apparently depending on the presence of the hydroxide. Accordingly by comparing the activity of normal nickel acetate with that of modified nickel acetate, a method

of estimating the degree of hydrolysis of the latter salt is obtained. The author finds for a  $N/100$  solution, less than 1% is hydrolysed.

E. H.

**Acetic Esters.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 285—313).—By the action of acetyl chloride or acetic anhydride on the magnesium halide compounds of the tertiary alcohols (compare Houben, Abstr., 1906, i, 520), or, in some cases, by the action of magnesium alkylhalides on the aldehydes, ketones, or esters from which the tertiary alcohols are prepared by Grignard's reaction, the following acetates have been obtained.  $\alpha\alpha\beta$ -Trimethylpropyl acetate,  $\text{CHMe}_2\cdot\text{CMe}_2\cdot\text{OAc}$ , a liquid, having  $D^{20}$  0.9226,  $n_D$  1.41831 (compare Kondakoff, Abstr., 1894, i, 113; Friedel, Abstr., 1873, 488), which is hydrolysed by distillation with solid potash, and is rapidly transformed by cold fuming hydrochloric acid into the *chloride*, a very mobile liquid, b. p. 111—113°.  $\alpha\alpha$ -Dimethylbutyl acetate,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OAc}$ , a liquid, b. p. 142—143°/752 mm.,  $D^{20}$  0.9114,  $n_D$  1.41433. *tert*-Butyl acetate,  $\text{CMe}_3\cdot\text{OAc}$ , a liquid, b. p. 95°/750 mm. (Butleroff, *Annalen*, 1867, 144, 7, gives 96°; Kondakoff gives 51°),  $D^{20}$  0.8958,  $n_D$  1.39469. Both of these esters react like the first towards alkalis and halogen acids.  $\alpha\alpha\beta\beta$ -Tetramethylpropyl acetate,  $\text{CMe}_3\cdot\text{CMe}_2\cdot\text{OAc}$ , a liquid with a faint camphor-like smell, b. p. 158—160°/766 mm., 96—97°/80 mm.,  $D^{20}$  0.8906,  $n_D$  1.42611, m. p. -51°, which, when impure, is decomposed by distillation at the ordinary pressure, forming Butleroff's  $\beta\gamma\gamma$ -trimethyl- $\alpha$ -butylene (Abstr., 1875, 1248),



a liquid having b. p. 78—80°/750 mm.,  $D^{20}$  0.7188. The acetate reacts very readily with the halogen acids, fuming hydrochloric acid, giving the *chloride* in the form of a white solid, m. p. 130°. On the other hand, it is not hydrolysed by an hour's boiling with alcoholic potash. Whilst primary and secondary alcohols readily form acetates when treated with acetyl chloride, and these acetates are attacked with difficulty by hydrochloric acid, the converse is true for the tertiary alcohols. The author shows that the difference between the boiling points of the acetates and those of the corresponding alcohols increases in passing from primary to tertiary, and that the acetylation of primary, secondary, and tertiary alcohols produces an increasing rise in the boiling point, as the radicle combined with the  $\cdot\text{CH}_2\cdot\text{OH}$ ,  $\cdot\text{CH}\cdot\text{OH}$ , and  $\cdot\text{C}\cdot\text{OH}$  groups is increasingly methylated.

E. H.

**Theory of Saponification.** II. JULIUS MARCUSSEN (*Ber.*, 1907, 40, 2905—2915. Compare Abstr., 1906, i, 924).—A reply to Lewkowitsch (this vol., i, 10). The high acetyl value of an incompletely hydrolysed fat is not due to the presence of mono- and diglycerides, but depends partly on the existence of acids soluble in water and of hydroxy-acids, and partly on the absorption of atmospheric oxygen.

C. S.

**Peat Wax.** ROMAN ZALOZIECKI and JOACHIM HAUSMANN (*Zeitsch. angew. Chem.*, 1907, 20, 1141—1143).—A brownish-yellow wax is obtained from peat to the extent of about 1% by extraction with

alcohol. This substance on treatment with ether is separated into two portions; the fraction readily soluble in ether forms a dark green, wax-like mass with an agreeable odour, whilst the insoluble fraction is a brown substance.

The soluble fraction yields on hydrolysis a greenish-coloured *acid*, m. p.  $184^{\circ}$ , which, from the results of analysis and molecular weight determinations, probably has the formula  $C_{10}H_{25}O_5$ , and an *alcohol*. This alcohol is identical in composition with that obtained from the portion insoluble in ether on hydrolysis; it is a yellow, gelatinous substance, m. p.  $124-130^{\circ}$ , and probably has the formula  $C_{20}H_{40}O_4$ . The *acid* which the insoluble portion yields on hydrolysis does not melt under  $260^{\circ}$ , and probably has the formula  $C_{21}H_{35}O_7$ .

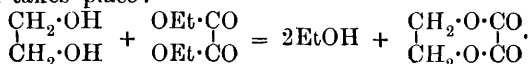
The authors consider that the wax obtained from peat is formed during the decomposition of the vegetable matter, and is not present as such in the original plants; they further maintain that peat wax is not identical with the wax obtained from algæ, as stated by Krämer and Spilker (Abstr., 1900, i, 73; 1902, i, 333), and is in no way connected with the formation of mineral oil.

W. H. G.

**Cyclic Esters from Ethylene Glycol and from Glycerol.** CARL A. BISCHOFF (*Ber.*, 1907, 40, 2803—2813).—Ethylene glycolate may be prepared either from glycollic acid and ethylene glycol or from monosodium ethylene glycol and ethyl chloroacetate in alcoholic solution or in suspension in benzene.

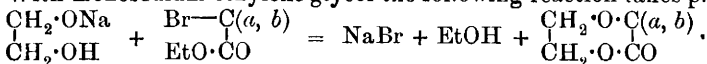
*Ethylene bromoacetate*,  $\begin{matrix} CH_2 \cdot O \cdot CO \cdot CH_2 Br \\ CH_2 \cdot O \cdot CO \cdot CH_2 Br \end{matrix}$ , obtained from monosodium glycol and bromoacetyl bromide, boils at  $125-130^{\circ}/20$  mm.

When glycol is heated with an excess of diethyl oxalate, the following reaction takes place:



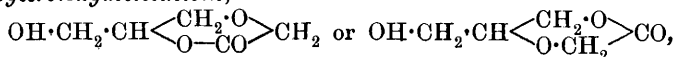
The resulting cyclic compound has m. p.  $171-172^{\circ}$ , and is isomeric with the compound with m. p.  $143^{\circ}$  (Bischoff and Walden, Abstr., 1895, i, 17).

With monosodium ethylene glycol the following reaction takes place:



The following compounds, prepared in this manner, are viscid oils: *ethylene  $\alpha$ -oxypropionate*,  $C_5H_8O_3$ , b. p.  $119-120^{\circ}/30$  mm.; *ethylene  $\alpha$ -oxybutyrate*,  $C_6H_{10}O_3$ , b. p.  $104-106^{\circ}/20$  mm.; *ethylene  $\alpha$ -oxyisobutyrate*,  $C_6H_{10}O_3$ , b. p.  $105^{\circ}/20$  mm.; *ethylene  $\alpha$ -oxyisovalerate*,  $C_7H_{12}O_3$ , b. p.  $120-125^{\circ}/17$  mm.

*Glyceroloxylactone*,



obtained from monosodium glycerol and ethyl bromoacetate, is a viscid, yellow oil, b. p.  $170-175^{\circ}/5$  mm.

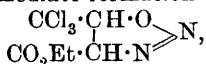
*Glycerol  $\alpha$ -oxypropiolactone*,  $OH \cdot CH_2 \cdot CH \begin{matrix} CH_2 \cdot O \\ O-CO \end{matrix} CHMe$  (?), ob-

tained from monosodium glycerol and ethyl  $\alpha$ -bromopropionate, has b. p. 200—210°/13 mm.

*Glycerol  $\alpha$ -oxybutyrolactone*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{O} \\ \text{O}\cdot\text{CO}\end{smallmatrix}\rangle\text{CHEt}$  (?), has b. p. 200—215°/10 mm.

*Glycerol  $\alpha$ -oxyisobutyrolactone*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{O} \\ \text{O}\cdot\text{CO}\end{smallmatrix}\rangle\text{CMe}_2$ , has b. p. 185—195°/8 mm. A. McK.

**Synthesis of  $\beta$ -Ketonic Esters by Means of Ethyl Diazoacetate.** FRITZ SCHLOTTERBECK (*Ber.*, 1907, 40, 3000—3002).—Ethyl  $\gamma$ -trichloroacetoacetate,  $\text{CCl}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is formed by the action of ethyl diazoacetate on chloral, the action probably being accompanied by the intermediate formation of the compound



from which nitrogen is eliminated. It is a colourless liquid,  $D^{18}$  1.41, b. p. 233—234° (corr.)/749 mm. and b. p. 118° (corr.)/11 mm. Mewes gives b. p. 223—225° and Genvresse b. p. 221—223°. Its alcoholic solution gives an intensely red coloration with ferric chloride.

A. McK.

**New Synthesis of Suberic Acid by Means of Organo-magnesium Compounds.** NICOLAI D. ZELINSKY and JOHANNES GUTT (*Ber.*, 1907, 40, 3049—3050).—In attempting to synthesise glutaric acid from trimethylene bromide, magnesium and carbon dioxide a small quantity of suberic acid was isolated, but no glutaric acid. There was also obtained trimethylene and propylene and neutral substances having no constant b. p. Suberic acid must be formed through the coalescing of two trimethylene residues to form hexamethylene- $\alpha\zeta$ -dimagnesium bromide. W. R.

**Derivatives of Saccharin.** HEINRICH KILIANI, P. LOEFFLER, and O. MATTHES (*Ber.*, 1907, 40, 2999).—Parasaccharone (*Abstr.*, 1904, i, 975),  $[\alpha]_D -107.8^\circ$ ; the barium and magnesium salts are described.

The quinine salts have been used for the separation and identification of the saccharins (*Abstr.*, 1904, i, 975); the rotatory power of these salts was determined as a possible means of identification, but the differences in the molecular rotations is found to be comparatively small. Quinine saccharate,  $[\alpha]_D -102.6^\circ$ ; quinine isosaccharate,  $[\alpha]_D -118.2^\circ$ ; quinine metasaccharate,  $[\alpha]_D -89.5^\circ$ , is soluble to the extent of 1 part in 25 parts of 50% alcohol; quinine parasaccharate,  $[\alpha]_D -105.7^\circ$ . G. Y.

**Comparative Action of Barley Extracts and Malt on the More Resistant Dextrins.** JULES WOLFF (*Compt. rend.*, 1907, 144, 1368—1370. Compare this vol., i, 482).—Barley extract acted only feebly, and after forty-eight hours ceased to act altogether, whilst malt extract gradually transformed the dextrins into maltose.

N. H. J. M.

**Oxalic Aldehyde [Glyoxal].** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 94—118).—The author has put forward the proposition that the accumulation of acid groups,  $\cdot\text{CCl}$ ,  $\cdot\text{CO}$ ,  $\cdot\text{CHO}$ ,  $\cdot\text{CN}$ , &c., in neighbouring positions in carbon compounds increases their volatility, or that in a compound containing one of these groups the substitution of a second acid group in a position near the first causes a considerably less increase in boiling point than did the substitution of the first. Harries and Temme's unimolecular glyoxal (this vol., i, 183) is claimed as a fresh confirmation of this view, since its boiling point ( $51^\circ$ ) is only  $30^\circ$  above that of acetaldehyde, whereas the boiling point of the latter exceeds that of ethane by  $111^\circ$ . By the comparison of the boiling points of a large number of aldehydes, ketones, and alkyloxy-, keto-, and halogen-nitriles, it is shown that the rule no longer holds when the acid groups are separated by the group  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ .

Other examples show that this influence of acid groups is the greater, the less the amount of hydrogen contained in the group displaced.

Unimolecular glyoxal is also an example of the rule that compounds containing the group  $\cdot\text{CO}\cdot\text{CO}\cdot$  are coloured, and that the colour disappears when the  $\text{CO}\cdot$  groups are reduced to  $\cdot\text{CH}\cdot\text{OH}$  or  $\cdot\text{CH}_2$  groups.

E. H.

**Preparation of Some Aliphatic Ethers of ortho-Ketones.**  
**Preparation of Esters of ortho-Acids.** H. REITTER and EDGAR HESS (*Ber.*, 1907, 40, 3020—3025).—Homologues of Claisen's acetone orthoethyl ether,  $\text{CMe}_2(\text{OEt})_2$ , are described. One of the methods given by Claisen for the preparation of the latter substance was by means of nascent orthoformic ester, that is, from formiminoether and alcohol, thus:  $\text{COMe}_2 + \text{OEt}\cdot\text{CH}\cdot\text{NH}_2\text{Cl} + 2\text{EtOH} = \text{NH}_4\text{Cl} + \text{H}\cdot\text{CO}_2\text{Et} + \text{CMe}_2(\text{OEt})_2$ . The authors find that higher homologues are obtained by replacing the anhydrous hydrogen cyanide necessary in Claisen's reaction by acetonitrile, propionitrile, and phenylacetonitrile respectively.

Contrary to the experience of Pinner, the nitriles of acetic and propionic acids may be converted into esters of ortho-acids. The reaction,  $\text{OEt}\cdot\text{CR}\cdot\text{NH}_2\text{Cl} + 2\text{EtOH} = \text{NH}_4\text{Cl} + \text{CR}(\text{OEt})_3$ , proceeds without the addition of a ketone.

*Orthomethylethylketone diethyl ether*,  $\text{CMeEt}(\text{OEt})_2$ , obtained from methyl ethyl ketone, absolute alcohol, and acetoiminoether hydrochloride, has b. p.  $120^\circ$ .

*Orthodiethylketone diethyl ether*,  $\text{CEt}_2(\text{OEt})_2$ , obtained from diethyl ketone, alcohol, and acetoiminoether hydrochloride, has b. p.  $154^\circ$ .

*Orthodipropylketone diethyl ether*,  $\text{CPr}_2(\text{OEt})_2$ , has b. p.  $69\text{—}70^\circ/12\text{ mm.}$

*Ethyl orthoacetate*,  $\text{CMe}(\text{OEt})_3$ , has b. p.  $145\text{—}146^\circ/748\text{ mm.}$

*Ethyl orthopropionate*,  $\text{CEt}(\text{OEt})_3$ , has b. p.  $161^\circ/766\text{ mm.}$

A. McK.

**Colloidal Properties of Starch.** EUGÈNE FOUARD (*Compt. rend.*, 1907, 144, 1366—1368. Compare this vol., i, 391).—The stronger

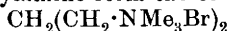
mineral acids, including sulphurous, phosphorous, and hydrofluosilicic acids, coagulate soluble starch, but the weak acids, including organic acids, carbonic and boric acids, and complex inorganic acids, such as silico- and phospho-tungstic acids, exert no coagulative action. There is a limit of concentration for each coagulating acid, beyond which it exerts no action, and this limit is the lower the more completely the acid is ionised. Hardy and Perrin's rule that at equal concentrations in hydrogen ions the acids have the same coagulating power, applies therefore, with the reservation, that an excess of ions or neutral molecules exerts an antagonistic action to coagulation.

The addition of alkalis to soluble starch retards coagulation, and the efficiency of the four alkalis tried are in the descending order, potassium hydroxide, lime, baryta, ammonia, and the rule holds that all alkaline solutions at equal concentration of hydroxyl ions exert the same retarding action. Excess of alkali inhibits coagulation altogether. Baryta behaves in an anomalous manner, owing to its reacting with the soluble starch, and it is for this reason that it falls below lime as a retarding agent.

Carefully purified starch can be converted into the soluble variety by prolonged contact with water at 60°. T. A. H.

**Action of Nitric Acid on Starch.** A. G. DOROSCHEWSKY and ADAM RAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 427—439).—The inversion of potato starch by means of nitric acid proceeds in several stages, the last one of which is of a unimolecular character. When the experiments are conducted in sealed tubes, the time taken for complete inversion is inversely proportional to the strength of acid employed (Abstr., 1884, 46, 36), but acids above 0.4% result in the oxidation of the sugar to the corresponding acid. Whilst other investigators, using hydrochloric and sulphuric acids (*Zeit. anal. Chem.*, 1896, 35, 609), have shown that the factor for calculating dextrose into starch is 0.917—0.941, for nitric acid it is 0.907, the theoretical being 0.900. To determine what sugars are actually produced after the disappearance of a certain amount of dextrin, their osazones have been prepared, but they have not been identified finally so far. Z. K.

**Preparation of Quaternary Ammonium Bases by Means of Alkali from Additive Products of Tertiary Amines with Alkylene Dibromides.** R. LUCIUS (*Arch. Pharm.*, 1907, 245, 246—258).—Ethylene and trimethylene dibromides, when heated with trimethylamine, triethylamine, tribenzylamine, or tropine, unite with 1 or 2 mols. of the base. When the additive products are heated with alcoholic potassium hydroxide, potassium bromide is precipitated and a solution of the quaternary base is obtained; in the case of the additive products with 1 mol. of the base, the alkyl halogen atom is eliminated at the same time along with an atom of hydrogen, an unsaturated derivative being formed. For instance, trimethylene dibromide and trimethylamine form the compounds



and  $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_3\text{Br}$  (the first is the less soluble of the two);



these yield solutions of the bases  $\text{CH}_2(\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH})_2$  and  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$

respectively. Most of the bases were isolated and analysed in the form of platinichlorides. The formulæ and melting points of the new substances described are enumerated below (the platinichlorides decomposed as they melted).

From ethylene dibromide. With triethylamine:  $\text{C}_2\text{H}_4(\text{NEt}_3\text{Br})_2$ , 245—246°;  $\text{C}_2\text{H}_4[\text{NEt}_3]_2\text{PtCl}_6$ , 211°;  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{NEt}_3\text{Br}$ , 241—242°;  $[\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{NEt}_3]_2\text{PtCl}_6$ , 237—238°;  $[\text{CH}_2\cdot\text{CH}\cdot\text{NEt}_3]\text{PtCl}_6$ , 208°. With tribenzylamine:  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})_3\text{Br}$ , 263°;

$[\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})_3]_2\text{PtCl}_6$ , 226—227°;  $[\text{CH}_2\cdot\text{CH}\cdot\text{N}(\text{CH}_2\text{Ph})_3]\text{PtCl}_6$ , 216°.

From trimethylene dibromide. With trimethylamine:

$\text{CH}_2[\text{CH}_2\cdot\text{NMe}_3]_2\text{PtCl}_6$ , 274—275°;  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\text{Br}$ , 208°;  $[\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3]\text{PtCl}_6$ , 258—259°. With triethylamine:  $\text{CH}_2(\text{CH}_2\cdot\text{NEt}_3\text{Br})_2$ , 245°;

$\text{CH}_2[\text{CH}_2\cdot\text{NEt}_3]_2\text{PtCl}_6$ , 220°;  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_3\text{Br}$ , 227—228°;  $[\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_3]_2\text{PtCl}_6$ , 247—249°;  $[\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NEt}_3]\text{PtCl}_6$ , 213°. With tribenzylamine:  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})_3\text{Br}$ , 259—260°;

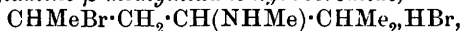
$[\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})_3]_2\text{PtCl}_6$ , 230—231°;  $[\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})_3]\text{PtCl}_6$ , 218—219°. With tropine:  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{C}_8\text{H}_{15}\text{O})\text{Br}$ , 310°;  $[\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{C}_8\text{H}_{15}\text{O})]_2\text{PtCl}_6$ , 255°;  $[\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{N}(\text{C}_8\text{H}_{15}\text{O})]\text{PtCl}_6$ , 253—254°. C. F. B.

**Preparation of Amino-alcohols from Unsaturated Methyl Ketones.** I. MORITZ KOHN (*Monatsh.*, 1907, 28, 423—437).—An investigation to see whether methyl ketones, similar in constitution to mesityl oxide, combine like this compound with amines (Hochstetter and Kohn, *Abstr.*, 1904, i, 18; Kohn, 1904, i, 932). It is found that isobutylidenacetone and benzylidenacetone combine with methylamine, forming ketonic bases, which when reduced with sodium amalgam yield the corresponding amino-alcohols.

*Methyl-β-methylaminoisoamylcarbinol* (*γ-methylamino-β-methylhexan-ε-ol*),  $\text{CHMe}_2\cdot\text{CH}(\text{NHMe})\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ , prepared by reducing with sodium amalgam a hydrochloric acid solution of the ketonic amine which results by combining isobutylidenacetone with methylamine, is a colourless oil, b. p. 199—202°. When treated with methyl iodide, the tertiary base yields an oily *methiodide*, which when treated successively with silver and auric chlorides yields the *aurichloride*,  $\text{C}_{10}\text{H}_{23}\text{ON}\cdot\text{HAuCl}_4$ , in the form of scaly crystals, m. p. 105—114°.

With formaldehyde, the amino-alcohol forms 3:6-dimethyl-4-isopropyltetrahydro-1:3-oxazine,  $\text{O} \begin{smallmatrix} \text{CH}_2-\text{NMe} \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix} \text{CHPr}^\beta$ , an oil, b. p. 179—181°; the *aurichloride*,  $\text{C}_9\text{H}_{19}\text{ON}\cdot\text{HAuCl}_4$ , is a sandy powder; the *platinichloride*,  $(\text{C}_9\text{H}_{19}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$ , is a yellowish-red, crystalline substance. The *methiodide*, when treated successively with silver and auric chlorides, yields the *aurichloride*,  $\text{C}_{10}\text{H}_{21}\text{ON}\cdot\text{HAuCl}_4$ , which crystal-

lises in short needles, m. p. 136—139°. When treated with hydrogen bromide, methyl- $\beta$ -methylaminoisoamylcarbinol is converted into  $\epsilon$ -bromo- $\gamma$ -methylamino- $\beta$ -methylhexane hydrobromide,



which on treatment with 33% aqueous potassium hydroxide is converted into 1:2-dimethyl-4-isopropyltrimethylenimine,  $\text{CH}_2 \left\langle \begin{smallmatrix} \text{CHPr}^\beta \\ \text{CHMe} \end{smallmatrix} \right\rangle \text{NMe}$ , a

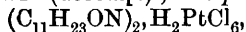
colourless, limpid liquid, b. p. 125—129°; the *aurichloride* is an oil; the *picrate*,  $\text{C}_{14}\text{H}_{20}\text{O}_7\text{N}_4$ , crystallises in glistening needles, m. p. 128—131°. The *methiodide* on successive treatment with silver and auric chlorides forms the *aurichloride*, obtained as a precipitate; the *platinichloride*,  $(\text{C}_9\text{H}_{10}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ , forms small, brilliant, granular crystals. In the same manner are obtained the *ethiodide*, the *aurichloride*,  $\text{C}_{10}\text{H}_{21}\text{N} \cdot \text{HAuCl}_4$ , which forms small, woolly needles, and the *platinichloride*,  $(\text{C}_{10}\text{H}_{21}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ , a yellowish-red precipitate.

$\alpha$ -Methylamino- $\alpha$ -phenylbutane- $\gamma$ -ol,  $\text{NHMe} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$ , is prepared by the reduction of the compound obtained by the interaction of methylamine with benzylidenacetone. It crystallises from light petroleum in white, fibrous needles, m. p. 56—57°; b. p. 153—154°/17—18 mm.; the *picrate*,  $\text{C}_{17}\text{H}_{20}\text{O}_8\text{N}_4$ , forms granular crystals, m. p. 140°. From the *methiodide* of the methyl ether an *aurichloride*,  $\text{C}_{13}\text{H}_{21}\text{ON} \cdot \text{HAuCl}_4$ , was prepared, which crystallises in light yellow leaflets, m. p. 131—134°. The *nitroso*-derivative,  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2$ , is obtained by acting on the amino-alcohol with nitrous acid as a thick, yellow oil. Formaldehyde unites with the amino-alcohol with the formation of 4-phenyl-3:6-dimethyltetrahydro-1:3-oxazine,  $\text{O} \left\langle \begin{smallmatrix} \text{CH}_2 - \text{NMe} \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{CHPh}$ , a colourless oil, b. p. 134°/15 mm.; the *aurichloride*,  $\text{C}_{12}\text{H}_{17}\text{ON} \cdot \text{HAuCl}_4$ , melts at 153—157°.

W. H. G.

**Preparation of Amino-alcohols from Unsaturated Methyl Ketones.** II. MORITZ KOHN and JAKOV GIACONI (*Monatsh.*, 1907, 28, 461—478. Compare preceding abstract).—The compound, obtained by the addition of methylamine to  $\alpha$ -isomethylheptenone, yields when reduced in hydrochloric acid solution with sodium amalgam methyl- $\beta$ -methylaminoisooheptylcarbinol ( $\delta$ -methylamino- $\beta$ -methylheptane- $\zeta$ -ol),  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NHMe}) \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$ , a colourless liquid, b. p. 106—107°/16 mm.; the *aurichloride* and *platinichloride* are resinous. The *methiodide* yields, on successive treatment with silver and auric chlorides, the *aurichloride*,  $\text{C}_{11}\text{H}_{25}\text{ON} \cdot \text{HAuCl}_4$ , which crystallises in shining, yellow scales, m. p. 120°. The *nitroso*-derivative,  $\text{C}_9\text{H}_{20}\text{O}_2\text{N}_2$ , is a dark yellow oil. The amino-alcohol condenses with formaldehyde, forming 3:6-dimethyl-4-isobutyltetrahydro-1:3-oxazine,  $\text{O} \left\langle \begin{smallmatrix} \text{CH}_2 - \text{NMe} \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{CH} \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , a colourless, mobile liquid, b. p. 83.5—84°/13 mm. The *aurichloride*,  $\text{C}_{10}\text{H}_{21}\text{ON} \cdot \text{HAuCl}_4$ , is a light yellow powder, m. p. 134° (decomp.); the *platinichloride*,  $(\text{C}_{10}\text{H}_{21}\text{ON})_2 \cdot \text{H}_2\text{PtCl}_6$ , forms orange-red needles; the *picrate* is an oil. On successive treatment with methyl iodide, silver and auric chlorides, the base forms the *aurichloride*,  $\text{C}_{11}\text{H}_{23}\text{ON} \cdot \text{HAuCl}_4$ , a crystalline

substance, m. p. 123—124° (decomp.); the *platinichloride*,



is a red substance, m. p. 134—135°. The amino-alcohol condenses with ethyl chlorocarbonate, forming 2-*oxy*-3:6-*dimethyl*-4-*isobutyltetra-*

*hydro*-1:3-*oxazine*,  $\text{O} \begin{array}{c} \text{CO} \text{---} \text{NMe} \\ \text{CHMe} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , a pale yellow

oil, b. p. 170.5°/11 mm., and with ethylene oxide, forming the *basic glycol*,  $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Pr}^s) \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , a thick, colourless liquid, b. p. 161—162°/13 mm.; the *aurichloride*, obtained at first as a light yellow precipitate, quickly changes into an oil. The compound, obtained by heating the amino-alcohol with concentrated hydrobromic acid in a sealed tube at 95—100°, is converted by 50% potassium hydroxide into 1:2-*dimethyl*-4-*isobutyltrimethylenimine*,

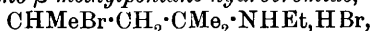
$\text{CH}_2 \begin{array}{c} \text{CH}(\text{C}_4\text{H}_9) \\ \text{---} \text{CHMe} \end{array} \text{NMe}$ , a colourless, mobile liquid, b. p. 152—154°;

the *aurichloride* is an unstable oil; the *picrate* crystallises in light yellow needles, m. p. 93—94°. The *methiodide* can be converted into the corresponding *aurichloride*,  $\text{C}_{10}\text{H}_{21}\text{N} \cdot \text{HAuCl}_4$ , a pale yellow, crystalline substance, m. p. 63—64°; the *platinichloride*,  $(\text{C}_{10}\text{H}_{21}\text{N})_2, \text{H}_2\text{PtCl}_6$ , forms small, pale red crystals decomposing at 170—171°. The *ammonium* base, formed by the action of moist silver oxide on the *methiodide*, loses water when distilled with 50% potassium hydroxide, yielding an *unsaturated* base,  $\text{C}_{10}\text{H}_{21}\text{N}$ , which is obtained as a colourless, mobile liquid, b. p. 168—171°; the *aurichloride* is an oil; the *platinichloride*,  $(\text{C}_{10}\text{H}_{21}\text{N})_2, \text{H}_2\text{PtCl}_6$ , is a crystalline substance, m. p. 135—138°; the *picrate* crystallises in long, pale yellow needles, m. p. 84—85°. The *additive* compound, formed with methyl iodide, yields on successive treatment with silver and auric chlorides the *aurichloride*,  $\text{C}_{11}\text{H}_{23}\text{N} \cdot \text{HAuCl}_4$ , obtained as a light yellow precipitate, m. p. 75—80°; the *platinichloride*,  $(\text{C}_{11}\text{H}_{23}\text{N})_2, \text{H}_2\text{PtCl}_6$ , forms small, pale red crystals, m. p. 155—156°. When treated with moist silver oxide, the *methiodide* yields an *ammonium* base, which on distillation with water decomposes into trimethylamine, water, and an *unsaturated hydrocarbon*,  $\text{C}_8\text{H}_{14}$ ; this is a colourless, mobile liquid, b. p. 120—122°, with a decided turpentine-like odour. One mol. of the hydrocarbon in carbon tetrachloride solution combines with 1 mol. of bromine at the ordinary temperature.

W. H. G.

**Derivatives of Diacetonalkamine. VI.** MORITZ KOHN and OTTO MORGENSTERN (*Monatsh.*, 1907, 28, 479—508. Compare Kohn, *Abstr.*, 1904, i, 378, 932, 933; 1905, 928; this vol., i, 338).—Various diacetonalkamines have been prepared and their derivatives investigated.

Ethyldiacetonalkamine combines with hydrogen bromide, forming *δ*-*bromo*-β-*ethylamino*-β-*methylpentane hydrobromide*,



since this compound when treated with concentrated potassium hydroxide is converted into 2:4:4-*trimethyl*-1-*ethyltrimethylenimine*,

$\text{CH}_2 \begin{array}{c} \text{CMe}_2 \\ \text{---} \text{CHMe} \end{array} \text{NEt}$ , a colourless, mobile liquid, b. p. 117—118°. The

*aurichloride*,  $\text{C}_8\text{H}_{17}\text{N} \cdot \text{HAuCl}_4$ , is a powder, m. p. 115—116°; the

*platinichloride*,  $(C_8H_{17}N)_2H_2PtCl_6$ , crystallises in hexagonal prisms and decomposes at  $170^\circ$ ; the *picrate*,  $C_{14}H_{20}O_7N_4$ , forms yellow needles, m. p.  $176.5-177.5^\circ$  (decomp.). The *methiodide* is identical with the ethiodide of 1:2:4:4-tetramethyltrimethylenimine (see this vol., i, 339). When treated with moist silver oxide, the methiodide is converted into an *ammonium* base, which when distilled with strong potassium hydroxide loses water and yields an unsaturated *base*,  $C_9H_{19}N$ , a colourless liquid, b. p.  $154-156^\circ$ , with a disagreeable odour; the *aurichloride* is an unstable oil; the *platinichloride*,  $(C_9H_{19}N)_2H_2PtCl_6$ , forms prismatic crystals, m. p.  $159-160^\circ$ ; the *picrate* is a crystalline substance, m. p.  $85.5-86.5^\circ$ ; the *picrolonate* is a yellow powder, m. p.  $137^\circ$ . The base combines with methyl iodide, forming a *methiodide*, which on successive treatment with silver and auric chlorides is converted into the *aurichloride*,  $C_{10}H_{21}N \cdot HAuCl_4$ , a coarse powder; the *platinichloride*,  $(C_{10}H_{21}N)_2H_2PtCl_6$ , crystallises in prisms, m. p.  $155-156^\circ$  (decomp.). The methiodide on treatment with moist silver oxide is converted into an *ammonium* base, which on distillation with water decomposes, forming dimethylethylamine (Knorr and Pschorr, Abstr., 1905, i, 922), water, and a *hydrocarbon*,  $C_6H_{10}$ , b. p.  $74-75^\circ$ . This hydrocarbon is oxidised by potassium permanganate with the formation of acetone, acetic acid, and formic acid, and by nitric acid with the formation of oxalic acid. From its mode of formation and behaviour on oxidation, the hydrocarbon probably has the formula  $CMe_2 \cdot CH \cdot CH \cdot CH_2$ , and the base from which it is derived is therefore probably  $\delta$ -methylethylamino- $\delta$ -methyl- $\Delta^a$ -amylene,  $NMeEt \cdot CMe_2 \cdot CH \cdot CH \cdot CH_2$ .

*Methylethyldiacetonalkamine* [*methyl- $\beta$ -methylethylaminoisobutylcarbinol*],  $OH \cdot CHMe \cdot CH_2 \cdot CMe_2 \cdot NMeEt$ , is prepared by the interaction of methyldiacetonalkamine and ethyl iodide. It is a colourless liquid, b. p.  $197-198^\circ$ ; the *benzoate*,  $C_{16}H_{25}O_2N$ , is a colourless, viscid liquid, b. p.  $177/15$  mm.; the *platinichloride*,  $2C_9H_{21}ON \cdot H_2PtCl_6$ , crystallises in the regular system; the *aurichloride* is an unstable powder; the *picrate* is an oil. From the *methiodide* are formed the corresponding *aurichloride*,  $C_{10}H_{23}ON \cdot HAuCl_4$ , obtained as a fine powder, m. p.  $90^\circ$ , and the crystalline *platinichloride*,  $(C_{10}H_{23}ON)_2H_2PtCl_6$ .

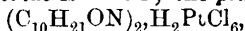
Methylethyldiacetonalkamine combines with hydrogen bromide, forming a compound which is converted by potassium hydroxide into an unsaturated *base*,  $C_9H_{19}N$ , b. p.  $154-156^\circ$ , identical with that obtained from the methiodide of 2:4:4-trimethyl-1-ethyltrimethylenimine.

W. H. G.

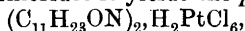
**Derivatives of Diacetonealkamine.** VII. MORITZ KOHN and KARL SCHLEGL (*Monatsh.*, 1907, 28, 509-528).—Ethanoldiacetonalkamine (Kohn, Abstr., 1905, i, 928) has been further investigated and the formula previously given to this compound shown to be correct. Several derivatives of methyldiacetonalkamine are also described.

Ethanoldiacetonalkamine, when heated with acetic anhydride, is converted into the *diacetate*,  $C_9H_{19}N(OAc)_2$ , a colourless liquid, b. p.  $160/17$  mm. When oxidised by chromic acid, ethanoldiacetonalkamine is converted into sarcosine (methylglycine), acetone, acetic acid, and carbon dioxide.

*Methylallyldiacetonalkamine* [methyl- $\beta$ -methylallylaminoisobutylcarbinol],  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NMe}\cdot\text{C}_3\text{H}_5$ , is obtained by the action of allyl iodide on methyldiacetonalkamine as a colourless oil, b. p. 212—215°; the *aurichloride* is an oil; the *platinichloride*,



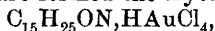
forms small, orange crystals; when treated successively with methyl iodide, silver and auric chlorides it yields the *platinichloride*,



obtained as small crystals.

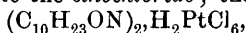
*Methylpropyldiacetonalkamine* [methyl- $\beta$ -methylpropylaminoisobutylcarbinol],  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NMePr}$ , similarly prepared by using propyl iodide, is a colourless liquid, b. p. 213—215°; the *aurichloride* is unstable; the *platinichloride*,  $2\text{C}_{10}\text{H}_{23}\text{ON}, \text{H}_2\text{PtCl}_6$ , forms small, reddish-yellow crystals, m. p. 195° (decomp.). The *methochloride* gives a *platinichloride*,  $(\text{C}_{11}\text{H}_{25}\text{ON})_2, \text{H}_2\text{PtCl}_6$ , which forms small, red crystals, m. p. 150°.

*Benzylmethyldiacetonalkamine* [methyl- $\beta$ -benzylmethylaminoisobutylcarbinol],  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NMe}\cdot\text{CH}_2\text{Ph}$ , obtained by using benzyl chloride, is a colourless oil, b. p. 169—171°/18 mm.; the *aurichloride* is an oil; the *platinichloride*,  $(\text{C}_{14}\text{H}_{23}\text{ON})_2, \text{H}_2\text{PtCl}_6$ , is a brick-red, crystalline powder decomposing at 197—198°; from the *methiodide*, a solid, white substance, are formed the crystalline *aurichloride*,



m. p. 82—84°, and the *platinichloride*,  $(\text{C}_{15}\text{H}_{25}\text{ON})_2, \text{H}_2\text{PtCl}_6$ , a brick-red, crystalline powder decomposing at 167—168°.

Dimethyldiacetonalkamine combines with ethyl iodide when heated in a sealed tube, forming an *ethiodide*, which on treatment with silver chloride is converted into the *ethochloride*; the *platinichloride*,



forms small, orange crystals which decompose at 156—158°; the *aurichloride*,  $\text{C}_{10}\text{H}_{23}\text{ON}, \text{HAuCl}_4$ , crystallises in yellow scales, m. p. 88—90°.

The unsaturated *base*,  $\text{C}_8\text{H}_{17}\text{N}$ , obtained by treating with strong potassium hydroxide the compound formed by acting on dimethyldiacetonalkamine with hydrogen bromide, is not identical with the *base*,  $\text{C}_8\text{H}_{17}\text{N}$ , obtained from 1 : 2 : 4 : 4-tetramethyltrimethylenimine (Kohn, this vol., i, 338), although the b. p. 138—140° is the same; the *aurichloride* is an unstable oil; the *platinichloride*,  $(\text{C}_8\text{H}_{17}\text{N})_2, \text{H}_2\text{PtCl}_6$ , forms small, orange-red crystals which decompose at 176°; the *picrate*,  $\text{C}_{14}\text{H}_{20}\text{O}_7\text{N}_4$ , crystallises in long, yellow needles, m. p. 175° (decomp.). With methyl iodide, the unsaturated base forms an *additive* compound, from which is obtained a *platinichloride*,  $(\text{C}_9\text{H}_{19}\text{N})_2, \text{H}_2\text{PtCl}_6$ , crystallising in reddish-yellow needles which decompose at 177°. The *methiodide* is converted by moist silver oxide into an *ammonium* base, which decomposes when boiled with water into trimethylamine, water, and a hydrocarbon,  $\text{C}_6\text{H}_{10}$ , identical with that obtained by Kohn and Morgenstern (following abstract).

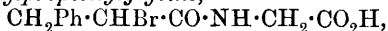
W. H. G.

**Derivatives of Diacetonealkamines.** VIII. MORITZ KOHN and OTTO MORGENSTERN (*Monatsh.*, 1907, 28, 529—536).—With the object

of examining the products formed by the oxidation of the hydrocarbon,  $C_8H_{10}$ , obtained by Kohn (this vol., i, 328) from 1:2:2:4-tetramethyltrimethylenimine, it has again been prepared by this method, and is found to be identical with the hydrocarbon obtained by the authors from 2:4:4-trimethyl-1-ethyltrimethylenimine and methylethyl-diacetonalkamine, and by Kohn and Schlegl from dimethyldiacetonalkamine (preceding abstracts). Now it has been shown (this vol., i, 628) that the hydrocarbon is probably  $\delta$ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene,  $CMe_2 \cdot CH \cdot CH \cdot CH_2$ ; the unsaturated base, through which it is obtained from 2:4:4-trimethyl-1-ethyltrimethylenimine and methylethyl-diacetonalkamine, is therefore in all probability  $\delta$ -methylethylamino- $\delta$ -methyl- $\Delta^{\alpha}$ -amylene,  $NMeEt \cdot CMe_2 \cdot CH_2 \cdot CH \cdot CH_2$ . It was also to be expected that the unsaturated base,  $C_8H_{17}N$ , obtained from 1:2:4:4-tetramethyltrimethylenimine, would be identical with that obtained from dimethyldiacetonalkamine, namely,  $\delta$ -dimethylamino- $\delta$ -methyl- $\Delta^{\alpha}$ -amylene,  $NMe_2 \cdot CMe_2 \cdot CH_2 \cdot CH \cdot CH_2$ ; but this is not the case (Kohn and Schlegl, preceding abstract). However, although differing from the latter compound, it nevertheless gives rise to the same hydrocarbon, so that it is probably  $\delta$ -dimethylamino- $\beta$ -methyl- $\Delta^{\beta}$ -amylene,  $NMe_2 \cdot CHMe \cdot CH \cdot CMe_2$ .  
W. H. G.

**Synthesis of Polypeptides. XIX.** EMIL FISCHER (*Annalen*, 1907, 354, 1—54. Compare this vol., i, 486).—*Derivatives of Phenylalanine*.—[With PAUL BLANK.]—Polypeptides consisting of combinations of phenylalanine with glycine, alanine, or leucine (compare Abstr., 1904, i, 867, 890) are formed together with cinnamoyl-glycine, -alanine, or -leucine, from  $\alpha$ -bromodihydrocinnamic acid, by conversion of this into  $\alpha$ -bromopropionyl chloride, action of the chloride on glycine, alanine, or leucine in aqueous sodium hydroxide solution cooled by ice, and treatment of the product with 23% ammonia. The compounds described are inactive, having been prepared from racemic compounds; two stereoisomeric forms of phenylalanyl-leucine have been obtained.

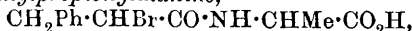
*$\alpha$ -Bromo- $\beta$ -phenylpropionylglycine,*



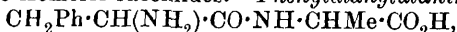
crystallises in microscopic prisms or scales, m. p.  $149^\circ$  (corr.). *i*-Phenylalanylglycine (Abstr., 1905, i, 863) forms a light blue, crystalline copper salt, and when treated with hydrogen chloride in alcoholic solution yields the *anhydride*,  $CH_2Ph \cdot CH \cdot \begin{matrix} CO \cdot NH \\ NH \cdot CO \end{matrix} \cdot CH_2$ , m. p.  $280^\circ$  (corr. partial decomp.).

*Cinnamoyl-glycine*,  $CHPh \cdot CH \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , crystallises from water in long, colourless needles, m. p.  $197^\circ$  (corr.).

*$\alpha$ -Bromo- $\beta$ -phenylpropionylalanine,*



crystallises in long prisms, m. p.  $193^\circ$  (corr. decomp.), and may be a mixture of two isomeric racemides. *Phenylalanylalanine*,



crystallises in colourless, microscopic needles, m. p. about  $241^\circ$  (corr. decomp.), and forms a copper salt crystallising in characteristic, stellate

groups of needles and dissolving in water to a cornflower-blue solution.

*α-Bromo-β-phenylpropionyl-leucine,*



is obtained in two forms, which are separated by treatment with benzene. The isomeride *B* crystallises from benzene in microscopic needles, m. p.  $148^\circ$  (corr.), and yields *phenylalanyl-leucine B*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{H}$ , crystallising in small prisms, m. p.  $224.5^\circ$  (corr.), with a bitter taste; the *copper* salt crystallises in small prisms. The *propionyl-leucine A* is insoluble in benzene, crystallises from boiling toluene in hexagonal leaflets, m. p.  $166.5^\circ$  (corr.), and yields *phenylalanyl-leucine A*, which crystallises from hot water in needles, m. p.  $196^\circ$ , and has solubilities closely resembling those of its isomeride.

*Derivatives of i-Valine.*—[With JULIUS SCHENKEL.]—Polypeptides containing the group  $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot$  are prepared from *α-bromoisovaleric acid* by the general methods of synthesis previously described. The acid chloride acts readily on *α-amino-acids*, but the subsequent substitution of bromine by the amino-group takes place only at  $100^\circ$  with poor yields, or in some cases does not take place. The action of *α-bromoisovaleryl chloride* on *i-alanine* leads to the formation of two racemic isomerides.

*α-Bromoisovaleryl chloride*, prepared by the action of thionyl chloride on the acid, is obtained as a transparent, mobile liquid, b. p.  $59^\circ/15$  mm., crystallises when cooled by liquid air and attacks the mucous membrane.

*α-Bromoisovalerylglycine*,  $\text{CHMe}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises from water in large prisms, m. p.  $139\text{—}141^\circ$  (corr.) evolving gas.

*dl-Valylglycine*,  $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises in thin, colourless prisms, m. p.  $251^\circ$  (corr.), is almost tasteless, is only slightly acid to litmus, and forms a *copper* salt crystallising in hexagonal prisms. A small amount of a product which decolorises permanganate in sodium carbonate solution and is probably a glycine derivative of dimethylacrylic acid is formed together with the dipeptide.

*Valylglycine anhydride*,  $\text{CHMe}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\end{smallmatrix}\right\rangle\text{CH}_2$ , formed by heating valylglycine over a free flame, crystallises in thin prisms, m. p.  $252^\circ$  (corr.).

*α-Bromoisovalerylalanine A*,  $\text{C}_8\text{H}_{14}\text{O}_3\text{NBr}$ , crystallises from hot water in colourless, flat needles, m. p.  $165\text{—}168^\circ$  (corr.), and is converted by ammonia into *valylalanine A*,  $\text{C}_8\text{H}_{16}\text{O}_3\text{N}_2$ , which crystallises in small, rhombic leaflets, m. p.  $246^\circ$  (corr.), is almost tasteless, has a slight acid reaction to litmus, and forms a *copper* salt crystallising in blue prisms. *Valylalanine anhydride*,  $\text{C}_8\text{H}_{14}\text{O}_2\text{N}_2$ , formed from valylalanine *A*, crystallises in colourless needles, m. p.  $246^\circ$  (corr.), and is probably a mixture of two isomerides.

*α-Bromoisovalerylalanine B*, obtained on evaporating the mother liquors from the *A*-isomeride, crystallises in prisms, m. p.  $129\text{—}132^\circ$  (corr.); it is doubtful if this has been obtained free from its isomeride.

*i-Valine anhydride*,  $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$ , prepared by heating *r-valine*, crystal-

lises in long, colourless needles, m. p. 303° (corr.), and is indifferent to acids or alkalis.

*Resolution of Diketopiperazines and Dipeptides of Tyrosine.*—[With WALTHER SCHRAUTH.]—The resolution of the diketopiperazines by means of alkalis, which takes place with great ease in the case of glycine anhydride, is hindered by the presence of alkyls, so that it occurs no longer with leucine anhydride (Abstr., 1906, i, 324). This is the case also with valine anhydride, derived from  $\alpha$ -aminoisovaleric acid.

The resolution of diketopiperazines derived from mixed dipeptides may lead to the formation of two isomeric dipeptides. This possibility has been studied particularly in the case of *dl*-leucylglycine anhydride,  $C_4H_9 \cdot CH < \begin{smallmatrix} NH \cdot CO \\ CO \cdot NH \end{smallmatrix} > CH_2$ , which on hydrolysis is found to yield leucylglycine and glycylleucine in the proportion, 2 : 1. Similar results have been obtained with *i*-leucylalanine anhydride, leucylalanine and alanylleucine being formed in about the proportion 3 : 2.

The resolution of diketopiperazines has been employed now in the preparation of previously unknown derivatives of tyrosine. Hydrolysis of glycyl-*l*-tyrosine anhydride with dilute alkalis at 35° leads to the formation of *l*-tyrosylglycine together with only small amounts of the known isomeride, glycyl-*l*-tyrosine. A substance which is probably *tyrosyltyrosine* is obtained in the same manner from tyrosine anhydride.

Glycyl-*l*-tyrosine anhydride,  $OH \cdot C_6H_4 \cdot CH_2 \cdot CH < \begin{smallmatrix} NH \cdot CO \\ CO \cdot NH \end{smallmatrix} > CH_2$ , prepared by the action of ammonia on ethyl chloroacetyl-*l*-tyrosine at 0°, crystallises in needles, m. p. about 295° (corr.),  $[\alpha]_D^{20} + 125 \cdot 4^\circ$ , and is probably identical with Fischer and Aberhalden's product from silk-fibroin (Abstr., 1906, i, 718).

*l*-Tyrosylglycine is obtained as a hygroscopic, amorphous mass; the hydrochloride of the ethyl ester,  $C_{18}H_{18}O_4N_2 \cdot HCl$ , crystallises in colourless needles, m. p. 230—235° (corr.),  $[\alpha]_D^{20} + 14 \cdot 1^\circ$ ; the *platinichloride*,  $(C_{18}H_{18}O_4N_2)_2 \cdot H_2PtCl_6$ , m. p. 224—227° (corr. decomp.). The *l*-tyrosylglycine and its derivatives are probably not pure, since the resolution of optically active diketopiperazines is accompanied by partial racemisation (compare Abstr., 1906, i, 145).

*Ethyl glycyl-l-tyrosine platinichloride* crystallises in golden, microscopic plates, and decomposes when heated or boiled with water.

*Methyl l-tyrosine*,  $C_{10}H_{13}O_3N$ , crystallises in colourless needles, m. p. 135—136° (corr.),  $[\alpha]_D^{20} + 25 \cdot 75^\circ$ , and is soluble in alkalis, but not in alkali carbonates. *l*-Tyrosine anhydride, formed by heating the methyl ester in methyl alcoholic solution at 100°, or in the absence of a solvent at 135—140°, crystallises in colourless needles, m. p. 277—280° (corr. decomp.),  $[\alpha]_D^{20} - 223 \cdot 8^\circ$ , and gives Millon's reaction. Prolonged heating of the methyl ester leads to partial racemisation, the product containing only 10% of *l*-tyrosine anhydride; the remaining 90% consists of a mixture of the two possible modifications of *i*-tyrosine anhydride, forming needles and stout crystals, m. p. about 300° (corr.). The supposed *tyrosyltyrosine*, obtained in small amount by the hydrolysis of the anhydride with sodium hydroxide, forms an



amorphous mass, gives Millon's reaction, and on esterification and treatment with ammonia yields tyrosine anhydride.

*Isomeric Leucyl-leucines and their Anhydrides.*—[With ARTHUR H. KOELKER.]—Leucyl-leucine has been obtained previously only in one active, the *ll*-, and a racemic form, whereas four active and two racemic modifications are possible theoretically. The missing forms have been prepared now by the general methods described previously (Abstr., 1906, i, 810). *r*-Leucine is resolved by means of its formyl derivative into its optical isomerides (Abstr., 1906, i, 72); one of these is converted by the action of bromine and nitric oxide into the active bromoisohexoic acid, Walden's transformation taking place. The four active leucyl-leucines and the two racemic compounds are formed by combination of the active bromoisohexoic acids with the active leucines.

The *i*-leucyl-leucine previously described is termed leucyl-leucine *A*, and is *d*-leucyl-*l*-leucine + *l*-leucyl-*d*-leucine. It is found now that in the preparation of *i*-bromoisohexoyl-leucine, a small amount of an isomeride is formed, from which the second racemic dipeptide, leucyl-leucine *B* = *d*-leucyl-*d*-leucine + *l*-leucyl-*l*-leucine, is obtained by the action of ammonia.

*l*-*α*-Bromoisohexoyl-*l*-leucine,  $C_{12}H_{22}O_3NBr$ , crystallises in thin prisms, m. p.  $128^\circ$  (corr.),  $[\alpha]_D^{20} - 34.97^\circ$  in ethyl acetate,  $[\alpha]_D^{20} - 53.22^\circ$  in *N*/2 sodium hydroxide solution, and gradually decomposes in alkaline solution.

*d*-Leucyl-*l*-leucine,  $C_{12}H_{24}O_3N_2$ , m. p.  $285^\circ$  (corr.),  $[\alpha]_D^{20} - 67.97^\circ$ , and is hygroscopic.

*trans*-Leucine anhydride,  $C_{12}H_{22}O_2N_2$ , m. p.  $287-289^\circ$  (corr.), is optically inactive.

*d*-*α*-Bromoisohexoyl-*d*-leucine,  $[\alpha]_D^{20} + 34.70^\circ$  in ethyl acetate, or  $[\alpha]_D^{20} + 53.03^\circ$  in *N*/2 sodium hydroxide solution.

*l*-Leucyl-*d*-leucine,  $[\alpha]_D^{20} + 68.95^\circ$ , yields the *trans*-anhydride.

*l*-*α*-Bromoisohexoyl-*d*-leucine crystallises in small octahedra,  $[\alpha]_D^{20} - 15.82^\circ$ .

*d*-Leucyl-*d*-leucine crystallises from alcohol,  $[\alpha]_D^{20} + 13.16^\circ$  in *N*-sodium hydroxide.

*d*-Leucine anhydride,  $[\alpha]_D^{20} + 46.02-48.67^\circ$ .

*i*-*α*-Bromoisohexoyl-leucine *B* crystallises from ether in thin prisms, m. p.  $120-121^\circ$  (corr.).

*i*-Leucyl-leucine *B* crystallises in small leaflets, m. p.  $267-268^\circ$  (corr. decomp.); the hydrochloride and nitrate form small prisms; the copper salt is crystalline.

The action of *i*-*α*-bromoisohexoic acid on *l*-leucine leads to the formation of a mixture of *d*-*α*-bromoisohexoyl-*l*-leucine and *l*-*α*-bromoisohexoyl-*l*-leucine; the former is separated by solution of the mixture in ethyl acetate and addition of light petroleum. The *ll*-isomeride is purified by conversion into the dipeptide and recrystallisation of this from alcohol.

The rate of hydrolysis of *d*-leucyl-*l*-leucine by 10% hydrochloric acid at  $99-100^\circ$  has been determined, and the results are expressed in a curve.

G. Y

**Formation of Calcium Cyanamide and of Calcium Carbide.** E. RUDOLFI (*Zeitsch. anorg. Chem.*, 1907, 54, 170—184. Compare Kühling, this vol., ii, 166; Bredig, this vol., i, 396).—The conditions under which calcium cyanamide is formed from calcium carbide and nitrogen and directly from its components have been investigated.

When commercial carbide, containing 82% of the pure substance, is heated in a porcelain tube in an electric furnace and nitrogen (dry or moist) passed over it, no appreciable amount of cyanamide is formed below 700°; beyond this point the amount of nitrogen absorbed increases regularly with the temperature and duration of the experiment. The rate of reaction is greatly increased by the addition of calcium chloride, but only when the temperature is sufficiently high to fuse the salt. Dry nitrogen gives rather better results than the moist gas.

The experiments on the formation of cyanamide from carbon, calcium oxide, and nitrogen were carried out in a charcoal tube immersed in an electric furnace, the temperatures being measured with an optical pyrometer. It was first shown that calcium carbide is formed from the oxide and nitrogen only when the temperature is raised to 1800—1819°, the temperature for this equilibrium (under a partial pressure of 1/5 atmosphere carbon monoxide) found by Rothmund (*Abstr.*, 1902, ii, 454) being much too low. When the oxide and carbon were heated in nitrogen, cyanamide and carbide were both formed at 1738—1753°, but neither could be detected at lower temperatures. It is therefore considered that the formation of calcium carbide precedes that of cyanamide; the fact that the equilibrium temperature is rather lower in the latter series of experiments is due in all probability to the much smaller pressure of carbon monoxide. The equilibrium temperature is in fair agreement with that calculated by Nernst's formula connecting equilibrium and temperature.

When calcium cyanamide is heated in a current of carbon monoxide it is partially reduced to carbide; this reaction is being investigated further.

G. S.

**Halogen Compounds of Molybdenum and Tungsten.** ARTHUR ROSENHEIM (*Zeitsch. anorg. Chem.*, 1907, 54, 97—103. Compare *Abstr.*, 1905, ii, 717; 1906, i, 603).—The compound previously obtained by the action of excess of potassium cyanide on the compound  $\text{Mo}(\text{OH})_2(\text{SCN})_3 \cdot 2\text{C}_5\text{H}_5\text{N}$  is now shown to have the formula  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  ascribed to it by its discoverer, Chilesotti (*Abstr.*, 1905, i, 177), and not that formerly suggested by Rosenheim and Koss (*loc. cit.*). By titration with potassium permanganate, however, it is shown that, contrary to the view of Chilesotti, it is a compound of *quinquevalent* molybdenum, and it has so far been found impossible to determine its constitution. Electrical conductivity measurements appear to show that it has the simple formula in solution, and cryoscopic determinations have not thrown much light on the subject.

The compound is readily soluble in water, and is stable towards

acids and dilute alkalis. By double decomposition in aqueous solution, many other salts of the same acid have been prepared, but only the following have been fully investigated. The *thallium* salt,  $\text{Ti}_4\text{Mo}(\text{CN})_8$ , occurs in long, lustrous, reddish-yellow needles, slightly soluble in water. The *cadmium* salt,  $\text{Cd}_2\text{Mo}(\text{CN})_8 \cdot 8\text{H}_2\text{O}$ , forms light yellow, microscopic needles, insoluble in water. From the solution of the last-named salt in boiling concentrated ammonia, the *cadmium ammine*,  $\text{Cd}_2(\text{NH}_3)_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ , was obtained in deep yellow needles on cooling. The corresponding *copper ammine*,  $\text{Cu}_2(\text{NH}_3)_4\text{Mo}(\text{CN})_8 \cdot 7\text{H}_2\text{O}$ , has also been obtained; it occurs in deep green needles.

The crystallographic characters of the potassium and thallium salts are given. G. S.

**Double Platinocyanides of Calcium, Strontium, and Barium, &c.** HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1907, 43, 356—368).—Crystallographic descriptions are given of the following salts:  $\text{Pt}(\text{CN})_4\text{Ca} \cdot 5\text{H}_2\text{O}$ ;  $\text{Pt}(\text{CN})_4\text{Sr} \cdot 5\text{H}_2\text{O}$ ;  $\text{Pt}(\text{CN})_4\text{Ba} \cdot 5\text{H}_2\text{O}$ ;  $\text{Pt}(\text{CN})_4\text{NaK} \cdot 3\text{H}_2\text{O}$ ;  $\text{Pt}(\text{CN})_4\text{Mg} \cdot 7\text{H}_2\text{O}$ ;  $\text{Pt}(\text{CN})_4\text{Y}_3 \cdot 7\text{H}_2\text{O}$ .

L. J. S.

**Some New Platinocyanides.** LEONARD A. LEVY (*Proc. Camb. Phil. Soc.*, 1907, 14, 159—160).—In continuation of the investigation on the platinocyanides of hydrazine and hydroxylamine (Levy and Sisson, *Trans.*, 1906, 89, 125), the following salts have been prepared.

*Guanidine platinocyanide*,  $(\text{CH}_5\text{N}_3)_2\text{H}_2\text{Pt}(\text{CN})_4$ , prepared by the interaction of guanidine carbonate and barium platinocyanide, forms long, silky, white needles.

1 : 4-*Diphenyl-3 : 5-endo-anilo-4 : 5-dihydro-1 : 2 : 4-triazole* (*nitron*) *platinocyanide*,  $(\text{C}_{20}\text{H}_{16}\text{N}_4)_2\text{Pt}(\text{CN})_4$ , prepared by adding an aqueous solution of hydroplatinocyanic acid to an acetic acid solution of nitron, crystallises in shining grey plates.

*Uranyl platinocyanide*, prepared by double decomposition between uranyl sulphate and barium platinocyanide, separates from its aqueous solution at the ordinary temperature as red crystals with strong green metallic reflexion; imperfect, yellow crystals are obtained by evaporating the solution on a water-bath, which become reddish-green when cooled. The two forms probably represent different degrees of hydration. The reddish-green form changes into the yellow form at  $39^\circ$ .

W. H. G.

**Dimagnesium Derivative of  $\alpha$ -Dibromopentane.** VICTOR GRIGNARD and G. VIGNON (*Compt. rend.*, 1907, 144, 1358—1360).— $\alpha$ -Dibromopentane, prepared by von Braun's method (*Abstr.*, 1904, i, 841), reacts readily with magnesium, in presence of ether, forming a mobile, slightly coloured *dimagnesium* derivative. On treatment with carbon dioxide, this is converted into *cyclohexanone*, *pimelic acid*, and probably *decamethylenedicarboxylic acid*, brilliant cottony flocks, m. p.  $124$ — $125^\circ$ . Ethyl acetate reacts with the dimagnesium derivative, forming *tert.*-methylcyclohexanol and a *hydrocarbon*, b. p.  $70$ — $110^\circ$ , which may be methylcyclohexene produced by dehydration of the alcohol. Diacetyl reacts with the dimagnesium derivative, forming a

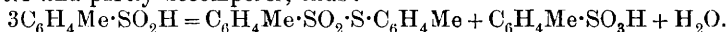
viscous, yellow liquid, b. p. 122—126°/14 mm., with an unpleasant butyric odour, which may be *dimethylcycloheptanediol*. The corresponding *diacetate* boils at 129—131°/12 mm. T. A. H.

**The Four Dinitro-derivatives of *o*-Dibromobenzene.** GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 843—846).—1 : 2-Dibromo-4 : 5-dinitrobenzene, prepared by Schiff (Abstr., 1891, 44), crystallises in the rhombic, bipyramidal class of the trimetric system [ARTINI.  $a : b : c = 0.7085 : 1 : 0.4961$ ].

1 : 2-Dibromo-3 : 5-dinitrobenzene (Schiff, *loc. cit.*) forms crystals belonging to the prismatic class of the monoclinic system [ARTINI.  $a : b : c = 0.8708 : 1 : 0.5683$ ;  $\beta = 89^\circ 32'$ ].

When 1 : 2-dibromo-3-nitrobenzene is nitrated with a mixture of nitric and sulphuric acids, it yields: (1) 1 : 2-dibromo-3 : 5-dinitrobenzene; (2) 1 : 2-dibromo-3 : 4-dinitrobenzene,  $C_6H_2Br_2(NO_2)_2$ , which separates from ethyl acetoacetate or carbon disulphide in faintly green, prismatic crystals, m. p. 109°, belonging to the prismatic class of the monoclinic system (ARTINI.  $a : b : c = 0.5717 : 1 : 0.6912$ ;  $\beta = 63^\circ 41'$ ); (3) 1 : 2-dibromo-3 : 6-dinitrobenzene,  $C_6H_2Br_2(NO_2)_2$ , which crystallises from carbon disulphide in almost white scales, or from a mixture of alcohol and ether in prisms or plates, m. p. 156.4°, belonging to the prismatic class of the monoclinic system [ARTINI.  $a : b : c = 1.7263 : 1 : 1.4846$ ]. T. H. P.

**Electrolytic Reduction of *p*-Toluenesulphonyl Chloride.** FRITZ FICHTER and W. BERNOULLI (*Zeitsch. Elektrochem.*, 1907, 13, 310—312).—When a solution of *p*-toluenesulphonyl chloride in 2*N*-alcoholic hydrogen chloride is electrolysed, the main product is the corresponding sulphinic acid, which is partly converted into the ethyl ester and partly decomposes, thus:



In presence of titanium trichloride and using a nickel gauze cathode the main product is *p*-tolyl mercaptan. The same result is obtained by reducing a suspension of the sulphonyl chloride in aqueous sulphuric acid at 80° with a lead cathode. The best method, however, is to use a saturated solution of *p*-toluenesulphonyl chloride in 2*N*-alcoholic sulphuric acid to which a quantity of the solid substance is added, this is stirred rapidly in a porous cell by means of a lead cathode. A water-cooled coil of lead tubing serves as anode; a cathodic current density of 0.13 ampere per sq. cm. gives a good yield of the mercaptan. T. E.

**Ditolane Hexachloride.** WILLY MARCKWALD and L. KARZAG (*Ber.*, 1907, 40, 2994—2996. Compare Wislicenus and Blank, Abstr., 1889, 261; Löb, Abstr., 1903, i, 811).—The authors have repeated Wislicenus and Blank's work and confirm their results, except that they find the supposed ditolane hexachloride to be an isomorphous mixture of tolane tetrachloride and  $\alpha$ -tolane dichloride. The formation of the isomorphous mixture on prolonged fusion of the tetrachloride with  $\beta$ -tolane dichloride results from transformation of the  $\beta$ - into the  $\alpha$ -dichloride on prolonged heating.  $\alpha$ -Tolane dichloride

has m. p.  $150^{\circ}$ ; toluene tetrachloride, m. p.  $161.5^{\circ}$ . The graph representing the m. p. of mixtures of these substances is a straight line; the molecular mixture, m. p.  $156^{\circ}$ ; the mixture obtained by partial reduction of toluene tetrachloride melts at a lower temperature in consequence of containing a slight excess of the dichloride. G. Y.

**Triphenylmethyl.** ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1907, 40, 3056—3058).—A reply to Gomberg (*this vol.*, i, 504). C. S.

**Dibenzylideneacetone and Triphenylmethane. IX.** ADOLF VON BAEYER (*Ber.*, 1907, 40, 3083—3090).—Largely a criticism of the quinonoid theory of coloured salts derived from triphenylcarbinol, &c. (compare Gomberg, *this vol.*, i, 504). The salts formed by the union of ferric chloride with the halogen derivatives of tri-*p*-chloro- (bromo-, iodo-) triphenylmethane have been prepared, and the decomposing effect of alkali or water in the presence of acetone examined. In all cases it was found that the halogen acid liberated was that derived from the ferric chloride and the carbinol haloid; no trace of the removal of the nucleus halogen atoms could be detected.

[With HANS AICHELIN].—*Tri-p-chlorotriphenylmethyl bromide*,  
 $C(C_6H_4Cl)_3Br$ ,

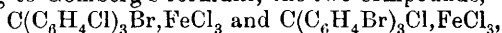
forms long, colourless needles, m. p.  $148^{\circ}$ . *Tri-p-bromotriphenylmethyl chloride ferrichloride*,  $C_{19}H_{12}Cl_4Br_3Fe$ , forms a brick-red, crystalline powder, m. p.  $237^{\circ}$ .

*Tri-p-chlorotriphenylmethyl bromide ferrichloride*,  $C_{19}H_{12}Cl_6BrFe$ , forms brown plates with a bluish-green lustre, m. p.  $217^{\circ}$ .

*Tri-p-iodotriphenylmethyl chloride ferrichloride*,  $C_{19}H_{12}Cl_4I_3Fe$ , forms olive-green crystals, which when rubbed yield a red powder.

*Tri-p-chlorotriphenylmethyl bromide ferribromide*,  $C_{19}H_{12}Cl_3Br_4Fe$ , forms brownish-green prisms and plates, m. p.  $216^{\circ}$ .

According to Gomberg's formulæ, the two compounds,



should behave similarly towards water or alkali as the quinonoid grouping is the same, but it is shown that the former yields 1Br and 3Cl, and the latter, 4Cl. J. J. S.

**Hexahydrophenylglycine.** NICOLAI D. ZELINSKY and B. ARZIBACHEFF (*Ber.*, 1907, 40, 3053—3055. Compare Zelinsky and Stadnikoff, *this vol.*, i, 425).—*Hexahydrophenylglycine* (cyclohexylglycine),  $C_6H_{11} \cdot NH \cdot CH_2 \cdot CO_2H$ , m. p.  $227-228^{\circ}$  (decomp.), is obtained by the hydrolysis of the nitrile; this results from the interaction of cyclohexylamine hydrochloride, 40% formaldehyde, and concentrated aqueous potassium cyanide in the cold, and is isolated from absolute ether in the form of the hydrochloride,  $C_6H_{11} \cdot NH \cdot CH_2 \cdot CN, HCl$ , m. p.  $193-194^{\circ}$  (decomp.). The acid forms a vivid blue copper salt,  $C_{16}H_{24}O_4N_2Cu, H_2O$ , and a nitroso-compound,  $C_6H_{11} \cdot N(NO) \cdot CH_2 \cdot CO_2H$ , m. p.  $117.5-118^{\circ}$ . C. S.

**Constitution of Xanthoxanil.** SIEGFRIED RUHEMANN (*Ber.*, 1907, 40, 3015—3017).—A reply to Wohl and Freund (*ibid.*, 2304), who

suggest a formula for xanthoxanil different from the author's (Trans., 1906, 89, 1236—1847).  
A. McK.

**Preparation of the Aniline Derivatives of Succinic Acid and of Phthalic Acid.** J. BISHOP TINGLE and MARSHALL P. CRAM (*Amer. Chem. J.*, 1907, 37, 596—604).—An account is given of improved methods for preparing succinanil, succinanilic acid, succinanilide, phthalanil, and phthalanilic acid. Phthalanilide is best prepared by the method of Rogoff (Abstr., 1897, i, 470).  
E. G.

**Substituted Bromoanilines.** J. R. HILL (*Proc. Camb. Phil. Soc.*, 1907, 14, 166—170).—The following compounds, obtained by acting on the corresponding tertiary aniline in glacial acetic acid with bromine, were prepared with the object of obtaining, by the addition of allyl or benzyl iodide, two series of substituted ammonium compounds containing an asymmetric nitrogen atom. These compounds, since they contain a brominated phenyl group, would differ in this respect from those investigated by Thomas and Jones (Trans., 1906, 89, 280), and hence admit of the study of the effect produced on the optical activity by the introduction of the bromine atom into the phenyl group.

Only in the case of the methylethylbromoaniline has it been possible to determine the position of the bromine atom. The quaternary hydroxide obtained from the methiodide of this compound gave on distillation *p*-bromodimethylaniline; the other quaternary hydroxides on distillation gave back the original bromoaniline. None of the methiodides of these compounds are decomposed by strong potassium hydroxide solutions.

*p*-Bromomethylethylaniline is an oil, b. p. 149—152°/13 mm. (compare Claus and Howitz, Abstr., 1884, 1005); the *methiodide*, m. p. 189°, and *picrate*, m. p. 138°, are both crystalline substances. The base combines with allyl iodide, yielding *p*-bromophenylmethylethylallylammonium iodide, which forms crystals, m. p. 134°.

*Methylisopropylbromoaniline*,  $\text{NMePr}^{\beta} \cdot (\text{C}_6\text{H}_4\text{Br})$ , crystallises in lustrous plates, m. p. 34°; the *hydrobromide*, m. p. 69°, *methiodide*, m. p. 167°, and *picrate*, m. p. 138°, are crystalline compounds; with allyl iodide is obtained *bromophenylmethylisopropylallylammonium iodide*,  $\text{C}_{13}\text{H}_{19}\text{NBrI}$ , a crystalline substance, m. p. 150°.

*Methylpropylbromoaniline*,  $\text{C}_{10}\text{H}_{14}\text{NBr}$ , is an oil, b. p. 149—152°/5 mm.; the *methiodide*, m. p. 167°, and *picrate*, m. p. 126°, form well-defined crystals.

*Methylisobutylbromoaniline*,  $\text{C}_{11}\text{H}_{16}\text{NBr}$ , is an oil, b. p. 169—173°/9 mm.; the *methiodide*, m. p. 167—168°, and *picrate*, m. p. 136—137°, are readily obtained in a crystalline form.

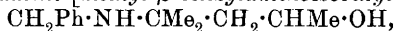
*Methylisoamylbromoaniline*,  $\text{C}_{12}\text{H}_{18}\text{NBr}$ , is an oil, b. p. 165—170°/5 mm.; the *methiodide*, m. p. 176°, and *picrate*, m. p. 89°, are crystalline substances.  
W. H. G.

**Resolution of Salts of Asymmetric Nitrogen Compounds and Weak Organic Acids.** MISS ANNIE HOMER (*Proc. Camb. Phil. Soc.*, 1907, 14, 196—198).—Inactive phenylbenzylmethylisopropyl-

ammonium hydroxide may be resolved by repeated crystallisation of the *d*-hydrogen tartrate,  $(C_{17}H_{22}N)C_4H_5O_6 \cdot H_2O$ . Attempts were therefore made to resolve inactive mixtures of *d*- and *l*-mandelic acids and of *d*- and *l*-valeric acids by means of active phenylbenzylmethylisopropylammonium iodide (Thomas and Jones, *Trans.*, 1906, **89**, 280), but a complete resolution could not be effected, owing to the fact that the solutions, being dilute, have to remain for some considerable time before crystallisation takes place and hence racemisation occurs during the process. If a concentrated solution of the active ammonium hydroxide could be obtained, it is probable that a complete resolution might be effected.

W. H. G.

**Derivatives of Diacetonalcamine. IX. MORITZ KOHN** (*Monatsh.*, 1907, **28**, 537—541).—Diacetonalcamine and benzyl chloride do not react together at the ordinary temperature, but when heated together a violent reaction takes place with the formation of benzyl diacetonalcamine [*methyl-β-benzylaminoisobutylcarbinol*],



and tribenzylamine. This latter compound is undoubtedly produced by the interaction of benzyl chloride with ammonia formed by the decomposition of the diacetonalcamine during the violent reaction.

Benzyl diacetonalcamine forms a colourless oil, b. p. 164—165°/15mm.; the *aurichloride*,  $C_{13}H_{21}ON \cdot HAuCl_4$ , crystallises in glittering scales, m. p. 157—160°; the *platinichloride*,  $(C_{13}H_{21}ON)_2 \cdot H_2PtCl_6$ , is crystalline. The *nitroso*-derivative,  $C_{13}H_{20}O_2N_2$ , crystallises from light petroleum in thin needles, m. p. 48°.

W. H. G.

**Aromatic Dithiocarbamates. II. SIMA M. LOSANITSCH** (*Ber.*, 1907, **40**, 2970—2977).—The product obtained from the action of carbon disulphide on amines depends on the basicity of the amine. Thus, whilst ammonia and primary or secondary aliphatic amines form dithiocarbamates, aromatic amines, in general, yield thiocarbamides. On the other hand, it has been found (*Abstr.*, 1892, 55; Delepine, *Abstr.*, 1902, i. 702) that in the presence of ammonia, primary and secondary aromatic amines form ammonium dithiocarbamates. The present work was undertaken to determine which aromatic amines are capable of forming dithiocarbamates directly, and which only with the assistance of a stronger base; the constitution of the dithiocarbamates formed by the action of carbon disulphide on two amines also has been determined.

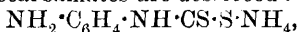
Aniline, *p*-toluidine, *α*- and *β*-naphthylamines, *o*-, *m*-, and *p*-phenylenediamines, *m*-tolylenediamine, benzidine, and *o*-tolidine form dithiocarbamates only in the presence of ammonia, or, in some cases, of phenylhydrazine or piperidine. This influence of ammonia, phenylhydrazine, and piperidine diminishes in the order in which these substances are named: thus benzidine in presence of ammonia forms a bisdithiocarbamate, but only a monodithiocarbamate with the assistance of phenylhydrazine, whilst it does not react with carbon disulphide in presence of piperidine. In the product,  $NR'R'' \cdot CS \cdot SH, NHR_2$ , formed

by the action of carbon disulphide on a mixture of amines, the group  $\text{NR}'\text{R}''$  is derived from the weaker base; hence an amine may function differently as it reacts in presence of a stronger or a more feeble base. Thus phenylhydrazine forms *ammonium anilinodithiocarbamate*,  $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{SNH}_4$ , but *phenylhydrazonium phenyldithiocarbamate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{SH}\cdot\text{NH}_2\cdot\text{NHPh}$ , in presence of ammonium and aniline respectively. Similarly, piperidine forms *ammonium piperylenedithiocarbamate*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CS}\cdot\text{SNH}_4$ , and *piperidonium phenyldithiocarbamate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{SH}\cdot\text{C}_5\text{H}_{10}\text{N}$ .

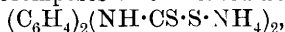
Ammonium aryldithiocarbamates are yellow, crystalline salts which yield diarylthiocarbamides, ammonia, ammonium sulphide, carbon disulphide, and an odour of thiocarbimide when heated. The phenylhydrazonium and piperidonium salts are white, crystalline substances, and are more stable than the ammonium salts.

Halogen, hydroxy-, and nitro-derivatives of aniline, toluidine, and naphthylamine, as also mono-, di-, and tri-aminoazobenzenes, diazoaminobenzene, triphenylguanidine, diphenylamine, and pyrrole do not form dithiocarbamates with carbon disulphide alone or in presence of ammonia, phenylhydrazine, or piperidine.

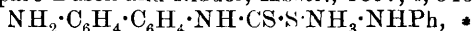
The following dithiocarbamates are described:



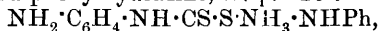
from *o*-phenylenediamine and ammonia, decomposes when heated yielding a product, m. p.  $260^\circ$ ; from *m*-phenylenediamine and ammonia, m. p.  $90^\circ$ ; from *p*-phenylenediamine, decomposes when heated yielding a product, m. p.  $250^\circ$ .  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{NH}_4$ , from *m*-tolylene-diamine, m. p.  $100^\circ$ , decomposes when heated above its m. p.



from benzidine and ammonia, m. p.  $240^\circ$  after decomposing and resolidifying.  $(\text{C}_6\text{H}_3\text{Me})_2(\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{NH}_4)_2$ , from *o*-toluidine, m. p.  $116^\circ$  (decomp.).  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CS}\cdot\text{S}\cdot\text{NH}_4$ , from piperidine and ammonia, decomposes at  $130^\circ$ .  $\text{NHPh}\cdot\text{CS}\cdot\text{S}\cdot\text{NH}_3\cdot\text{NHPh}$ , from aniline and phenylhydrazine, needles, m. p.  $82^\circ$  (compare Busch and Ridder, Abstr., 1897, i, 343).



from benzidine and phenylhydrazine, m. p.  $120^\circ$  (decomp.), and when further heated resolidifies, m. p.  $189^\circ$ .  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CS}\cdot\text{S}\cdot\text{NH}_3\cdot\text{NHPh}$ , from piperidine and phenylhydrazine, m. p.  $128^\circ$ .



from *p*-phenylenediamine and phenylhydrazine, colourless needles, m. p.  $109^\circ$ . A *dithiocarbamate*, m. p.  $122^\circ$ , is obtained from phenylhydrazine, tetrahydroquinoline, and carbon disulphide.  $\text{NHPh}\cdot\text{CS}\cdot\text{S}\cdot\text{C}_5\text{H}_{11}\text{N}$ , from piperidine and aniline, leaflets, m. p.  $97^\circ$ , yields phenylthiocarbimide when boiled with water.  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{S}\cdot\text{C}_5\text{H}_{11}\text{N}$ , from piperidine and *p*-phenylenediamine, colourless crystals, m. p.  $114$ — $115^\circ$ .

The action of carbon disulphide on aniline and tetramethylammonium hydroxide leads to the formation of a mixture of diphenylthiocarbamide and *tetramethylammonium phenylcarbamate*; the two substances crystallise together in needles, m. p.  $150^\circ$ , which decompose at the ordinary temperature, forming phenylthiocarbimide, yield diphenylthiocarbamide and phenylthiocarbimide when boiled with water or treated with acids, and dissolve in aqueous alkalis, forming a yellow solution and depositing diphenylthiocarbamide.

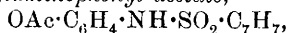
G. Y.



**Bivalency of Glucinum. Glucinum Picrate.** BORIS GLASSMANN (*Ber.*, 1907, 40, 3059—3060).—*Glucinum picrate*,  $\text{Gl}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2 \cdot 3\text{H}_2\text{O}$ , is obtained by neutralising a warm, aqueous solution of picric acid with glucinum carbonate. The molecular weight of the anhydrous picrate, determined by the cryoscopic method in acetophenone, is 465. The presence of moisture in the solvent causes an elevation of the freezing point, due probably to the hydration of the picrate. C. S.

**Nitration of Derivatives of *p*-Aminophenol.** FRÉDÉRIC REVERDIN [and FRITZ DINNEN] (*Ber.*, 1907, 40, 2848—2857; *Bull. Soc. Chim.*, [iv], 1, 624. Compare *Abstr.*, 1905, i, 54, 430; 1906, i, 165, 748; this vol., i, 37).—This is a study of the nitration, under varying conditions, of derivatives of *p*-aminophenol in which the hydroxylic and an amino-hydrogen atom are substituted by *p*-toluenesulphonyl and acetyl or benzoyl.

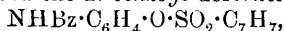
4-*p*-Toluenesulphonylaminophenyl acetate,



prepared from acetic anhydride and 4-*p*-toluenesulphonylaminophenol, crystallises in rose-coloured leaflets, m. p. 138—139°, and is hydrolysed by cold dilute alkalis, hot aqueous sodium carbonate, or concentrated sulphuric acid.

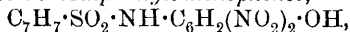
4-*p*-Toluenesulphonylaminophenyl benzoate,  $\text{C}_{20}\text{H}_{17}\text{O}_4\text{NS}$ , crystallises in needles, m. p. 170°.

From 4-aminophenyl *p*-toluenesulphonate are prepared the *N*-acetyl, m. p. 146°, and the *N*-benzoyl derivative,



white needles, m. p. 218°.

3:5-Dinitro-4-*p*-toluenesulphonylaminophenol,



crystallising in needles, m. p. 157—158°, is formed by the action of nitric acid, D 1·52, on the acetate at -10—0°, and, on hydrolysis with concentrated sulphuric acid on the water-bath, yields 3:5-dinitro-4-aminophenol. The action of a mixture consisting of 45% of nitric acid, D 1·4, and 55% of concentrated sulphuric acid on the acetate in acetic anhydride solution leads to the formation of a substance crystallising from alcohol in white needles, m. p. 145—146°, which contains only 4·81% of nitrogen; 3:5-dinitro- and small amounts of 3-nitro-4-aminophenol are obtained on hydrolysis of the mother liquors from this, or of the product of the action of nitric acid, D 1·52, on the acetate in acetic anhydride solution.

Nitration of the benzoate with nitric acid leads to the formation of nitro-*p*-toluenesulphonyl-4-amino-3:5-dinitrophenylnitrobenzoate,  $\text{NO}_2 \cdot \text{C}_7\text{H}_6 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , yellow needles, m. p. 189—190°, or with a mixture of nitric and sulphuric acids in acetic anhydride solution to the formation of a product which, on hydrolysis, yields 3-nitro-4-aminophenol.

Nitration of 4-acetylaminophenyl *p*-toluenesulphonate with nitric acid, D 1·4, leads to the formation of 3-nitro-4-acetylaminophenyl nitro-*p*-toluenesulphonate,  $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$ , yellow leaflets, m. p. 146°, or with a mixture of nitric acid, D 1·4, and

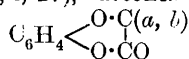
sulphuric acid in acetic anhydride solution, to the formation of 3-nitro-4-acetylaminophenyl *p*-toluenesulphonate,  $C_{15}H_{14}O_6N_2S$ , yellow leaflets, m. p.  $134^\circ$ , or with a mixture of nitric acid, D 1.52, and sulphuric acid in acetic anhydride solution, to the formation of a *product*, which, on hydrolysis, yields 3-nitro-4-aminophenol. The mononitro-derivative, m. p.  $134^\circ$ , is formed also by the action of acetyl nitrate on 4-acetylaminophenyl *p*-toluenesulphonate in acetic anhydride solution. The introduction of a second nitro-group into the phenol nucleus takes place to only a small extent when the dinitro-derivative, m. p.  $146^\circ$ , is treated with nitric acid, D 1.52.

Nitration of 4-benzoylaminophenyl *p*-toluenesulphonate by means of nitric acid, D 1.52, or of a mixture of nitric and sulphuric acids, leads to the formation of a *trinitro*-derivative, m. p.  $145$ — $150^\circ$ , which, on hydrolysis, yields 3-nitro-4-aminophenol and nitrotoluenesulphonic and *m*-nitrobenzoic acids. This trinitro-derivative is formed also to a small extent on nitration of the *N*-benzoyl compound with the acid mixture in acetic anhydride solution, whilst nitration with acetyl nitrate leads to the formation of a *product* which, on hydrolysis, yields a mixture of nitro- and dinitro-aminophenols. A small amount of dinitroaminophenol is formed further by hydrolysis of the *product* of the action of nitric acid, D 1.52, on the trinitro-compound.

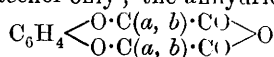
The iodo-acid, m. p.  $114$ — $115^\circ$ , derived from dinitrophenoxyacetic acid (Reverdin and Bucky, Abstr., 1906, i, 748), is found now to be 4-iodo-2:5-dinitrophenol, whilst the product, m. p.  $201$ — $202^\circ$ , is 4-iodo-2:5-dinitrophenoxyacetic acid. G. Y.

**Action of Nitric Acid on Phenol Ethers.** HERMANN THOMS and ADOLF SCHÜLER (*Arch. Pharm.*, 1907, 245, 284—286).—Examples are tabulated which show that: (1) dimethoxybenzenes all yield nitro-derivatives readily; (2) as the methoxy-groups accumulate, the entry of nitro-groups is retarded, only taking place when a para-position is free, and oxidation to a quinone is favoured; (3) alkyl (propyl) groups favour the entry of nitro-groups, which may take place in a para-position to the alkyl group even when this must be accompanied by elimination of methoxyl from the position in question. C. F. B.

**Preparation of Cyclic Esters and Ethers of Catechol.** CARL A. BISCHOFF and EMANUEL FRÖHLICH (*Ber.*, 1907, 40, 2779—2790).—Whilst oxalic esters of the type  $C_6H_4 \begin{smallmatrix} \diagup O \cdot CO \\ \diagdown O \cdot CO \end{smallmatrix}$  were obtained from each of the dihydroxybenzenes (Bischoff and von Hedenström, Abstr., 1903, i, 27), lactones of the type

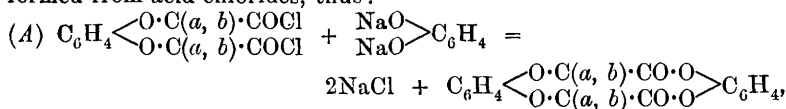


were obtained from catechol only; the anhydride type

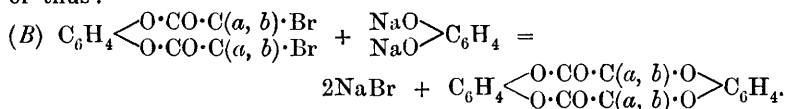


was represented in the ortho-series only. In the present communication the influences of the ortho-, meta-, and para-positions of the

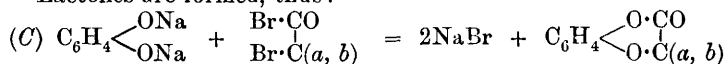
hydroxyl group, on the one hand, and of the groups *a* and *b* (H, Me, Et, and Pr<sup>β</sup>), on the other, on the formation of lactones and bis-esters respectively have been examined. The latter esters can be formed from acid chlorides, thus:



or thus:



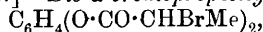
Lactones are formed, thus:



Catecholbisoxylacetic acid, obtained by the action of monochloroacetic acid on catechol, has m. p. 177—178°. The *chloride*,  $\text{C}_6\text{H}_4(\text{O} \cdot \text{CH}_2 \cdot \text{COCl})_2$ , obtained by the action of thionyl chloride on the acid, has b. p. 213°/41 mm., and separates from a mixture of benzene and light petroleum in crystals, m. p. 49—50°. The cyclic compound, obtained by the action of the chloride on disodium catechol in accordance with *A*, was a resin, which began to crystallise in prisms after several months, but could not be recrystallised; it was not analysed.

Catechol-*α*-oxypropionyl lactone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \cdot \text{CO} \\ \text{O} \cdot \text{CHMe} \end{array}$ , was obtained from disodium catechol and ethyl *α*-bromopropionate.

[With H. HOFFMANN.]—*Bis-α-bromopropionylcatechol*,



obtained from disodium catechol and *α*-bromopropionyl bromide separates from alcohol in colourless leaflets, m. p. 62°.

*Bis-α-bromobutyrylcatechol*,  $\text{C}_6\text{H}_4(\text{O} \cdot \text{CO} \cdot \text{CHBrEt})_2$ , obtained from disodium catechol (1 mol.) and bromobutyryl bromide (2 mols.), separates from alcohol in colourless leaflets, m. p. 75—76°. If molecular proportions of the sodium compound and the acid bromide are used, *catechol-*

*mono-α-oxybutyrolactone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \cdot \text{CHEt} \\ \text{O} \cdot \text{CO} \end{array}$ , is formed as a reddish-yellow oil, b. p. 131°/25 mm.

*Bis-α-bromoisobutyrylcatechol*,  $\text{C}_6\text{H}_4(\text{O} \cdot \text{CO} \cdot \text{CBrMe}_2)_2$ , prepared from disodium catechol (1 mol.) and bromoisobutyryl bromide (2 mols.), is an oil with b. p. 195—200°/20 mm. When molecular proportions of sodium compound and acid bromide are used, the main product is catechol *α*-oxyisobutyrolactone.

*Bis-α-bromoisovalerylcatechol*,  $\text{C}_{16}\text{H}_{20}\text{O}_4\text{Br}_2$ , is a colourless oil, b. p. 220—225°/20 mm. *Catecholoxysovalerolactone*,  $\text{C}_{11}\text{H}_{12}\text{O}_3$ , is a colourless oil, b. p. 128°/20 mm. A. McK.

**Resorcinol and Quinol Esters of Halogenated Fatty Acids.** CARL A. BISCHOFF and EMANUEL FRÖHLICH (*Ber.*, 1907, 40, 2790—2803. Compare preceding abstract).—The authors describe

representatives of the type  $C_6H_4[O\cdot CO\cdot C(a, b)Br]_2$ , and also reactions undergone by the compound  $C_6H_4(O\cdot CH_2\cdot COCl)_2$ .

Resorcinolmono-oxyacetic acid,  $OH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$ , is formed, together with the dioxy-acid, by the action of ethyl monochloroacetate on a mixture of sodium ethoxide and resorcinol in ethyl alcoholic solution. Its ethyl ester separates from benzene in monoclinic pyramids, m. p.  $55^\circ$ . Various data quoted by Carter and Lawrence (Trans., 1900, 77, 1222) are confirmed. *Resorcinoldioxyacetyl chloride*,  $C_6H_4(O\cdot CH_2\cdot COCl)_2$ , is an oil, b. p.  $232^\circ/12-60$  mm. (decomp.).

[With F. ULMANN.]—*Bisbromopropionylresorcinol*,  
 $C_6H_4(O\cdot CO\cdot CHBr\cdot Me)_2$ ,

obtained by the action of bromopropionyl bromide on disodium resorcinol in benzene solution, separates from alcohol in colourless crystals, m. p.  $66^\circ$ , and b. p.  $217-220^\circ/10$  mm. As products of its interaction with disodium resorcinol, tribromoresorcinol and resorcinol bis- $\alpha$ -oxypropionic acid were obtained. The interaction with disodium catechol and disodium quinol gave tarry products.

*Bis- $\alpha$ -bromobutyrylresorcinol*,  $C_6H_4(O\cdot CO\cdot CHEtBr)_2$ , is a bright yellow oil, b. p.  $225-227^\circ/19$  mm. *Bis- $\alpha$ -bromoisobutyrylresorcinol* has m. p.  $61^\circ$  and b. p.  $227-228^\circ/20$  mm.

*Bis- $\alpha$ -bromoisovalerylresorcinol*,  $C_6H_4(O\cdot CO\cdot CHBr\cdot CHMe)_2$ , is a viscid, yellow oil, b. p.  $222-228^\circ/15$  mm.

[With DIFFERT.]—*Quinoldioxyacetyl chloride*,  $C_6H_4(O\cdot CH_2\cdot COCl)_2$ , obtained from the corresponding acid previously prepared by Carter and Lawrence (*loc. cit.*), forms colourless crystals, m. p.  $84^\circ$ , and has b. p.  $240^\circ/12-100$  mm. (decomp.). It interacts with disodium quinol to form quinolbisoxyacetylquinol,  $C_6H_4\begin{smallmatrix} O\cdot CH_2\cdot CO\cdot O \\ O\cdot CH_2\cdot CO\cdot O \end{smallmatrix}C_6H_4$ .

*Bis- $\alpha$ -bromopropionylquinol*,  $C_6H_4(O\cdot CO\cdot CHMeBr)_2$ , obtained from  $\alpha$ -bromopropionyl bromide and disodium quinol, separates from benzene in colourless prisms, m. p.  $110^\circ$ . It interacts with disodium catechol to form catecholoxypropiolactone,  $C_6H_4\begin{smallmatrix} O\cdot CHMe \\ O\cdot CO \end{smallmatrix}$ , m. p.  $51^\circ$ .

*Bis- $\alpha$ -bromobutyrylquinol*,  $C_6H_4(O\cdot CO\cdot CHEtBr)_2$ , forms colourless leaflets, m. p.  $67-68^\circ$ . *Bis- $\alpha$ -bromoisobutyrylquinol* forms colourless needles, m. p.  $120^\circ$ . *Bis- $\alpha$ -bromoisovalerylquinol* separates from alcohol in colourless leaflets, m. p.  $53^\circ$ .  
 A. McK.

**Preparation of Quinonoid Sulphur Compounds.** THEODOR ZINCKE and W. GLAHN (*Ber.*, 1907, 40, 3039—3049).—The similarity between oxygen and sulphur suggested the possibility of preparing thioquinones of the type  $O\cdot C_6H_4\cdot S$ , and this investigation deals with the results obtained in the attempt. 2:6-Dibromophenol-4-sulphonyl chloride,  $C_6H_3O_3ClBr_2S$ , which crystallises in colourless needles, m. p.  $127-128^\circ$ , is easily prepared, the bromine shielding the hydroxyl group from the attack of the phosphorus pentachloride. On reduction with zinc and hydrochloric acid in alcoholic solution, 2:6-dibromothioquinol,  $SH\cdot C_6H_3Br_2\cdot OH$ , is obtained, crystallising in glistening needles, m. p.  $82^\circ$ . All attempts to convert this into the corresponding thiobenzoquinone have been fruitless; nitric acid oxidises it to

picric acid, and ferric chloride gives 2:2':6:6'-*tetrabromo-4:4'-diphenol disulphide*,  $C_{12}H_6O_2Br_4S_2$ , which crystallises in pale yellow needles, m. p. 152—153°. 2:6-*Dibromothioquinol diacetate* has m. p. 137—138°. With methyl iodide, the thioquinol yields, according to the conditions employed, a sulphide or a sulphonium iodide. When 1 mol. of the thioquinol dissolved in a solution of sodium methoxide (1 mol.) in methyl alcohol is treated with 1 mol. of methyl iodide in

the cold, 2:6-*dibromophenol 4-methyl sulphide*,  $OH \begin{array}{c} \text{Br} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \\ \diagdown \quad \diagup \\ \text{Br} \end{array} SMe$ , is

formed, and crystallises in needles, m. p. 47—48°. Nitric acid oxidises the compound to picric acid. The *acetate*,  $C_9H_8O_2Br_2S$ , has m. p. 99°. When a dilute solution of sodium nitrite is carefully added to a cold solution of the dibromomethylthiophenol in glacial acetic acid, 2-*bromo-6-nitrophenol 4-methyl sulphide*,  $C_7H_6O_3NBrS$ , is formed. It crystallises in red needles, m. p. 108°; the *acetate*,  $C_9H_8O_4NBrS$ , crystallises in dark yellow needles, m. p. 109—110°. Nitric acid in glacial acetic acid converts this sulphide into 2-*bromo-*

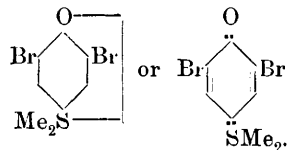
6-*nitrophenol-1-methylsulphoxide*,  $OH \begin{array}{c} NO_2 \\ \diagup \quad \diagdown \\ \text{C}_6H_3 \\ \diagdown \quad \diagup \\ \text{Br} \end{array} SMeO$ , crystallising in

yellow needles, m. p. 147—148°; the *acetate*, yellow needles, m. p. 106—107°. When 2 mols. of sodium methoxide and 2 of methyl iodide interact with the thioquinol at the b. p., 2:6-*dibromophenol-*

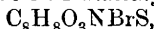
4-*dimethylsulphonium iodide*,  $OH \begin{array}{c} \text{Br} \\ \diagup \quad \diagdown \\ \text{C}_6H_3 \\ \diagdown \quad \diagup \\ \text{Br} \end{array} SMe_2I$ , separates on cooling.

It crystallises from water in silky needles which lose methyl iodide at about 100°. The corresponding *sulphonium chloride*,  $C_8H_9OClBr_2S$ , obtained by the interaction of silver chloride and iodide in aqueous solution, crystallises in white, silky needles, losing methyl chloride at 160°. By shaking silver oxide with an aqueous solution of the sulphonium iodide, an anhydro-compound, 2:6-*dibromo-1:4-dimethyl-*

*thioniumquinone*, is obtained. It may also be obtained by using alkali hydroxides. From water it crystallises in white plates, m. p. 251—252° (decomp.). Water regenerates the sulphide. 2:6-*Dinitro-1:4-dimethylthioniumquinone*,  $C_8H_8O_5N_2S$ , obtained by heating the sulphonium iodide



with nitric acid (D 1.4), crystallises in glistening, yellow leaflets, m. p. 263—264° (decomp.). Hydroxylamine and phenylhydrazine are without action on the compound. The *hydrochloride* and *sulphate* are colourless, and it forms a *platinichloride*,  $(C_8H_9O_5N_2S)_2PtCl_6$ . If, however, the nitration be carried out in glacial acetic acid solution with less acid, 2-*bromo-6-nitro-1:4-dimethylthioniumquinone*,



is the product. It is more stable than the dinitro-compound, crystal-

lises in yellow needles, m. p. 270—271° (decomp.), and forms more stable salts and a *platinichloride*,  $(C_8H_9O_3NBrS)_2PtCl_6$ .

*2:6-Dinitrophenol 4-methyl sulphide*,  $C_7H_6O_5N_2S$ , prepared by digesting the dinitrodimethylthioniumquinone with 25% hydrobromic acid, forms dark red needles, m. p. 104—105°; the *acetate*, yellow needles, m. p. 129—130°. The corresponding *sulphoxide*,  $C_7H_6O_6N_2S$ , forms light yellow leaflets, m. p. 150°; the *acetate*, yellow needles, m. p. 137° (decomp.).

The conclusion is drawn that the more probable formula for the thionium compounds is the quinonoid. W. R.

**The Ethereal Function in Dichloromethylenecatechol.** RAYMOND DELANGE (*Compt. rend.*, 1907, 144, 1278—1280).—The conversion of compounds containing the group  $:O_2:CCl_2$  into the corresponding carbonates containing the group  $:O_2:CO$  by the action of cold water (Abstr., 1904, i, 313, 741) is found to be a general reaction. Thus *ethyl dichloropiperonylate*,  $CCl_2:O_2:C_6H_3:CO_2Et$ , having b. p. 156—157°/9 mm., gives the *carbonate*,  $CO:O_2:C_6H_3:CO_2Et$ , which has b. p. 169—171°/12 mm., whilst *dichloropiperonyl chloride*,  $CCl_2:O_2:C_6H_3:COCl$ , having b. p. 149—151°/13 mm., gives a mixture of the *carbonate*,  $CO:O_2:C_6H_3:CO_2H$ , and 3:4-dihydroxybenzoic acid.

Fittig and Remsen (*Annalen*, 1869, 149, 157) by the action of water on tetrachloropiperonal,  $CCl_2:O_2:C_6H_3:CHCl_2$ , obtained a substance which they considered to be dichloropiperonal,  $CCl_2:O_2:C_6H_3:CHO$ . The author having obtained tetrachloropiperonal as crystals, m. p. 34°, b. p. 162—164°/14 mm., has prepared Fittig and Remsen's compound, which, however, he considers to be, not dichloropiperonal, but *dichloromethylcatechol carbonate*,  $CO:O_2:C_6H_3:CHCl_2$ , since (1) the group  $:O_2:CCl_2$  is more readily attacked by water than is the group  $\cdot CHCl_2$ ; (2) when boiled with water or dilute acids it gives 3:4-dihydroxybenzaldehyde; (3) it does not combine with sodium hydrogen sulphite, and (4) when treated with phosphorus pentachloride it does not regenerate tetrachloropiperonal, but remains unchanged.

Potassium hydroxide acts very violently on the dichloromethylenic ethers, forming compounds containing the group  $:O_2:C:C:O_2:$ ; thus propyl catechol dichloromethylene ether gives the compound  $C_6H_3Pr^a:O_2:C:C:O_2:C_6H_3Pr^a$ , b. p. 242—243°/10 mm., which by dissolving in sulphuric acid and pouring the solution into water gives propylcatechol carbonate and *propylcatecholmethylenedisulphonic acid*,  $C_6H_3Pr^a:O_2:C(SO_3H)_2$ , m. p. 52°. E. H.

**Diphenyl Derivatives of Hydroxyquinol Trimethyl Ether [1:2:4-Trimethoxybenzene]. Action of Nitric Acid on Hydroxyquinol Trimethyl Ether.** ADOLF SCHÜLER (*Arch. Pharm.*, 1907, 245, 262—283).—When the triacetate of hydroxyquinol, prepared from quinone by Thiele's method (Abstr., 1900, i, 505), is added to methyl or ethyl alcoholic sodium methoxide or ethoxide, and the resulting sodium derivative is methylated by the addition of methyl sulphate gradually and with constant shaking, then, if the 1:2:4-trimethoxybenzene formed is separated by distillation with steam instead of by shaking with ether, a by-product crystallises

from the residue after distillation. This substance appears to be a 2:4:5:2':4':5'-*hexahydroxydiphenyl*,  $C_6H_2(OMe)_3 \cdot C_6H_2(OMe)_3$  (molecular weight determined cryoscopically in naphthalene); m. p. 177°. The fact that it does not yield a nitro-derivative makes it probable that no para-hydrogen atom is present; boiling with concentrated hydriodic acid converts it into 4:5:4':5'-*tetrahydroxydiphenylene-2:2'-oxide*,  $O \begin{array}{c} \diagup C_6H_2(OH)_2 \\ \diagdown C_6H_2(OH)_2 \end{array}$ , m. p. 252°, which decomposes without melting when it is heated and forms an *acetyl* derivative.

1:2:4-Trimethoxybenzene forms a mononitro-derivative when nitrated in acetic acid solution in the cold; as the corresponding amino-derivative is oxidised readily to a quinone, probably the nitro-group is in the para-position to one of the methoxyl groups. 5-Nitro-1:2:4-trimethoxybenzene,  $NO_2 \cdot C_6H_2(OMe)_3$ , m. p. 129°, is yellow. It is reduced by tin and hydrochloric acid to 5-amino-1:2:4-trimethoxybenzene,  $NH_2 \cdot C_6H_2(OMe)_3$ , m. p. 94·5—95°; *hydrochloride*, m. p. 210° (decomp.); *benzoyl* derivative, m. p. 139·5—140°; this base is unstable in the air; 50% nitric acid, and nitrous acid also, oxidise it to 2:5-dimethoxy-p-benzoquinone,  $C_6H_2O_2(OMe)_2$ , which is yellow, decomposes without melting when it is heated, and is reduced by sulphurous acid to 2:5-dihydroxy-1:4-dimethoxybenzene,  $C_6H_2(OH)_2(OMe)_2$ , m. p. 170° (not 166°, Nietzki and Rechberg, Abstr., 1890, 968).

A dinitro-derivative of 1:2:4-trimethoxybenzene could not be obtained; the substance, m. p. 131°, described under this name (Will, Abstr., 1888, 457) was the mononitro-derivative just described. When a solution of the ether is added to dilute nitric acid and a reaction is induced by heating cautiously, oxidation takes place to a yellow substance, which decomposes without melting when it is heated, and appears to be a diphenylquinone with some such constitution as  $OMe \cdot C_6H_2O_2 \cdot C_6H_2O_2 \cdot OMe$ .  
C. F. B.

### Transformation of Anethole Glycol into Anisylacetone.

MARC TIFFENEAU and DAUFRESNE (*Compt. rend.*, 1907, 144, 1354—1356. Compare Abstr., 1902, i, 666; 1904, i, 63, 133; 1906, i, 662, 724, 965; 1907, i, 130).—In previous papers the transformation of  $\alpha$ -glycols into aldehydes or ketones has been dealt with, and in view of Balbiano and Paolini's statement that  $\alpha$ -glycols of the type  $OH \cdot CHAr \cdot CHR \cdot OH$ , where Ar is an aryl radical, are converted by treatment with zinc chloride into hydrocinnamaldehydes, it has been thought desirable to ascertain whether the reaction represented by the scheme

$OH \cdot CHAr \cdot CHR \cdot OH \rightarrow CHAr \cdot CR \cdot OH \rightarrow CH_2Ar \cdot COR$ ,  
previously suggested (Tiffeneau, Abstr., 1907, i, 404), is of general application.

The diacetyl derivative of anethole glycol, obtained by heating anethole dibromide, dissolved in acetic acid, with lead or silver acetate (Balbiano and Paolini, Abstr., 1902, i, 808), has  $D^{20}_D$  1·127, b. p. 187—189°/12 mm. The  $\alpha$ -acetoxy- $\beta$ -bromo-derivative, simultaneously produced (Hoering, Abstr., 1905, i, 903), has  $D^{20}_D$  1·46, and b. p. 180—185°/14 mm., and on distillation is partially decomposed, yielding

the *bromo-derivative*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CMeBr}$ . This has  $D_0$  1.325 and distils at  $153\text{--}154^\circ$  under 15 mm. pressure. When anethole dibromide dissolved in acetic acid is heated with zinc acetate, *p*-methoxyhydratropaldehyde is produced.

Anethole glycol,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_5(\text{OH})_2$  (Balbiano and Nardacci, Abstr., 1902, i, 808), on distillation under reduced pressure, furnishes a crystalline *substance*, m. p.  $98^\circ$ , b. p.  $240\text{--}250^\circ/14$  mm., which may be the corresponding diethylenic oxide, and when treated with sulphuric acid is converted into anisylacetone. T. A. H.

**Action of Organo-magnesium Compounds on Phthalide.** ALEXANDER LUDWIG (*Ber.*, 1907, 40, 3060—3065).—The behaviour of organo-magnesium compounds with alkylated phthalimides (Sachs and Ludwig, Abstr., 1904, i, 266; Béis, *ibid.*, i, 503) and “saccharins” (Sachs and Ludwig, *ibid.*, i, 876) led the author to examine the reaction between the Grignard reagent and phthalide. With an excess (3 mols.) of the reagent it proceeds thus:  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{O} \rightarrow$

$\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CR}_2 \cdot \text{OH} \\ \text{CH}_2 \cdot \text{OH} \end{smallmatrix} \right\rangle$ , and this primary-tertiary alcohol yields by solution in sulphuric acid an intensely coloured liquid from which water precipitates colourless *as-dialkyl-o-xylylene oxides*,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CR}_2 \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{O}$ , which the author proposes to call dialkylphthalans.

The following compounds are described: *o-methylolphenyldimethylcarbinol*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}_2 \cdot \text{OH}$ , m. p.  $63\text{--}64^\circ$ ; *1:1-dimethyl-1:2-dihydroisobenzofuran* (*as-dimethyl-o-xylylene oxide*, *dimethylphthalan*),  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CMe}_2 \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{O}$ , is an oil with a terpene-like odour; *o-methylolphenyldiethylcarbinol*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}^t\text{Et}_2 \cdot \text{OH}$ , m. p.  $81\text{--}82^\circ$ ; *o-methylolphenyldiisopropylcarbinol*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPr}^i_2 \cdot \text{OH}$ , m. p.  $107\text{--}108^\circ$ ; *o-methylolphenyldibenzylcarbinol*,

$\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CH}_2\text{Ph})_2 \cdot \text{OH}$ , m. p.  $133\text{--}134.5^\circ$ , and its *acetyl* derivative, m. p.  $103\text{--}104^\circ$ . The preceding carbinol is insoluble in concentrated sulphuric acid, but when the solution in glacial acetic acid is boiled with concentrated hydrochloric acid and diluted with water, *dibenzylphthalan*,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{C}(\text{CH}_2\text{Ph})_2 \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{O}$ , m. p.  $88\text{--}89^\circ$ , is obtained, which forms crystals 2—3 cm. in length. C. S.

**Thiobenzoic Acids.** EMIL FROMM and PH. SCHMOLDT (*Ber.*, 1907, 40, 2861—2870).—Both benzoyl disulphide and thiobenzoyl disulphide contain the grouping  $\text{—}\ddot{\text{C}} \cdot \text{S} \cdot \text{S} \cdot \ddot{\text{C}}\text{—}$ , and are consequently found to follow Fromm's rule (Abstr., 1906, i, 656), being decomposed on heating or on treatment with alkalis, ammonia, and amines with the separation of sulphur.

Benzoyl disulphide is most readily prepared by the action of potassium ferricyanide on dilute solutions of thiobenzoates; it is decomposed by potassium hydroxide with the formation of thiobenzoic and benzoic acids and liberation of sulphur.



Thiobenzoyl disulphide cannot be prepared by acting on phenyl-carbithionic acid (dithiobenzoic acid) with potassium ferricyanide, but is readily obtained by Houben and Pohl's method (Abstr., 1906, i, 847). It is decomposed by alcoholic potassium hydroxide into phenyl-carbithionic and benzoic acids with liberation of sulphur, and by aniline with the formation of thiobenzanilide and the separation of sulphur.

When either thiobenzoic acid, benzoyl sulphide, or benzoyl disulphide are distilled, they decompose yielding the same decomposition products, namely, hydrogen sulphide, sulphur, benzoic acid, and tolane tetrasulphide, a compound isomeric with thiobenzoyl disulphide (Houben and Pohl, *loc. cit.*).

$$\begin{array}{c} \text{S-CPh-S} \\ \text{S-CPh-S} \end{array}$$

*Tolane tetrasulphide*,  $\frac{1}{\text{S}} \frac{1}{\text{CPh}} \frac{1}{\text{S}} \frac{1}{\text{S}}$ , forms colourless crystals, m. p. 164°;

it is not decomposed by ammonia or aniline, but is converted by alcoholic potassium hydroxide into 2:3:4:5-tetraphenylthiophen. This latter compound is also obtained from tolane tetrasulphide on reduction and by distillation over copper powder.

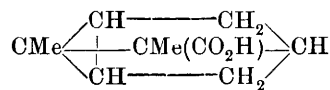
When lead phenylcarbithionate (dithiobenzoate) is submitted to dry distillation, it decomposes into lead sulphide, sulphur, and *tolane disulphide*,  $\text{CPh} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{CPh}$ , which crystallises in needles, m. p.

174—175°, and is similar to tolane tetrasulphide in properties, being stable towards aniline and converted by potassium hydroxide, by distillation with copper powder, or by reduction, into 2:3:4:5-tetraphenylthiophen.

Benzylidene chloride is converted by sodium sulphide into  $\beta$ -trithiobenzaldehyde, and by sodium hydrosulphide into benzyl disulphide; phenylcarbithionic acid is not formed in the latter case as stated by Klinger (Abstr., 1882, 1058).

W. H. G.

**Constituents of Ethereal Oils—Teresantalic Acid, its Derivatives, and Constitution.** FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 3101—3107. Compare Guerbet, Abstr., 1900, i, 242; Müller, *ibid.*, i, 678).—The optical properties of teresantalic acid derivatives indicate that these compounds belong to a saturated tricyclic series of quite different constitution, however, from the tricyclic santalol and eksantalol series (this vol., i, 431). The annexed formula is suggested for teresantalic acid.



Teresantalic acid has  $[\alpha]_D^{25} 70^\circ 24'$ . The *methyl* ester,  $\text{C}_{11}\text{H}_{16}\text{O}_2$ , obtained by leaving the silver salt with an excess of methyl alcohol in a spacious separating funnel for some time, has b. p. 85—86°/11 mm.,  $D_{20}^{20} 1.032$ , and  $n_D 1.47053$ . When reduced with sodium and alcohol, the ester yields *teresantalol*,  $\text{C}_{10}\text{H}_{16}\text{O}$ , which may be crystallised from light petroleum; m. p. 113°, b. p. 95—98°/9 mm.,  $[\alpha]_D +11^\circ 58'$ . It sublimes with the greatest readiness. The *acetate* has b. p. 102—103°/9—10 mm.,  $D_{20}^{20} 1.019$ ,  $n_D 1.470$ . *Teresantalyl chloride*,  $\text{C}_{10}\text{H}_{15}\text{Cl}$ , obtained by the action of phosphorus pentachloride on an ethereal

solution of the alcohol, has b. p.  $78-85^{\circ}/9$  mm. and  $D^{20}$  1.0656. *Teresantalan*,  $C_{10}H_{16}$ , has b. p.  $165-168^{\circ}$ ,  $D^{20}$  0.892, and  $n_D$  1.48033. The hydrochloride of teresantalic acid has m. p.  $199^{\circ}$ , and when reduced yields *dihydroteresantalic acid*,  $C_{10}H_{16}O_2$ , m. p.  $226^{\circ}$ . The corresponding *methyl ester*,  $C_{11}H_{18}O_2$ , has b. p.  $88^{\circ}/9$  mm.,  $D^{20}$  1.0034,  $n_D$  1.46757, and is laevorotatory.

*Dihydroteresantalol*,  $C_{10}H_{18}O$ , obtained by reducing either the above methyl ester or, better, teresantalol, has b. p.  $171^{\circ}$ ; *dihydroteresantalyl chloride*,  $C_{10}H_{17}Cl$ , has b. p.  $70-75^{\circ}/9$  mm., and *dihydroteresantalan*,  $C_{10}H_{18}$ , b. p.  $48-58^{\circ}/9$  mm. These reduction products have a saturated dicyclic constitution. J. J. S.

**Ethyl Hexahydrobenzoylacetate.** NICOLAI D. ZELINSKY and D. SCHWEDOFF (*Ber.*, 1907, 40, 3055—3056).—*Ethyl hexahydrobenzoylacetate*,  $C_6H_{11}\cdot CO\cdot CH_2\cdot CO_2Et$ , b. p.  $135-137^{\circ}/18$  mm.,  $D^{18}$  0.9678, is obtained by the action of equal molecular quantities of ethyl acetate and hexahydrobenzoate on finely-divided sodium. Ferric chloride produces an intense violet-red coloration. C. S.

**1:4-Diaminohexahydroterephthalic Acid.** NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1907, 40, 2888—2890. Compare this vol., i, 720).—1:4-Diaminohexahydroterephthalonitrile,  $C_6H_8(CN)_2(NH_2)_2$ , is formed when diketohexamethylene (*cyclohexane-1:4-dione*) is condensed with potassium cyanide and ammonium chloride in concentrated aqueous solution in the cold. It separates in the form of colourless crystals which decompose at  $193^{\circ}$  without melting. It is extremely unstable and is decomposed even by cold water. It is hydrolysed to the corresponding acid when added to ice-cold concentrated sulphuric acid, kept for two days, and then warmed on the water bath. When cold, the *sulphate*,  $C_6H_8(CO_2H)_2(NH_2)_2\cdot H_2SO_4$ , crystallises out. It does not melt at  $285^{\circ}$  and is hydrolysed by water. The *acid*,  $C_6H_8O_4N_2$ , forms a crystalline powder insoluble in the ordinary solvents, but dissolves in both alkalis and dilute mineral acids. It does not melt at  $295^{\circ}$ . A platinichloride could not be obtained. A small amount of a second amino-acid was obtained from the mother liquor from which the diaminohexahydroterephthalic acid had separated. J. J. S.

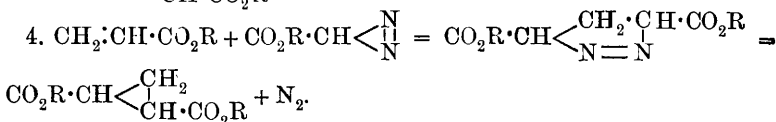
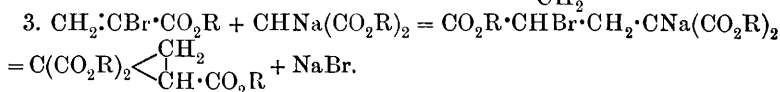
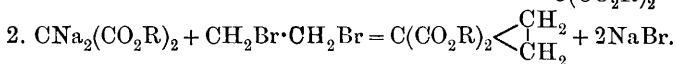
**1:4-Dihydroxyhexahydroterephthalic Acid.** NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1907, 40, 2890—2891).—1:4-Dihydroxyhexahydroterephthalonitrile,  $C_6H_8(OH)_2(CN)_2$ , has been synthesised from *cyclohexane-1:4-dione* (diketohexamethylene) and hydrogen cyanide. It is sparingly soluble in water, alcohol, or ether, m. p.  $152-154^{\circ}$  (decomp.). When hydrolysed by adding it gradually to concentrated sulphuric acid, diluting with two volumes of water, and boiling for an hour, it yields the corresponding *acid*,  $C_6H_8(OH)_2(CO_2H)_2$ , which crystallises from hot water in colourless needles, m. p.  $122^{\circ}$ , with partial sublimation and decomposition. It is only sparingly soluble in cold water or cold alcohol. The *barium salt* crystallises in prisms containing  $3H_2O$ . J. J. S.

*cyclo*Trimethylene Compounds. III. Synthesis of *cyclo*-Propanecarboxylic Acids. ARTHUR KÖTZ [and, in part, G. KAYSER, A. KEMPE, J. SIELISCH] (*J. pr. Chem.*, 1907, [ii], 75, 433—516. Compare Kötz and Stalman, *Abstr.*, 1903, i, 741; Kötz, *ibid.*, 742).—The first half of this paper consists of an account of the properties and the methods of synthesis of the *cyclo*propanecarboxylic acids. It is shown that the stability of the *cyclo*propane nucleus depends on the nature and position of the substituting groups, resolution of the ring taking place only between two carbon atoms, to one of which is attached a carboxyl group, whilst the other carries at least one substituting group other than carboxyl. The resolution takes place the more easily the fewer the hydrogen atoms attached to the two carbons concerned. The ring cannot be resolved in the absence of carboxyls, or between two carbon atoms each carrying a carboxyl, or if the compound contains a  $\text{CH}_2$  and two  $\text{C}\cdot\text{CO}_2\text{H}$  groups.

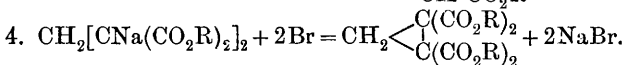
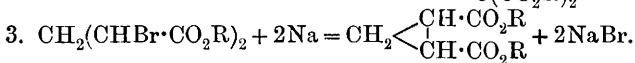
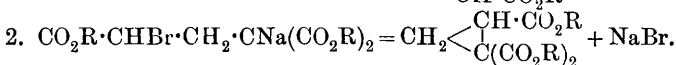
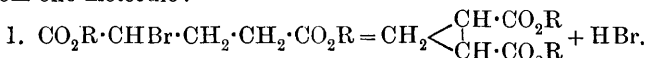
The methods of synthesis of the *cyclo*propanecarboxylic acids fall under three heads:

I. Synthesis from three molecules, each supplying one ring carbon atom:  $3\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{R} + 3\text{Br} = \text{CO}_2\text{R}\cdot\text{C}(\text{CN})\begin{smallmatrix} \text{C}(\text{CN})\cdot\text{CO}_2\text{R} \\ \text{C}(\text{CN})\cdot\text{CO}_2\text{R} \end{smallmatrix} + 3\text{NaBr}$ .

II. Syntheses from two molecules, one supplying one, the other, two, ring carbon atoms:

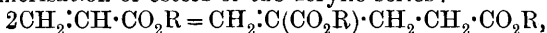


III. Syntheses in which the three-ring carbon atoms are derived from one molecule:



The propane-di-, -tri-, and -tetra-carboxylic esters required for the syntheses under III. are prepared by the general reactions:

1. Polymerisation of esters of the acrylic series:



and hydrolysis of the resulting alkylideneglutaric ester with formation of a propane- $\alpha\gamma$ -dicarboxylic acid and an aldehyde or a ketone.

2. Addition of ethyl malonate to esters of the acrylic series:  $\text{CH}_2\text{:CH}\cdot\text{CO}_2\text{R} + \text{CH}_2(\text{CO}_2\text{R})_2 = \text{CH}(\text{CO}_2\text{R})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$ .

3a. Addition of ethyl malonate to esters of the methylenemalononic series:  $\text{CH}_2\text{:C}(\text{CO}_2\text{R})_2 + \text{CH}_2(\text{CO}_2\text{R})_2 = \text{CH}_2[\text{CH}(\text{CO}_2\text{R})_2]_2$ .

3b. Action of dihaloids derived from aldehydes or ketones on ethyl sodiomalonate:  $\text{CRR}'\text{Br}_2 + 2\text{CHNa}(\text{CO}_2\text{Et})_2 = \text{CRR}'[\text{CH}(\text{CO}_2\text{R})_2]_2 + 2\text{NaBr}$ .

The esters of the acrylic series are formed by condensation of aldehydes and ketones with acetic acid, and those of the methylenemalononic series by condensation of aldehydes and ketones with ethyl malonate, or by the action of dihaloids derived from aldehydes or ketones, on ethyl disodiummalonate.

The following new experimental details are given in the second half of the paper.

*Ethyl  $\alpha$ -bromopropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate*, formed by bromination of ethyl propane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate cooled by ice, decomposes when distilled, and when treated with methyl alcoholic ammonia at the ordinary temperature yields ethyl cyclopropane-1 : 1 : 2 : 2-tetracarboxylate.

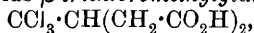
*Ethyl propyldidenemalonate*,  $\text{CHEt}\cdot\text{C}(\text{CO}_2\text{Et})_2$ , is obtained by heating ethyl malonate with propaldehyde and acetic anhydride under pressure at  $100^\circ$ , in a 90% yield, as a transparent liquid, b. p.  $115\text{--}125^\circ/12\text{ mm.}$ , and on prolonged shaking with concentrated ammonia is partly hydrolysed and partly decomposed forming propaldehyde and malonamide.

*Ethyl propyldenedimalonate*,  $\text{CHEt}[\text{CH}(\text{CO}_2\text{Et})_2]_2$ , formed by the action of ethyl sodiomalonate on ethyl propyldidenemalonate in ethereal solution, is obtained as a slightly yellow liquid, b. p.  $195\text{--}205^\circ/12\text{ mm.}$  When converted into its *disodio*-derivative and treated with iodine in ethereal solution, it yields ethyl ethylenetetracarboxylate, ethyl ethanetetracarboxylate, and *ethyl 3-ethylcyclopropane-1 : 1 : 2 : 2-tetracarboxylate*, b. p.  $211\text{--}240^\circ/12\text{ mm.}$ , which on hydrolysis with aqueous ammonia forms the *acid* as a reddish-brown, viscid mass with an odour resembling that of the fatty acids. The *silver* salt,  $\text{C}_9\text{H}_6\text{O}_8\text{Ag}_4$ , was analysed. *3-Ethylcyclopropane-1 : 2-dicarboxylic acid*, obtained by hydrolysis of the tetracarboxylic ester with alcoholic potassium hydroxide and evaporation of the product with hydrochloric acid in an atmosphere of carbon dioxide, forms a hygroscopic, white, crystalline mass; the *silver* salt,  $\text{C}_7\text{H}_8\text{O}_4\text{Ag}_2$ , was analysed; the *ethyl* ester, b. p.  $185\text{--}195^\circ/12\text{ mm.}$  (decomp.). On distillation, the dicarboxylic acid decomposes, yielding ethylparaconic acid and an oil which may be hydrosorbic acid.

*Ethyl  $\alpha\beta\gamma$ -triethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate*, b. p.  $195\text{--}230^\circ/12\text{ mm.}$  (decomp.), formed together with ethyl propyldidenemalonate and ethyl ethylmalonate by the action of sodium and ethyl iodide on ethyl propyldenedimalonate in alcoholic solution, yields ethylmalonamide when treated with concentrated ammonia, and on hydrolysis with hydrochloric acid forms  *$\alpha\beta\gamma$ -triethylglutaric acid*, obtained as a yellow, viscid mass, and analysed in the form of its *silver* salt,  $\text{C}_{11}\text{H}_{18}\text{O}_4\text{Ag}_2$ .

*Tri-γ-chlorocrotonic acid*,  $\text{CCl}_3 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$ , formed by hydrolysis of ethyl trichloroethylidenemalonate by means of boiling 27% hydrochloric acid, separates from water in stout crystals, m. p. 119°.

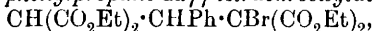
*Ethyl trichloroethylidenedimalonate*,  $\text{CCl}_3 \cdot \text{CH}[\text{CH}(\text{CO}_2\text{Et})_2]_2$ , prepared from ethyl trichloroethylidenemalonate and ethyl sodiomalonate, is obtained as a yellow oil which decomposes at 60°. On hydrolysis with hydrochloric acid, it yields *β-trichloromethylglutaric acid*,



which crystallises from benzene in nacreous leaflets, m. p. 159°.

*Ethyl 3-trichloromethylcyclopropane-1 : 1 : 2-tetracarboxylate*, m. p. 48°, is formed by the action of bromine on ethyl trichloroethylidenedimalonate or on its disodio-derivative.

*Ethyl α-bromo-β-phenylpropane-ααγγ-tetracarboxylate*,



decomposes on distillation; when treated with methyl alcoholic ammonia, it yields ethyl 3-phenylcyclopropane-1 : 1 : 2 : 2-tetracarboxylate, b. p. 228°/11 mm., which on hydrolysis is converted into 3-phenylcyclopropane-1 : 2-dicarboxylic acid, m. p. 175°. The oil, b. p. 100—200°/12 mm., described by Kötz and Stalman (*loc. cit.*), is shown to have been a mixture of benzaldehyde, ethyl malonate, and ethyl ethylenetetracarboxylate. In agreement with this, ethyl disodio-β-phenylpropane-ααγγ-tetracarboxylate is decomposed by dilute acids, forming ethyl malonate and ethyl benzylidenemalonate, together with only traces of ethyl 3-phenylcyclopropane-1 : 1 : 2 : 2-tetracarboxylate. Similarly, ethyl disodioethylidenedimalonate is decomposed by dilute acids, forming ethyl malonate and ethyl ethylenemalonate. The action of methyl iodide on ethyl dipotassio-β-phenylpropane-ααγγ-tetracarboxylate leads to the formation of ethyl methylmalonate and ethyl benzylidenemalonate.

*Ethyl α-bromoisopropylmalonate*, formed by the action of bromine on ethyl isopropylmalonate cooled by ice, is obtained as a colourless liquid, b. p. 119—123°/12 mm. or 215—230°/760 mm. When heated with diethylaniline in a reflux apparatus at 170—175°, it yields ethyl dimethylacrylate, ethyl malonate, and only small amounts of ethyl isopropylidenemalonate, b. p. 110—112°/12 mm.; when shaken with concentrated aqueous ammonia, this yields acetone and malonamide. Ethyl ββ-dimethylpropanetetracarboxylate (Lawrence, *Proc.*, 1899, 62), b. p. 190—195°/12 mm., is formed in a 90—95% yield by heating ethyl isopropylidenemalonate with ethyl sodiomalonate in ethereal solution at 60—70° under pressure; when treated with bromine alone it is converted only partially into the α-bromo-derivative, but on treatment with bromine in presence of iodine in sunlight, it yields ethyl ethanetetracarboxylate.

*Ethyl 3 : 3-dimethylcyclopropanetetracarboxylate*, formed by the action of methyl alcoholic ammonia on ethyl α-bromo-ββ-dimethylpropanetetracarboxylate, is obtained as a slightly yellow oil, b. p. 188—190°/10 mm., and on hydrolysis with alcoholic potassium hydroxide and subsequent boiling with hydrochloric acid, yields a mixture of *cis*- and *trans*-caronic acids (Perkin and Thorpe, *Trans.*, 1899, 75, 48).

The action of bromine on ethyl disodio-ββ-dimethylpropanetetracarboxylate cooled by ice leads to the formation of ethyl ethanetetra-

carboxylate, whilst the action of water on the disodio-ester leads to the formation of ethyl malonate and ethyl isopropylmalonate, and that of ethyl iodide in boiling alcoholic solution to the formation of ethyl isopropylmalonate and ethyl ethylmalonate.

Ethyl dimethylacrylate remains unchanged in ethereal solution in presence of sodium methoxide, free from alcohol, at the ordinary temperature (compare Pechmann, Abstr., 1901, i, 63; Pechmann and Röhm, *ibid.*, 253).

Ammonia reacts with ethyl methylenemalonate with development of heat and formation of hexamethylenetetra-amine.

*Ethyl m-nitrobenzylidenemalonate*, prepared by condensation of *m*-nitrobenzaldehyde with ethyl malonate in presence of piperidine at 80°, crystallises in rhombic plates, m. p. 73°, decolorises potassium permanganate in ethereal solution, and reacts with ethyl sodiomalonate with development of heat, forming *ethyl sodio-m-nitrobenzylidenedimalonate*. On treatment with dilute sulphuric acid, this yields the free ester as a viscid, yellow oil, which decomposes on distillation/12 mm., and is hydrolysed by alcoholic potassium hydroxide to *m-nitrobenzylidenedimalonic acid*, or by hydrochloric acid to  $\beta$ -*m*-nitrophenylglutaric acid. This is formed also by the action of bromine on the disodiodimalonate or of sodium hydroxide on the viscid, yellow *bromodimalonate*. *m-Nitrobenzylidenedimalonic acid* forms a yellowish-red, amorphous mass, decomposing above 150°; the *silver* salt,  $C_{13}H_7O_{10}NAg_4$ , was analysed.

Ethyl *m-nitrobenzylidenedimalonate* is reduced by sodium and methyl alcohol to a yellowish-red, unstable azoxy-derivative, but by aluminium amalgam in alkaline solution to *ethyl m-aminobenzylidenedimalonate*, which is obtained as a yellowish-red, viscid oil, and on hydrolysis with hydrochloric acid yields  $\beta$ -*m*-aminophenylglutaric acid *hydrochloride*. This is formed also by reduction of  $\beta$ -*m*-nitrophenylglutaric acid with stannous chloride and hydrochloric acids; it forms white crystals, m. p. 100—101°, becomes red on exposure to air, gives an intensely-yellow lignin reaction, and when diazotised and boiled with sulphuric acid yields  $\beta$ -*m*-hydroxyphenylglutaric acid, m. p. 112°.

*Ethyl p-nitrobenzylidenedimalonate*, formed by condensation of the monomalonate with ethyl sodiomalonate, is converted by hydrolysis with hydrochloric acid into *p*-nitrophenylglutaric acid. When reduced with stannous chloride and hydrochloric acid, diazotised, and boiled with sulphuric acid, this yields  $\beta$ -*p*-hydroxyphenylglutaric acid, which forms white crystals, m. p. 154—155°.

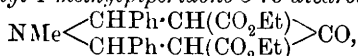
$\beta$ -*m*-2-Naphtholazophenylglutaric acid, formed by coupling diazotised  $\beta$ -*m*-aminophenylglutaric acid with  $\beta$ -naphthol in alkaline solution, is obtained as red, crystalline powder, m. p. 208°, is soluble in alkalis, and forms a red, insoluble *barium* salt. G. Y.

**Condensation of Ethyl Acetonedicarboxylate with Aldehydes Under the Influence of Ammonia and Amines. II.** PAVEL PETRENKO-KRITSCHENKO and M. LEWIN [and, in part, F. MENTSCHIKOWSKY] (*Ber.*, 1907, 40, 2882—2885).—Cinnamaldehyde and furfuraldehyde react with acetonedicarboxylic esters in the presence of ammonia in quite a different manner from benzaldehyde

(Abstr., 1900, i, 307; 1906, i, 452), the products being 1:5-diketones (compare Knoevenagel, Abstr., 1896, i, 210). *Ethyl cinnamylidenebis-acetonedicarboxylate*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}[\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}]_2$ , is formed when a slow stream of dry ammonia is passed into a benzene solution of cinnamaldehyde and ethyl acetonedicarboxylate. The yield is increased when the ammonia is replaced by diethylamine. It separates from benzene in colourless crystals, m. p. 132—133°.

Furfuraldehyde and methyl acetonedicarboxylate in the presence of ammonia give a small yield of *methyl furfurylidenebisacetonedicarboxylate*,  $\text{C}_4\text{OH}_3\cdot\text{CH}[\text{CH}(\text{CO}_2\text{Me})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}]_2$ , m. p. 162—175° (decomp.), which is sparingly soluble in hot alcohol. A by-product is an oily compound containing nitrogen. When diethylamine is used as the condensing agent, a product, m. p. 139—143°, is obtained. This is probably a mixture of the condensation product and the original ester.

*Ethyl 2:6-diphenyl-1-methylpiperidone-3:5-dicarboxylate*



obtained by the condensation of acetonedicarboxylic ester and benzaldehyde in the presence of methylamine, or by the action of methyl iodide on the secondary base previously described (Abstr., 1906, i, 452), crystallises from alcohol in well developed prisms, m. p. 85—86°. The *hydrochloride*,  $\text{C}_{24}\text{H}_{28}\text{O}_5\text{NCl}$ , m. p. 195—200°, is insoluble in water or benzene and may be crystallised from a mixture of chloroform and light petroleum. With nitrous acid the ester yields a *nitrosoamine*, m. p. 137—139°.

J. J. S.

**Hexahydrobenzaldehyde.** NICOLAI D. ZELINSKY and JOHANNES GUTT (*Ber.*, 1907, 40, 3050—3053. Compare Bouveault, Abstr., 1904, i, 61; Wallach, 1906, i, 564).—Hexahydrobenzaldehyde, obtained from cyclohexylcarbinol by oxidation with chromic acid, forms the *aldoxime*,  $\text{C}_7\text{H}_{13}\text{ON}$ , crystallising in needles, m. p. 90—91°; the *hydrochloride* has m. p. 107—108° (decomp). The solid polymeride of hexahydrobenzaldehyde (Wallach, *loc. cit.*) is  $(\text{C}_7\text{H}_{12}\text{O})_3$ . When dimethylaniline and hexahydrobenzaldehyde condense, a green dye is formed, and on dissolution in alcohol the *leuco-base* (?),  $\text{C}_{23}\text{H}_{32}\text{N}_2$ , is deposited as white needles, m. p. 148—149°; this substance, however, cannot be re-oxidised to the dye.

The m. p. of hexahydrobenzylidenesemicarbazone is 173—174° (Wallach, 167—168°; Bouveault, 176°).

W. R.

**Diphenylhydrazones of the Tolualdehydes.** F. RORIVE and BERNHARD TOLLENS (*Ber.*, 1907, 40, 3107. Compare Maurenbrecher, Abstr., 1906, i, 985).

J. J. S.

**Conversion of Piperonal into the Cyclic Carbonate of Protocatechualdehyde.** HERMANN PAULY (*Ber.*, 1907, 40, 3096—3100).—A good yield of Fittig and Remsen's dichloropiperonal,  $\text{CHO}\cdot\text{C}_6\text{H}_3\left\langle \begin{array}{c} \text{O} \\ \text{O} \end{array} \right\rangle \text{CCl}_2$  (*Annalen*, 1871, 159, 126), can be obtained by acting with phosphorus pentachloride on piperonal and pouring the

product on to ice, provided certain directions are followed. All acid must be completely removed by repeated washing with water. It crystallises from chloroform, has m. p. 96—97°, b. p. 178°/15 mm., and is stable when protected from moisture.

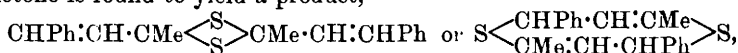
When heated with anhydrous oxalic acid at 130° and ultimately at 160°, it yields *protocatechualdehyde carbonate*,  $\text{CHO} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{CO}$ , which may be distilled under reduced pressure. Treatment with cold concentrated sulphuric acid, or with anhydrous formic acid at 80—90°, yields the same product. It forms rhombic crystals, m. p. 124° (corr.), b. p. 162° (corr.)/13 mm., or 289° under atmospheric pressure. It reacts with alcohols yielding the monoalkyl carbonates. When boiled with water, it loses carbon dioxide quantitatively, and in the presence of small amounts of tertiary amines this decomposition proceeds in the cold. It is, however, relatively stable in the presence of concentrated acids. J. J. S.

**Conversion of Substituted Adipic and Pimelic Acids into Cyclic Ketones.** H. G. BLANC (*Compt. rend.*, 1907, 144, 1356—1358).—When an acid of either of these groups is heated during some hours with acetic anhydride, it is converted into the corresponding anhydride, which, on slow distillation at the atmospheric pressure and at a temperature which varies for the different anhydrides, decomposes, yielding carbon dioxide and the corresponding cyclic ketone.

A number of these ketones have been prepared in this way, and of these the following are new: 1:1:4-*trimethylcyclopentane-5-one*, b. p. 152°, *oxime*, m. p. 62°; 1-*methyl-3-allylcyclopentane-4-one*, b. p. 188°, *semicarbazone*, m. p. 156°; 1:1:1-*trimethylcyclohexane-5-one*, b. p. 185°, *semicarbazone*, m. p. 170°. T. A. H.

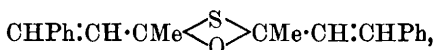
**Action of Ammonia Sulphide on Ketones.** EMIL FROMM and H. HÖLLER (*Ber.*, 1907, 40, 2978—2982).—Manchot and Krische's supposed diphenyldimethylthiopinacone (Abstr., 1905, i, 142) is a mixture of 2:4-diphenylthiophen (Baumann and Fromm, Abstr., 1895, i, 363) and sulphur. G. Y.

**Thio-derivatives of Ketones.** V. Duplobenzylidenethioacetone, a Substance with Extraordinary Additive Powers. EMIL FROMM and H. HÖLLER (*Ber.*, 1907, 40, 2982—2993. Compare Fromm and Baumann, Abstr., 1889, 852; Baumann and Fromm, Abstr., 1890, 25; 1895, i, 362; Fromm and Ziersch, Abstr., 1906, i, 931).—The formation of thio-derivatives by the action of hydrogen sulphide on mono- and 1:3-di-ketones in presence of hydrogen chloride has been described in previous papers. The study of this reaction has been extended now to an unsaturated ketone, benzylideneacetone. This ketone is found to yield a product,



which the authors term *duplobenzylidenethioacetone*. The former formula is preferred, as it explains the more easily the transformation of the substance into *duplobenzylideneoxythioacetone*,

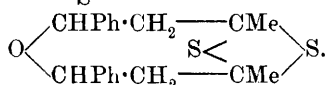




and the hydrolysis of this to benzylideneacetone.

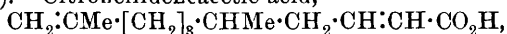
*Duplobenzylidenethioacetone*,  $\text{C}_{20}\text{H}_{20}\text{S}_2$ , separates from alcohol in crystals containing alcohol of crystallisation, which is lost readily on exposure to air, m. p.  $132\cdot5^\circ$ , forms an unstable *additive* compound with bromine, and when boiled with acids in alcoholic solution yields *duplobenzylideneoxythioacetone*,  $\text{C}_{20}\text{H}_{20}\text{O}_2\cdot\frac{1}{2}\text{H}_2\text{O}$ , m. p.  $186\cdot5^\circ$ , soluble in ether. On evaporation, the mother liquor from the preparation of this yields benzylideneacetone. The action of dilute acids on duplobenzylidenethioacetone in warm alcoholic solution leads to the formation of the oxythioacetone together with the following *additive* products:  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , m. p.  $229^\circ$ ;  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{HBr}\cdot\text{H}_2\text{O}$ , m. p.  $230^\circ$ ;  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ , m. p.  $177^\circ$ ;  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{N}_2\text{O}_3$ , m. p.  $197^\circ$ . An *additive* product,  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{HCl}$ , m. p.  $208^\circ$ , is formed by the action of hydrogen chloride on duplobenzylidenethioacetone in ethereal solution and absorbs water readily. These *additive* compounds may have the constitution (I)  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CMe}\begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{CMe}\cdot\text{CH}_2\cdot\text{CHPhX}$  or (II)

$\text{CHPh}:\text{CH}\cdot\text{CMe}\begin{smallmatrix} \text{SH}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{SHX} \end{smallmatrix} \text{CMe}\cdot\text{CH}:\text{CHPh}$ , are colourless, insoluble in ether, and when treated with boiling dilute alkalis or alkali carbonates yield *duplobenzylidenethioacetone hydrate*,  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{H}_2\text{O}$  needles, m. p.  $152^\circ$ , or benzylideneacetone on prolonged boiling. The hydrate does not form a benzoyl derivative, but is readily converted into the acid *additive* compounds, which have therefore probably the formula (I). The hydrate may have the constitution  $\text{CHPh}:\text{CH}\cdot\text{CMe}\begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{CMe}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$  or



The action of ammonia on the acid *additive* compounds leads to the formation of an *additive* compound,  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{NH}_3$ , which crystallises in needles, m. p.  $142^\circ$ , may have the annexed constitution, and is readily converted into the acid *additive* compounds by the action of cold dilute acids. An *additive* compound,  $\text{C}_{20}\text{H}_{20}\text{S}_2\cdot\text{NH}_3$ , m. p.  $148^\circ$ , formed by the action of ammonia on duplobenzylidenethioacetone, may be identical or isomeric with the preceding derivative. G. Y.

**Condensations with Citronellal.** II. HANS RUPE, S. PFEIFFER, and J. SPLITTGERBER (*Ber.*, 1907, 40, 2813—2817. Compare Abstr., 1903, i, 841).—Citronellideneacetic acid,



previously prepared from citronellal and malonic acid in the presence of pyridine, is a liquid with b. p.  $175\cdot5\text{--}177\cdot5^\circ/14\text{ mm}$ . Grünhagen (*Diss.*, 1898), using the same method, however, obtained the acid as a solid, m. p.  $51\text{--}52^\circ$ . The liquid, previously described, was a mixture of isomeric acids, one of which had the double linking in the  $\beta\gamma$ -position,

since a lactone could be obtained by treatment with sulphuric acid. This transference of the double linking had taken place owing to the presence of the pyridine.

The lactone,  $\text{CH}_2\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{smallmatrix}$ , has b. p. 161—163°/13 mm.

*βζ-Dimethyl-Δ<sup>α</sup>-nonene-αθ-ol*,

$\text{CH}_2\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ , obtained by the action of magnesium methyl iodide on citronellal, has b. p. 104—105°/10 mm.,  $D_4^{20}$  0.8578,  $[\alpha]_D^{20} + 0.55^\circ$ . Its acetate,  $\text{C}_{18}\text{H}_{24}\text{O}_2$ , has b. p. 118—119°/14 mm.

*βζ-Dimethylnonane-βθ-diol*,

$\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ , obtained by boiling the preceding alcohol with ethyl alcohol and sulphuric acid, has b. p. 144—145°/14 mm.

*βζ-Dimethyl-Δ<sup>α</sup>-nonene-θ-one*,  $\text{CH}_2\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COMe}$ , obtained by oxidising the dimethylnoneneol with potassium dichromate and sulphuric acid, has b. p. 93—94°/12 mm.,  $D_4^{20}$  0.8650,  $[\alpha]_D^{20} + 5.89^\circ$ ,  $n_D^{20}$  1.4496. Its semicarbazone separates from dilute alcohol in glistening leaflets, m. p. 82—83°. Its oxime has b. p. 133—134°/11 mm. A. McK.

**Bornyl and Fenchyl Derivatives.** IWAN KONDAKOFF and IWAN SCHINDELMEISER (*J. pr. Chem.*, 1907, [ii], 75, 529—538).—The action of phosphorus pentahaloids and of hydrogen haloids on secondary hydro-aromatic alcohols is discussed. Previously the product of the reaction has been an unstable, or a mixture of this with a stable, haloid derivative (Abstr., 1895, i, 549). It is found possible now to increase the amount of either haloid derivative by varying the experimental conditions. The present work was undertaken to determine if the action of hydrogen haloids on the esters of the secondary hydro-aromatic alcohols takes place in the same manner as the action of the hydrogen haloids on the alcohols, and, if possible, to obtain indications of an intermediate phase by means of which the complicated transformations of the alcohols might be explained.

Wagner and Brickner (Abstr., 1900, i, 46. Compare Hesse, Abstr., 1906, i, 375) showed that the action of phosphorus pentachloride on borneol leads to the formation of isobornyl chloride or camphene hydrochloride, which is unstable, and a stable chloride which these authors assumed to be Kindt's camphor. It is found now that *l*-borneol acetate, which on hydrolysis yields *l*-borneol, on treatment with hydrogen chloride in acetic acid solution at 125°, yields pinene hydrochloride, m. p. 124°; this has the same m. p. when mixed with Kindt's camphor, is optically inactive, and is hydrolysed partially to camphor when heated with water at 120°. This is the first case of the conversion of the acetate into the corresponding *sec*-chloride without simultaneous formation of a racemised stereoisomeride or a tertiary chloride.

Similar results are obtained with fenchyl acetate. Fenchyl alcohol sublimes in plates, m. p. 47°,  $[\alpha]_D - 15.22'$ , and probably contains traces of fenchone. The acetate, b. p. 91—91.5°/12 mm.,  $D^{20}$  0.972,

$[\alpha]_D - 63^\circ 24'$ ,  $n_D 1.4565$  (compare Bertram and Helle, Abstr., 1900, i, 398; Bouchardat and Lafont, Abstr., 1899, i, 156), is converted by hydrogen chloride in acetic acid solution at  $125-130^\circ$  into a chloride, b. p.  $68-74^\circ/11$  mm.,  $D^{20} 0.952$ ,  $n_D 1.4758$ , which is optically inactive, reacts with silver nitrate, and on treatment with alcoholic potassium hydroxide yields considerable amounts of *i*-fenchene, but remains for the most part unchanged. The chloride, b. p.  $76-78^\circ/12$  mm., obtained by the action of phosphorus pentachloride on fenchyl alcohol, does not react with silver nitrate. G. Y.

***iso*Fenchyl Alcohol and its Derivatives.** IWAN KONDAKOFF (*J. pr. Chem.*, 1907, [ii], 75, 539-548).—*iso*Fenchyl alcohol has been held by various authors to be (1) a mixture of structurally identical, but optically different, secondary alcohols (Bertram and Helle, Abstr., 1900, i, 398); (2) a mixture of tertiary alcohols or of a tertiary and a secondary alcohol; (3) a stereoisomeride of fenchyl alcohol (Abstr., 1900, i, 604), or (4) a mixture of two secondary alcohols of different types. As the experimental facts published previously do not admit of a decision between these views, the author gives now a number of observations made with *isofenchyl* alcohol and its derivatives.

*iso*Fenchyl alcohol, prepared from fenchene by Bertram and Helle's (*loc. cit.*), Kondakoff's (*loc. cit.*, Abstr., 1902, i, 478), or Wallach's (Abstr., 1901, i, 331) method, is a mixture of a liquid and a crystalline alcohol; a portion of the fenchene remains always unchanged. A fenchene, b. p.  $152-159^\circ$ ,  $D^{17.5} 0.860$ ,  $[\alpha]_D - 36^\circ 3'$ ,  $n_D 1.46643$ , formed an acetate, b. p.  $100-105^\circ/15$  mm.,  $D_4^{20} 0.9784$ ,  $[\alpha]_D + 5^\circ 33'$ ,  $n_D 1.46257$ ; the alcohol, m. p.  $61.5^\circ$ ,  $[\alpha]_D + 45^\circ 40'$ ; the unchanged fenchene, b. p.  $144-152^\circ$ ,  $D_4^{20} 0.8539$ ,  $\alpha_D - 21^\circ 10'$ . Another fenchene, b. p.  $155-158^\circ$ ,  $D_4^{20} 0.8677$ ,  $[\alpha]_D - 39^\circ 50'$ , yielded a residual fenchene, b. p.  $146-158^\circ$ ,  $D_4^{20} 0.8529$ ,  $\alpha_D - 12^\circ 02'$ ; the acetate was obtained in two fractions: b. p.  $90-95.5^\circ/15$  mm.,  $[\alpha]_D - 9^\circ 35'$ , and b. p.  $95.5-100^\circ/95$  mm.,  $[\alpha]_D - 7^\circ 38'$ . In both experiments an optically inactive acetate, b. p.  $95-97^\circ/15$  mm.,  $D_4^{20} 0.9752$ ,  $n_D 1.46168$ , was obtained. On hydrolysis, the *lævorotatory* acetate gave an alcohol,  $[\alpha]_D - 6.07^\circ$ , and the inactive acetate an alcohol,  $[\alpha]_D^{17.4} - 6.31^\circ$ . When mixed and distilled/10 mm., these alcohols gave a series of fractions: b. p.  $80-81^\circ$ ,  $D^{18.5} 0.961$ ,  $n_D 1.47751$ , optically inactive; b. p.  $81-82^\circ$ ,  $D^{20.5} 0.952$ ,  $[\alpha]_D - 2^\circ$ ,  $n_D 1.47654$ ; b. p.  $82-84.5^\circ$ ,  $[\alpha]_D - 5^\circ$ ; these three fractions did not solidify. A fourth fraction, b. p.  $84.5-87^\circ$ , yielded two crystalline alcohols: m. p.  $48-53^\circ$ , and m. p.  $54-55^\circ$ ,  $[\alpha]_D^{30.5} - 8.13^\circ$  in ethyl alcoholic, or  $-7.06^\circ$  in toluene, solution. Other preparations of crystalline *isofenchyl* alcohols had  $[\alpha]_D^{18} - 8.75^\circ$  and  $-11.6^\circ$  respectively. It is evident that no relation can be established between the original and residual fenchenes, or between the acetates and the alcohols derived from them.

When treated with phosphorus pentachloride, an *i-isofenchyl* alcohol, b. p.  $80-81^\circ$ , yielded a chloride which was obtained in two fractions: b. p.  $73-74^\circ/9$  mm.,  $D^{20} 0.996$ ,  $[\alpha]_D - 3^\circ 53'$ ,  $n_D 1.4812$ , and b. p.  $74-76^\circ/9$  mm.,  $[\alpha]_D - 5^\circ 2'$ . This chloride yielded silver chloride quantitatively with silver nitrate in alcoholic solution, gave with alcoholic potassium hydroxide an *isofenchyl* alcohol, b. p.  $71-74^\circ/$

8 mm.,  $D^{17.5}_D$  0.932,  $n_D$  1.46702, containing traces of chlorine together with small amounts of fenchene, and on treatment with water was converted completely into *isofenchyl* alcohol, m. p. 61.5–65°,  $[\alpha]^{18.5}_D + 12.63^\circ$ . Optical isomerisation must take place during the formation of the chloride. Similar results were obtained with other *isofenchyl* alcohol preparations.

The remainder of the paper contains a discussion of these results and of Bertram and Helle's observations (*loc. cit.*), together with a criticism of Semmler's views on the constitution of fenchone and its derivatives (*Chem. Zeit.*, 1905, 29, 1313). G. Y.

**Citral.** CARL HARRIES and ALFRED HIMMELMANN (*Ber.*, 1907, 40, 2823–2826).—In continuation of Harries and Langheld's work (*Abstr.*, 1906, i, 226) the action of ozone on Tiemann's citral *a* and citral *b* (*Abstr.*, 1899, i, 250) has been studied. The two citrals give the same results, which agrees with Tiemann's assumption that they are stereoisomerides. The product of the action of ozone on citral varies with the solvent; in light petroleum solution, Harries and Langheld's ozonide,  $C_{10}H_{16}O_5$ , but in carbon tetrachloride or glacial acetic acid solution a *diozonide* is formed.

The *diozonide*,  $O \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} O \cdot CMe_2 \\ O \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot O \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} O$ , is obtained as a

powder sparingly soluble in carbon tetrachloride; it is only slightly explosive, does not decolorise bromine, and when heated with water yields acetone, lævulaldehyde, and a syrup which is probably glyoxal; the formation of lævulaldehyde peroxide, which is obtained from caoutchouc diozonide, was not observed.

The mono-ozonide decolorises bromine in glacial acetic acid solution and is decomposed by hot water, forming hydrogen peroxide, lævulaldehyde, and acetone peroxide. G. Y.

**The Constituents of Ethereal Oils. I. Dihydroterpinene = Carvomenthene. II. Oil from Pilea. III. Addition of Hydrogen Chloride, &c., to Bicyclic Singly Unsaturated Systems. IV. Derivatives of Sabinene and Constitution of Terpinene.** FRIEDRICH W. SEMMLER (*Ber.*, 1907, 40, 2959–2968).—*Sabinene monohydrochloride*,  $C_{10}H_{16}HCl$ , is obtained, when care is taken to exclude moisture, by passing hydrogen chloride through an ethereal solution of the terpene; b. p. 82–86°/9 mm.,  $D^{20}$  0.970,  $n_D$  1.482,  $\alpha_D - 0^\circ 15'$ . The dihydrochloride is formed when moisture is present (compare this vol., i, 145).

On reduction of the monohydrochloride with sodium and alcohol, carvomenthene was obtained, b. p. 57–60°/9 mm.,  $D^{20}$  0.8184,  $n_D$  1.4566. To identify the compound it was oxidised by ozone, when a *ketoaldehyde*,  $C_{10}H_{18}O_2$ , was isolated, b. p. 119–125°/9 mm.,  $D^{20}$  0.9439,  $n_D$  1.44962; the *disemicarbazone* has m. p. 183°. On further oxidation of the aldehyde by potassium permanganate,  $\epsilon$ -keto- $\beta$ -isopropyl-heptonic acid,  $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH(Pr^{\beta}) \cdot CH_2 \cdot CO_2H$ , is obtained, b. p. 174–180°/9 mm.,  $D^{20}$  1.019,  $n_D$  1.45662; the phenylhydrazone has m. p. 102° (compare Baeyer, *Abstr.*, 1896, i, 248). The dihydro-

terpinene gives on treatment with nitrosyl chloride a *bisnitroso-chloride* of m. p.  $87^{\circ}$ , which yields with benzylamine the *nitrolamine*,  $\text{OH}\cdot\text{N}:\text{C}_{10}\text{H}_{18}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , m. p.  $107^{\circ}$ .

Menthene gives on oxidation with ozone,  $\zeta$ -*keto- $\gamma\gamma$ -dimethyloctaldehyde*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$ , b. p.  $122-124^{\circ}/9$  mm.,  $D^{20}_D$  0.959,  $n_D$  1.4483. The identity therefore of the dihydro-

terpinene with carvomenthene as obtained either from limonene, hydrochloride, or from  $\eta$ - and  $\psi$ -phellandrene or sabinene is therefore established (Abstr., 1903, i, 505, 641). The annexed constitution is ascribed to sabinene, and explains the optical activity of the monohydrochloride and the dihydrochloride formation.

The crude oil from *Pilea* has  $D^{15}_D$  0.8533–0.8520,  $n_D$  1.4686–1.4690,  $\alpha_D + 33^{\circ}52' - + 58^{\circ}20'$ . The main fraction has b. p.  $167-168^{\circ}$ ,  $D^{20}_D$  0.8402,  $n_D$  1.4695, and on oxidation with potassium permanganate gives a glycol,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , of b. p.  $150-154^{\circ}/9$  mm.,  $D^{20}_D$  1.0332,  $n_D$  1.4852, so that the dicyclic terpene is sabinene.

The author correlates the behaviour of sabinene towards hydrogen chloride with those of camphene and pinene in which new ring systems are produced.

W. R.

**$\beta$ -Amyrin Acetate from Balata.** N. H. COHEN (*Arch. Pharm.*, 1907, 245, 245).— $\alpha$ -Balalban (Tschirch and Schereschewski, Abstr., 1905, i, 713) is nothing more or less than  $\beta$ -amyrin acetate.

C. F. B.

**Digitoxin.** HEINRICH KILIANI (*Ber.*, 1907, 40, 2996–2998).—Cloetta has ascribed to digitoxin the formula  $\text{C}_{28}\text{H}_{46}\text{O}_{10}$ , and to “digalen” (amorphous digitoxin),  $\text{C}_{14}\text{H}_{23}\text{O}_5$  (*Münch. med. Woch.*, 1906, 53, 2282; 1907, 54, 987. Compare Kiliani, *ibid.*, 1907, 54, 886). Crystallised digitoxin is found now to have the molecular weight in chloroform, as determined ebullioscopically, 681 and 582, or in alcoholic solution, 676, and amorphous digitoxin in chloroform, 501, 507, and 515; the formula  $\text{C}_{34}\text{H}_{54}\text{O}_{11}$  requires 638, to which these results approximate (compare Abstr., 1899, i, 70). Digitoxin is readily decomposed; when it is boiled for a few minutes with 85% alcohol, the presence of a carbohydrate which reduces Fehling's solution may be detected. Cloetta's “digalen” is considered to have been an impure digitalein.

G. Y.

**Melanins.** FLORENCE M. DURHAM (*Proc. physiol. Soc.*, 1907, xlvii–xlvi; *J. Physiol.*, 35).—The pigments in the hairs of mice are yellow, black, and chocolate; the keratin may be removed either by dissolving it in strong sulphuric acid or stannous chloride. The three pigments, which are associated with a fat-like substance, exhibit certain differences in physical appearance and solubilities.

W. D. H.

**Pharmacological Behaviour of Hydroxybenzyltannins.** HERMANN HILDEBRANDT (*Arch. Expt. Path. Pharm.*, 1907, 56, 410–415. Compare Abstr., 1905, i, 153).—Condensation products

are readily obtained when an alcoholic solution of a phenol, formaldehyde, and tannic acid is poured into concentrated hydrochloric acid; the condensation consisting in the removal of a nucleus hydrogen atom of the phenol and also of the tannin by the oxygen of the aldehyde.

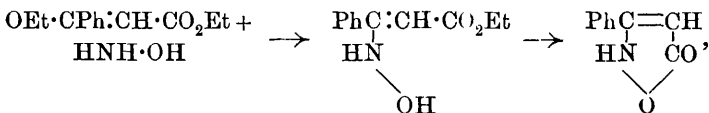
The acetyl and benzoyl derivatives of thymol, anisole, phenetole, and *o*-methoxybenzoic acid also react quantitatively with formaldehyde and tannin. Good yields are also obtained with resorcinol diethyl ether and  $\beta$ -naphthol methyl ether, but vanillic acid gives only a poor yield. *p*-Dibromobenzene gives a good yield, but *p*-cymene, benzene, and toluene do not form condensation products. The dibromobenzene-methylenetannin, when distilled with sodium hydroxide solution, yields dibromobenzene. Acetyltannin may also be used in place of tannin.

None of the condensation products which contain alkylated hydroxyl groups possess astringent properties. The carvacrol derivative has the most pronounced pharmacological properties, then follows the thymol derivative, and the effect of the *o*-cresol derivative is not so marked.

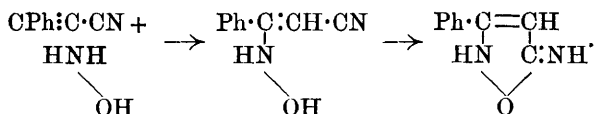
The pharmacological properties of most of the condensation products have been studied, and the question of the relationship between pharmacological properties and constitution is discussed. J. J. S.

#### Action of Hydroxylamine on Acetylenic Nitriles, Amides, and Esters, and on the Corresponding $\beta$ -Ketonic Compounds.

CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1907, 144, 1281—1283).—When hydroxylamine in methyl alcoholic solution acts on phenylpropionitrile, the substance  $C_9H_9ON_2$ , m. p.  $111^\circ$ , previously prepared by Obregia by the action of hydroxylamine on benzoyl-acetonitrile (Abstr., 1892, 324) and by Burns (Abstr., 1893, i, 314), is formed. It gives a *hydrochloride*, m. p.  $154$ — $155^\circ$ , and a *benzoyl* derivative, m. p.  $179$ — $180^\circ$ , and when boiled with concentrated hydrochloric acid forms a substance,  $C_9H_7O_2N$ , m. p.  $151$ — $152^\circ$  (decomp.), identical with the phenylisooxazolone prepared by Claisen and Zedel (Abstr., 1891, 468) and Hantzsch (Abstr., 1891, 739) from ethyl benzoylacetate, by Obregia from benzoylacetamide, by Posner (Abstr., 1906, i, 955) from  $\beta$ -hydroxylamino- $\beta$ -phenylpropionic acid, and by the authors from the action of free hydroxylamine on ethyl phenylpropionate, phenylpropionamide, or ethyl  $\beta$ -ethoxycinnamate. Owing to its formation from the latter substance,



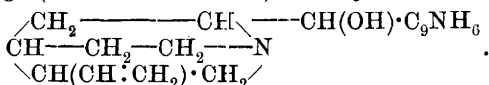
the authors consider that the substance  $C_9H_7O_2N$  is 3-phenyl-5-isooxazolone. The reaction with phenylpropionamide is effected similarly, whilst those with benzoylacetamide and ethyl benzoylacetate can be explained by supposing these substances to act in the enolic form. The compound  $C_9H_9ON_2$  must then be 3-phenyl-5-isooxazonimine, being formed from phenylpropionitrile, thus:



3-Phenyl-5-isooxazonimine is attacked by nitrous acid, but the product behaves quite differently from that formed by the action of nitrous acid on the aminoisooxazole prepared by Hanriot by the action of hydroxylamine on propionylpropionitrile (Abstr., 1892, 79), and the difference in constitution of the two products is probably due to propionylpropionitrile being a substituted, whilst benzoylacetone nitrile is a non-substituted,  $\beta$ -ketonic nitrile. The preceding reactions seem to be generally applicable; thus amylpropionitrile and hexoylacetone nitrile give a *substance*,  $\text{C}_8\text{H}_{14}\text{ON}_2$ , m. p.  $41^\circ$ , probably amylisooxazonimine, which forms a *hydrochloride*, m. p.  $104\text{--}106^\circ$ , and an *acetyl* derivative, m. p.  $87\text{--}88^\circ$ , and when heated with concentrated hydrochloric acid decomposes into methyl amyl ketone, hydroxylamine and ammonium chloride, and carbon dioxide, probably owing to a splitting up of the amylisooxazolone first formed. The latter substance has been obtained in the form of an *ammonium* salt,  $\text{C}_8\text{H}_{12}\text{O}_2\text{N}\cdot\text{NH}_4$ , m. p.  $174\text{--}175^\circ$  (corr. decomp.), and a *benzoyl* derivative, m. p.  $72\text{--}73^\circ$ . Similarly, hexylpropionitrile and heptoylacetone nitrile give a *substance*, m. p.  $32^\circ$ , probably hexylisooxazonimine, which forms an *acetyl* compound, m. p.  $82\cdot5\text{--}83^\circ$ . The acetylenic and  $\beta$ -ketonic non-substituted nitriles by condensation with hydroxylamines thus give the same cyclic compounds, namely, the isooxazonimines, whilst the acetylenic amides and esters and the corresponding  $\beta$ -ketonic amides and esters give the same isooxazolones.

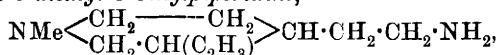
E. H.

**Oximes of 1-Methylcinchotoxine and 1-Methylcinchotintoxine and their Transformation by the Beckmann Reaction.** WILHELM KOENIGS [with KARL BERNHART and JOSEF IBELE] (*Ber.*, 1907, 40, 2873—2882).—It has been shown (this vol., i, 345) that cinchonic acid and 4-aminoquinoline are obtained on hydrolysing the product formed by the Beckmann transformation of the oxime of 1-methylcinchotoxine. It has now been found possible to isolate in addition to these compounds, 4-aminoethyl-1-methyl-3-vinylpiperidine and N-methylhomomeroquinine. The oxime of 1-methylcinchotintoxine behaves in a similar manner, yielding cinchonic acid, 4-aminoquinoline, 4-aminoethyl-1-methyl-3-ethylpiperidine, and N-methylhomocincholeupone. From their mode of formation it is probable that these new compounds possess the formulæ assigned to them, although this has not been proved. The author considers Rabe's cinchonine formula (this vol., i, 78) less probable than the one proposed by him some time ago (Abstr., 1900, i, 189), namely,



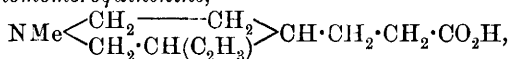
Rabe, in his last publication (this vol., i, 546), considers it probable that there is present in cinchonine a secondary alcohol group.

## 4-Aminoethyl-1-methyl-3-vinylpiperidine,



is a colourless oil, b. p.  $234^\circ/725$  mm.; the *oxalate*,  $\text{C}_{12}\text{H}_{22}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$ , forms small needles, m. p. approx.  $190^\circ$  (decomp.); the *aurichloride*,  $\text{C}_{10}\text{H}_{20}\text{N}_2 \cdot 2\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ , is a crystalline substance, m. p. approx.  $102^\circ$ ; the *platinichloride* decomposes at  $240^\circ$ ; the *picrate* crystallises in needles; the *tartrate* forms a crystalline powder.

## N-Methylhomomeroquinene,

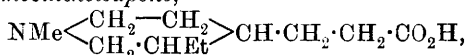


is an oil, as is likewise its *methyl ester*; the ester yields a crystalline *aurichloride*,  $\text{C}_{12}\text{H}_{21}\text{O}_2\text{N} \cdot \text{HAuCl}_4$ , m. p.  $122^\circ$ .

N-Methylcinchotintoxine, prepared by Rahe's method from cinchotine methiodide (Arlt, Abstr., 1899, i, 962), is a crystalline substance, m. p.  $74\text{--}76^\circ$ ; its *oxime*,  $\text{C}_{20}\text{H}_{27}\text{ON}_3$ , melts at  $65\text{--}80^\circ$ .

4-Aminoethyl-1-methyl-3-ethylpiperidine,  $\text{C}_{10}\text{H}_{22}\text{N}_2$ , yields an *oxalate*,  $\text{C}_{12}\text{H}_{24}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$ , which forms slender needles, m. p.  $180\text{--}192^\circ$  (decomp.); the *aurichloride*,  $\text{C}_{10}\text{H}_{22}\text{N}_2 \cdot 2\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ , crystallises in long needles, m. p.  $133\text{--}135^\circ$ ; the *platinichloride* forms small, yellowish-red needles, m. p.  $250^\circ$  (decomp.).

## N-Methylhomocincholeupone,



is a resinous substance; its *aurichloride*,  $\text{C}_{11}\text{H}_{21}\text{O}_2\text{N} \cdot \text{HAuCl}_4$ , is a crystalline substance, m. p. about  $120^\circ$ . The *ethyl ester* is likewise resinous; it yields an *aurichloride*,  $\text{C}_{13}\text{H}_{25}\text{O}_2\text{N} \cdot \text{HAuCl}_4$ , obtained as a yellow crystalline powder, m. p.  $80\text{--}100^\circ$ . W. H. G.

**Action of Halogens on Morphine Derivatives.** EDUARD VONGERICHTEN and OTTO HÜBNER (*Ber.*, 1907, 40, 2827—2831).—The action of halogens on morphine or codeine is totally different from that on  $\alpha$ - or  $\beta$ -methylmorphimethine, whereas  $\alpha$ - and  $\beta$ -methyl-dihydromorphimethines behave towards bromine in the same manner as morphine (Vongerichten, Abstr., 1897, i, 643), bromination taking place in the ring carrying the phenolic hydroxyl.

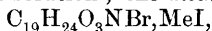
The action of bromine on  $\alpha$ -methylmorphimethine in chloroform solution leads to the formation of a *bromohydroxydihydromethylmorphimethine*,  $\text{C}_{19}\text{H}_{21}\text{O}_4\text{NBr}$ , which crystallises in leaflets, m. p.  $170^\circ$ , decomposes with loss of water at about  $180^\circ$ , gives with concentrated sulphuric acid a brownish-red coloration becoming brownish-green and blue on addition of water, and does not give a precipitate with silver nitrate after being heated with dilute sulphuric acid. The crystalline *methiodide* decomposes at about  $150^\circ$ ; the *acetyl derivative*,  $\text{C}_{21}\text{H}_{26}\text{O}_5\text{NBr}$ , m. p.  $118\text{--}138^\circ$  (decomp.), yields a white, flocculent, tertiary base when converted into the *hydrobromide* and treated with ammonia, forms an oily *methiodide*, and on treatment with acetic anhydride is converted into *diacetylmethylthebaol*, m. p.  $162^\circ$ . When heated with acetic anhydride at  $180^\circ$  under pressure, bromohydroxy- $\alpha$ -methyl-dihydromorphimethine yields a bromomorphol, m. p.  $165^\circ$ .

When heated in a current of hydrogen at  $180^\circ$ , bromo- $\alpha$ -methyl-



morphimethine,  $[\alpha]_D^{15} - 104.06^\circ$ , is transformed into *bromo-β-methylmorphimethine*,  $[\alpha]_D^{15} + 128.22^\circ$ . The *methiodide* of this is amorphous and dextrorotatory. *Bromo-α-methylmorphimethine methiodide* has  $[\alpha]_D^{15} - 110.71^\circ$ .

*Bromo-α-methyldihydromorphimethine*,  $C_{19}H_{24}O_3NBr$ , m. p.  $165^\circ$ , is formed by bromination of *α-methyldihydromorphimethine* in chloroform or glacial acetic acid solution; the *methiodide*,



m. p.  $264^\circ$ , is converted by boiling concentrated sodium hydroxide solution into *bromo-β-methyldihydromorphimethine methiodide*, m. p.  $277^\circ$ . *Bromo-β-methyldihydromorphimethine*, m. p.  $169^\circ$ , is formed by heating the *α* compound. G. Y.

**Pyrrolidone.** JULIUS TAFEL and OTTO WASSMUTH (*Ber.*, 1907, 40, 2831—2842).—This is a study of the properties of pyrrolidone, which has been easily obtainable since Tafel and Stern prepared it by electrolytic reduction of succinimide (*Abstr.*, 1900, i, 557). The molecular weight of pyrrolidone ( $C_4H_7ON = 85$ ) is found by the vapour density method at  $230^\circ/70-80$  mm. as  $87.3-90.3$ , but considerably higher,  $106-148.5$ , by the cryoscopic and ebullioscopic methods in benzene solution. Pyrrolidone has both basic and acid properties; with hydrogen chloride and bromide it forms two series of salts containing one equivalent of acid with one and two equivalents respectively of pyrrolidone. The second series belongs to Werner's abnormal ammonium salts (*Abstr.*, 1903, i, 234), and has the general constitution  $\begin{smallmatrix} NR_3 \\ NR_3 \end{smallmatrix} > HX$ .

This tendency of pyrrolidone to form double molecules appears also in the bromine additive product,  $\begin{smallmatrix} NR_3 \\ NR_3 \end{smallmatrix} > Br \cdot Br$ . Such formulæ are to be considered as merely schematic. Both series of hydrohaloid salts are strongly dissociated in aqueous solution.

*Dipyrrolidone hydrochloride*,  $(C_4H_7ON)_2 \cdot HCl$ , crystallises in spears, m. p.  $86-88^\circ$ ; *pyrrolidone hydrochloride*,  $C_4H_7ON \cdot HCl$ , hexagonal plates, m. p.  $128-131^\circ$ ; *dipyrrolidone hydrobromide*,  $(C_4H_7ON)_2 \cdot HBr$ , granular crystals, m. p.  $135-137^\circ$ ; *pyrrolidone hydrobromide*,  $C_4H_7ON \cdot HBr$ ,

m. p.  $108-121^\circ$ .

The action of bromine on pyrrolidone in chloroform solution leads to the formation of the hydrobromide, *l*-bromopyrrolidone, and *pyrrolidone perbromide*; on recrystallisation from chloroform, the bromo-compound remains in solution, the hydrobromide and perbromide separating in mixed crystals. On repeated recrystallisation, the perbromide is transformed gradually into the bromo-compound. The action of acetone on the perbromide, as also on *l*-bromopyrrolidone, leads to the formation of bromoacetone and dipyrrolidone hydrobromide.

*l*-Bromopyrrolidone is obtained in white crystals if formed in 40% sodium hydroxide solution; it is decomposed by hydrogen iodide forming pyrrolidone, hydrogen bromide, and iodine, or 2 mols. of hydrogen bromide, forming pyrrolidone hydrobromide perbromide, or 1 mol. of hydrogen bromide forming pyrrolidone and bromine.

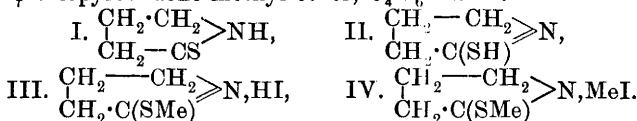
The *sodium* derivative of pyrrolidone,  $C_4H_6ONNa$ , m. p. about  $165^\circ$ , decomposes at higher temperatures. When treated with methyl iodide in benzene solution, it yields *1-methylpyrrolidone*,  $C_5H_9ON$ , which is obtained as a colourless oil, b. p.  $197-202^\circ/736$  mm., and on hydrolysis forms  *$\gamma$ -methylaminobutyric acid*,  $C_5H_{11}O_2N$ , m. p.  $143-145^\circ$ , decomposing slightly above its melting point.

*Ethyl pyrrolidone-1-acetate*,  $C_4H_6ON \cdot CH_2 \cdot CO_2Et$ , formed by the action of ethyl chloroacetate on sodium pyrrolidone, is obtained as an oil, b. p.  $280-283^\circ$ , and on hydrolysis yields *pyrrolidone-1-acetic acid*,  $C_6H_9O_3N$ , crystallising in needles, m. p.  $143^\circ$ ; the *potassium* salt has m. p.  $209-213^\circ$ .

*2-Chloropyrroline*,  $\begin{array}{c} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CCl \end{array} \gg N$ , prepared by the action of phosphorus pentachloride on pyrrolidone hydrochloride at  $85^\circ$ , crystallises in needles or leaflets, m. p.  $50-51^\circ$ . G. Y.

**Thiopyrrolidone.** II. JULIUS TAFEL and PAUL LAWACZEK (*Ber.*, 1907, 40, 2842—2848. Compare Abstr., 1905, i, 465).—Thiopyrrolidone, m. p.  $116^\circ$ , is prepared now in a 90% yield by heating pyrrolidone with phosphorus pentasulphide in xylene solution (compare Hantzsch, Abstr., 1889, 723).

The constitution of thiopyrrolidone is discussed; the sparing solubility in aqueous alkalis and the non-formation of a disulphide point to constitution I, whilst the alkali salts are considered to be derived from II, since their reaction with methyl iodide leads to the formation of  $\psi$ -thiopyrrolidone methyl ether,  $C_4H_6N \cdot SMe$ .



The  $\psi$ -thio-ether forms a hydriodide, III, and a methiodide, IV, which on treatment with an alkali decomposes, forming 1-methylpyrrolidone and methyl mercaptan.

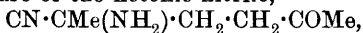
*Thiopyrrolidone methiodide*,  $C_5H_{10}NSI$ , crystallises in yellow needles, m. p.  $139^\circ$ , and when treated with concentrated potassium hydroxide yields *methyl- $\psi$ -thiopyrrolidone*,  $C_4H_6N \cdot SMe$ , which is formed also by the action of methyl iodide on potassium thiopyrrolidone. The *methyl ether* is obtained as a colourless, highly refracting, alkaline oil, b. p.  $170^\circ/755$  mm., and has an odour of mercaptan and pyrrolidine. On reduction with zinc dust and acetic acid, or electrolytically in sulphuric acid solution with a current density of 2.4 amperes, it yields methyl mercaptan and pyrrolidine. When oxidised with potassium permanganate in aqueous solution, the methyl ether yields potassium methanesulphonate and pyrrolidone. The *methiodide*,  $SMe \cdot C_4H_6N, MeI$ , crystallises in needles, m. p.  $122^\circ$ . G. Y.

**Synthesis of a Pyrrolinecarboxylic Acid.** NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1907, 40, 2886—2888. Compare Abstr., 1906, i, 425).—The nitriles of  $\alpha$ -amino-acids have been synthesised by the action of potassium cyanide and ammonium chloride on diketones.

2 : 5-Dimethylpyrroline-5-carboxylic acid,  $\begin{array}{c} \text{CH}=\text{CMe} \\ \text{CH}_2 \cdot \text{CMe}(\text{CO}_2\text{H}) \end{array} > \text{NH}$ , has

been obtained from the condensation product of acetylacetone and potassium cyanide. The *copper* salt,  $(\text{C}_7\text{H}_{10}\text{O}_2\text{N})_2\text{Cu}$ , separates from alcohol in pale blue crystals; the neutral solution of the salt is not affected by hydrogen sulphide, but in the presence of hydrochloric acid an immediate precipitate is formed. The *hydrochloride* of the amino-acid is extremely readily soluble in water or alcohol and crystallises in long needles.

The primary condensation product has b. p.  $108^\circ/17$  mm., and consists of a mixture of the ketonic nitrile,



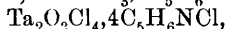
and of the nitrile of the pyrrolinecarboxylic acid. From the mixture, the *semicarbazone*,  $\text{C}_8\text{H}_{15}\text{ON}_5$ , of the amino-keto-nitrile has been isolated.

J. J. S.

### Chloro- and Bromo-Columbates and Chlorotantalates.

RUDOLF F. WEINLAND and LUDWIG STORZ (*Zeitsch. anorg. Chem.*, 1907, **54**, 223—243).—The first part of the paper contains a detailed account of the preparation and properties of chloro- and bromo-columbates of the types  $\text{CbOX}_3 \cdot \text{RX}$  and  $\text{CbOX}_3 \cdot 2\text{RX}$  ( $\text{R}$  = alkali metal or organic base,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) which have been already described (*Abstr.*, 1906, ii, 764). Attempts to prepare corresponding iodo-derivatives were unsuccessful owing to the insolubility of columbic acid in concentrated hydriodic acid. The so-called double columbium pyridine iodide described by Renz (*Abstr.*, 1903, i, 774) appears to have been pyridine periodide,  $\text{C}_5\text{H}_6\text{NI}_2$ .

The following tantalum double salts with pyridine and quinoline were prepared by the action of the base on tantalum pentachloride dissolved in alcohol containing hydrogen chloride:  $\text{TaOCl}_3 \cdot 2\text{C}_5\text{H}_6\text{NCl} \cdot 2\text{C}_2\text{H}_6\text{O}$ ;  $2\text{TaOCl}_3 \cdot 3\text{C}_5\text{H}_6\text{NCl} \cdot 2\text{C}_2\text{H}_6\text{O}$ ;



and  $\text{TaOCl}_3 \cdot 2\text{C}_9\text{H}_8\text{NCl} \cdot 2\text{C}_2\text{H}_6\text{O}$ . The first pyridine double salt was obtained from solutions free from water, the second and third from solutions containing increasing amounts of water. All the compounds form colourless crystals soluble in alcohol, but decomposed by water; they gradually become opaque on exposure to the air.

Attempts to prepare bromotantalates were unsuccessful owing to the insolubility of tantalum bromide in hydrogen bromide. G. S.

**Which Substances contain a Readily Resolvable, Single Carbon-Nitrogen Linking?** ERNST MOHR (*J. pr. Chem.*, 1907, [ii], **75**, 549—555).—von Braun and Steindorff have shown that

$\gamma$ -coniceine,  $\text{CH}_2 < \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \text{CH} : \text{C}(\text{C}_3\text{H}_7) \end{array} > \text{NH}$ , readily undergoes hydrolysis,

forming propyl  $\delta$ -aminobutyl ketone,  $\text{NH}_2 \cdot [\text{CH}_2]_4 \cdot \text{CO} \cdot \text{C}_3\text{H}_7$  (*Abstr.*, 1905, i, 812). The present paper is a discussion of the question: is the C-N linking in the grouping  $\text{C} : \text{C} \cdot \text{N}$  or  $\text{X} : \text{C} \cdot \text{N}$  always unstable or only so in particular cases? The conclusion is drawn that no general rule can be laid down, since whilst the linking in question is readily resolved in many substances, in others, such as aniline, it is extremely

stable. Between these extremes are substances which contain the grouping and in which are found all degrees of stability of the C-N linking. Thus there are amides which are hydrolysed with great ease, others in which the hydrolysis is normal, and finally those which can be hydrolysed only with difficulty. G. Y.

**An Optically Active Tetrahydroquinoline Compound.** F. BUCKNEY (*Proc. Camb. Phil. Soc.*, 1907, 14, 177—178. Compare Wedekind, *Abstr.*, 1905, i, 520).—It has been found possible to effect the resolution of allylkairolinium iodide into the two optically active forms, the salts, *d*-allylkairolinium *d*-bromocamphorsulphonate and *l*-allylkairolinium *d*-bromocamphorsulphonate, having been isolated. This is the first case of an optically active compound in which the activity is due to a nitrogen atom in a ring.

*Allylkairolinium iodide*,  $C_{13}H_{15}NI$ , prepared by adding allyl iodide to kairoline (methyltetrahydroquinoline), forms small, yellow, prismatic crystals, m. p.  $130^{\circ}$ .

*Allylkairolinium d-bromocamphorsulphonate*,  $C_{23}H_{32}O_4NBrS$ , prepared by the interaction of the silver salt of the acid with the above iodide, yields, when repeatedly crystallised from a mixture of ethyl acetate and a little toluene, two kinds of crystals: small, colourless, transparent crystals sparingly soluble in ethyl acetate, m. p.  $164^{\circ}$ , and silky needles readily soluble in ethyl acetate, m. p.  $153.5^{\circ}$ . The less soluble salt is evidently the *l*-base *d*-acid salt, since it gives  $[\alpha]_D + 39.1^{\circ}$  and  $[M]_D + 195^{\circ}$ , so that the basic ion,  $C_9H_{10}NMe \cdot C_3H_5$ , has the value  $[M]_D - 75^{\circ}$ . The more soluble compound is the *d*-base *d*-acid salt, since it gives  $[\alpha]_D + 68.6^{\circ}$  and  $[M]_D + 342^{\circ}$ , whence the value of  $[M]_D$  for the basic ion is  $+72^{\circ}$ .

The iodides could not be recovered from the *d*-bromocamphorsulphonates, being too soluble in water. W. H. G.

**Catalytic Action of Finely-divided Metals on Nitrogen Compounds.** MAURICE PADOA and UGO FABRIS (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 921—924. Compare this vol., i, 636).—The action of finely-divided nickel and hydrogen on acridine vapour at  $250^{\circ}$ — $270^{\circ}$  yields 2:3-dimethylquinoline (compare Rohde, *Abstr.*, 1887, 974) and not a methylated carbazole, which would be expected if the change were analogous with that occurring in the case of quinoline (see Padoa and Carughi, *Abstr.*, 1996, i, 765). T. H. P.

**Conductivities of the Isomeric Hydrogen Esters of Quinolinic and Cinchomeronic Acids.** ALFRED KIRPAL (*Monatsh.*, 1907, 28, 439—445).—With the object of determining the strength of the two carboxyl groups in quinolinic acid and cinchomeronic acid, electrical conductivity measurements of the hydrogen esters of the acids have been made.

2-Methyl 3-hydrogen quinolinate is not hydrolysed even in very dilute aqueous solutions; it has a conductivity constant,  $k=0.265$ . 3-Methyl 2-hydrogen quinolinate has a conductivity,  $k=0.138$ . From these values it is evident that the 3- or  $\beta$ -carboxyl group is stronger than the 2- or  $\alpha$ -carboxyl group, so that, employing the nomenclature

proposed by Wegscheider (Abstr., 1903, i, 146), 2-methyl 3-hydrogen quinolinate is the *b*-ester acid, whilst the isomeride is the *a*-ester acid.

Since quinolinic anhydride, when treated with methyl alcohol, is converted into 80% of the *b*-methyl ester acid, it follows that quinolinic acid does not follow Wegscheider's rule for the esterification of dibasic acids (Abstr., 1895, ii, 310; 1898, i, 238), for the weaker 2- or *a*-carboxyl group undergoes esterification more readily than the stronger 3- or *β*-carboxyl group.

*γ*-Methyl cinchomeronate has a conductivity  $k = 0.0665$ , whilst the *β*-methyl ester has the conductivity  $k = 0.0666$ , from which it follows that the two carboxyl groups have practically the same electrolytic dissociation constant. It would therefore be expected that equal quantities of the two esters would be obtained from the acid anhydride, but this is not the case, so that Wegscheider's rule is inapplicable likewise to cinchomeric acid.

It is probable that this abnormal behaviour is due to the influence of the nitrogen atom. W. H. G.

**Condensation Products of Carbazole and Diphenylene Oxide with Phthalic Anhydride.** RUDOLF STÜMMER (*Monatsh.*, 1907, 28, 411—422).—An investigation of the two compounds prepared originally by Goldschmiedt and Lipschitz (Abstr., 1905, i, 132) by the condensation of phthalic anhydride with carbazole and diphenylene oxide, but not investigated by these authors.

*Carbazole-N-carbonyl-o-benzoic acid*,  $C_{12}H_8N \cdot CO \cdot C_6H_4 \cdot CO_2H$ , prepared by the action of phthalic anhydride on carbazole in carbon disulphide solution in presence of aluminium chloride, crystallises from alcohol in white, rhombic plates; it sinters at  $150^\circ$ , m. p.  $190^\circ$ , at which temperature it dissociates into its components. The solution in concentrated sulphuric acid is colourless. The amorphous *silver* salt decomposes at  $146^\circ$ . The *methyl* ester,  $C_{21}H_{15}O_3N$ , prepared by the action of methyl iodide on the silver salt, forms small crystals, m. p.  $194$ — $201^\circ$  (decomp.). The *amide*,  $C_{20}H_{14}O_2N_2$ , obtained when ammonia acts on the acid chloride prepared by means of thionyl chloride, crystallises from pyridine in small, white plates, m. p.  $235$ — $238^\circ$  (decomp.).

*o-Diphenylene-oxide-ketobenzoic acid*,  $\begin{matrix} C_6H_4 \\ \text{O} \text{---} \end{matrix} > C_6H_3 \cdot CO \cdot C_6H_4 \cdot CO_2H$ ,

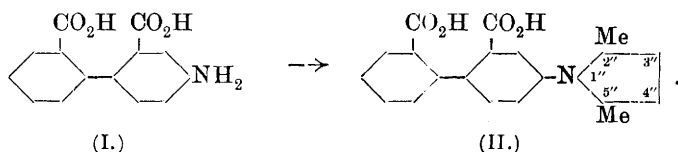
formed when a solution of phthalic anhydride and diphenylene oxide in light petroleum is treated with aluminium chloride, crystallises from methyl alcohol in small, colourless plates, m. p.  $208$ — $210^\circ$ . The *methyl* ester,  $C_{21}H_{14}O_4$ , obtained by treatment of the silver salt with methyl iodide, by esterification with alcohol and sulphuric acid, or by treatment of the acid chloride prepared by phosphorus trichloride with methyl alcohol, forms small, thin plates, m. p.  $99$ — $103^\circ$ , and dissolves in concentrated sulphuric acid to a yellowish-red solution. The isomeric *methyl* ester, prepared by the action of methyl alcohol on the acid chloride obtained by means of thionyl chloride, forms an amorphous, white powder, m. p.  $72$ — $105^\circ$  after sintering at  $55^\circ$ . It dissolves, as does the free acid, in concentrated sulphuric acid to an

intense dark red solution. The *amide*,  $C_{20}H_{13}O_3N$ , formed when ammonia acts on the acid chloride, is a white powder, m. p. 115—118°. The *oxime anhydride*,  $C_{20}H_{11}O_3N$ , obtained by the action of free hydroxylamine on the acid in excess of potassium hydroxide, crystallises in colourless needles, m. p. 203—206°. The *phenylhydrazone anhydride*,  $C_{23}H_{16}O_2N_2$ , prepared by the interaction of the acid and phenylhydrazine, forms colourless plates, m. p. 221—223°.

W. H. G.

**Syntheses of Pyrrole Derivatives of High Molecular Weights.** JULIUS SCHMIDT and RICHARD SCHALL (*Ber.*, 1907, 40, 3002—3011).—The authors have previously described (*Abstr.*, 1906, i, 23) the preparation of 6-amino-, 4-amino-, 6:6'-diamino-, and 4:4'-diamino-diphenic acids. Since certain naturally occurring compounds contain the pyrrole nucleus, the authors have utilised the acids in question in order to add on the diphenyl group to the pyrrole ring by interaction of the reactive amino-groups with  $\gamma$ -diketo-compounds.

4-Aminodiphenic acid, (I), for example, combines with acetonyl acetone to form 2":5"-dimethyl-4-pyrrolediphenic acid, (II):



The influence of steric retardation was noted in certain cases. Thus, whilst 4-amino- and 4:4'-diamino-diphenic acids readily form pyrrole derivatives, such derivatives could not be obtained from 6-amino-, 6:6'-diamino-, and 6-amino-6'-hydroxy-diphenic acids.

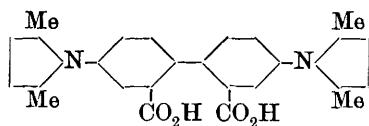
The diketones used were acetonylacetone and ethyl  $\beta$ -diacetylsuccinate. Pyrrole derivatives were not obtained when ethyl dibenzoylsuccinate was used. This is an instructive example of the fact that the reactivity of carbonyl groups is influenced by the groups attached to them.

Not only the pyrrole derivatives obtained, but also the amino-diphenic acids used in their preparation gave the so-called pyrrole reaction, causing pine-wood shavings moistened with hydrochloric acid to assume a red colour. This reaction, accordingly, is not so very trustworthy as a characteristic test for pyrrole compounds.

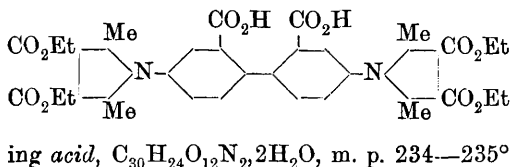
2":5"-Dimethyl-4-pyrrolediphenic acid, (II), when first prepared, is white, but is readily changed by air, assuming a red tint. It decomposes at 100—115°.

3":4"-Dicarbethoxy-2":5"-dimethyl-4-pyrrolediphenic acid, obtained from *p*-aminodiphenic acid and ethyl  $\beta$ -diacetylsuccinate, forms white needles, m. p. 229—230°. When saponified, it yields the corresponding acid,  $C_{22}H_{17}O_8N \cdot H_2O$ , which separates from dilute alcohol in colourless needles, m. p. 239—240°.

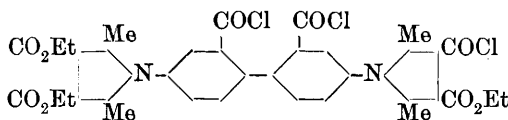
2'' : 5''-2''' : 5'''-Tetramethyl-4 : 4'-dipyrrolediphenic acid, obtained by the condensation of 4 : 4'-diaminodiphenic acid with acetonylacetone, crystallises in leaflets, m. p. 284—285° (decomp.).



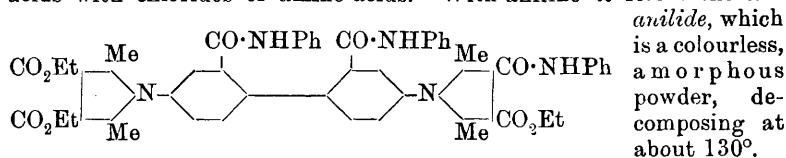
3'' : 4'' : 3''' : 4'''-Tetracarbethoxy-2'' : 5'' : 2''' : 5'''-tetramethyl-4 : 4'-dipyrrolediphenic acid, obtained from 4 : 4'-diaminodiphenic acid and ethyl  $\beta$ -diacetylsuccinate, crystallises in colourless leaflets, m. p. 285—286° (decomp.). When saponified, it forms the corresponding acid,  $C_{30}H_{24}O_{12}N_2 \cdot 2H_2O$ , m. p. 234—235° (decomp.).



When the tetracarbethoxy compound is warmed with an excess of phosphorus pentachloride, one carbethoxyl group only is attacked; the resulting trichloride has m. p. 175—177° and is comparatively stable towards water and alcohol. The corresponding triamide has m. p. 120—130° (decomp.).

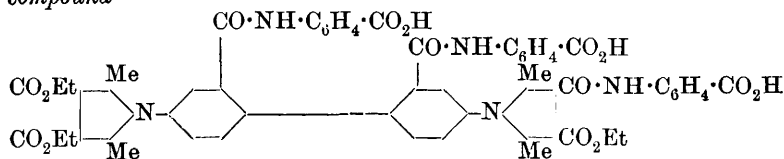


The trichloride combines with amino-compounds in a manner comparable with the formation of polypeptides by combination of amino-acids with chlorides of amino-acids. With aniline it forms the tri-



anilide, which is a colourless, amorphous powder, decomposing at about 130°.

When condensed with *p*-aminobenzoic acid, the trichloride forms the compound



which is an amorphous powder decomposing at 160—170°.

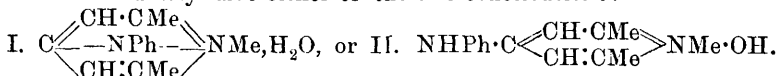
A. McK.

**Mechanism of the Synthesis of Quinoline Derivatives (Döbner's Reaction).** LOUIS J. SIMON and CHARLES MAUGUIN (*Compt. rend.*, 1907, 144, 1275—1278).—By using chloroform or benzene instead of alcohol in the condensation of  $\beta$ -naphthylamine with pyruvic acid and benzaldehyde, and also by acting on pure benzyldene- $\beta$ -naphthylamine (1 mol.) with pyruvic acid (1 mol.), the

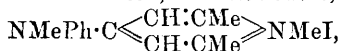




lutidine methiodide could be substituted by an atom of sulphur or selenium, it seemed of interest to determine if the action of aniline on 4-chlorolutidine would lead to the formation of the oxygen-free base, methylanilolutidine. The base, obtained on treating the immediate product of the reaction with an alkali, contains a stable molecule of water and may have either of the two constitutions:



In favour of I. is the addition of methyl iodide with formation of water and 4-anilino-*N*-methyl-lutidine at the ordinary temperature, as also the liberation of the base from its salt by alkalis, whereas the strong alkaline reaction of the base, its insolubility in ether, and the stability of the mol. of water, which cannot be removed without destruction of the whole molecule, point to constitution II. The authors consider that the product of the action of aniline on 4-chlorolutidine methiodide is the hydriodide of the base I., and that this base on liberation by an alkali immediately combines with water, forming the ammonium hydroxide base, II. When heated, the *methiodide*,



formed by the action of methyl iodide on the base I. or II., yields 4-methylanilinolutidine,  $\text{NMePh} \cdot \text{C} \begin{array}{c} \diagup \text{CH} \cdot \text{CMe} \\ \diagdown \text{CH} \cdot \text{CMe} \end{array} \text{N}$ , which is isomeric with the base I. This combines with water forming an ammonium hydroxide base,  $\text{NMePh} \cdot \text{C} \begin{array}{c} \diagup \text{CH} \cdot \text{CMe} \\ \diagdown \text{CH} \cdot \text{CMe} \end{array} \text{NH} \cdot \text{OH}$ , which has a strong alkaline reaction and is insoluble in ether, but differs from the first ammonium hydroxide base in that it loses water readily over sulphuric acid in a desiccator. These results agree with Michaelis's view that the alkaline reaction of the iminopyrines in aqueous or aqueous-alcoholic solution must be ascribed to the formation of ammonium hydroxide bases (Abstr., 1905, i, 476).

4-Anilinolutidine methiodide, obtained by the action of aniline on 4-chlorolutidine methiodide or of methyl iodide on 4-anilinolutidine (Conrad and Epstein, Abstr., 1887, 501), forms large, colourless needles, m. p. 223°.

4-Anilino-*N*-methyl-lutidinium hydroxide forms small, yellowish-white needles, m. p. 115°, and is stable at 110° in a current of hydrogen; the *hydrochloride*,  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{HCl}$ , forms colourless, hygroscopic needles; the *platinichloride*,  $(\text{C}_{14}\text{H}_{16}\text{N}_2)_2\text{H}_2\text{PtCl}_6$ , crystallises in yellow prisms, m. p. 218°; the *aurichloride* forms red needles, m. p. 159°; the *mercurichloride*, white plates, m. p. 175°; the *thiocyanate*,  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{HCNS}$ , m. p. 172°; the *picrate*, greenish-yellow leaflets, m. p. 178°.

4-Methylanilinolutidine methiodide crystallises in white leaflets, m. p. 166°; the *methochloride* forms a white, hygroscopic, crystalline mass. 4-Methylanilinolutidine is obtained as a colourless oil, b. p. 263—265°, which absorbs water, forming the *ammonium hydroxide base*, m. p. 75°. The *hydrochloride*,  $(\text{H}_2\text{O})$ , m. p. 214°, *platinichloride*,  $(\text{C}_{14}\text{H}_{16}\text{N}_2)_2\text{H}_2\text{PtCl}_6$ ,

yellowish-red needles, m. p.  $208^{\circ}$ , *aurichloride*,  $C_{14}H_{16}N_2 \cdot HAuCl_4$ , red crystals, m. p.  $118^{\circ}$ , *mercurichloride*, plates, m. p.  $126^{\circ}$ , *thiocyanate*, white needles, m. p.  $145^{\circ}$ , and *picrate* were analysed. G. Y.

**Piperazine and  $\alpha$ -Dihalogen-pentanes.** JULIUS VON BRAUN (*Ber.*, 1907, 40, 2935—2937).—Owing to the tendency of  $\alpha$ -dibromopentane to form a piperidine ring, the action of secondary bases on this substance or on the corresponding di-iodo-compound proceeds in this manner, to the exclusion of pentamethylene derivatives of the type  $HBr \cdot NR_2 \cdot [CH_2]_5 \cdot NR_2 \cdot HBr$  (this vol., i, 151).

Di-iodopentane and piperazine when heated on the water-bath combine together and give Aschan's diethylenedipiperidyl iodide (*Abstr.*, 1899, i, 542); the dibromopentane reacts more sluggishly, giving the corresponding bromide (Brühl, *Ber.*, 1874, 4, 738).

W. R.

**Pyrimidines. XX. Some Condensation Products of a Substituted  $\psi$ -Thiocarbamide. Synthesis of 1-Methyluracil.** TREAT B. JOHNSON and FREDERICK W. HEYL (*Amer. Chem. J.*, 1907, 37, 628—637).—It has been shown previously (Wheeler and Merriam, *Abstr.*, 1903, i, 524; Wheeler and Johnson, *Abstr.*, 1904, i, 624; Wheeler and Bristol, *Abstr.*, 1905, i, 482) that  $\psi$ -thiocarbamides undergo condensations more readily than the normal thiocarbamides. In the present paper, an account is given of the behaviour of a mono-substituted  $\psi$ -thiocarbamide towards some ketonic esters. It is found that condensation occurs with the formation of substituted thiolpyrimidines, which are converted by hydrochloric acid into uracil derivatives.

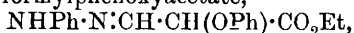
$\psi$ -Methylethylthiocarbamide hydriodide,  $NHMe \cdot C(SET) : NH, HI$ , obtained by the action of ethyl iodide on methylthiocarbamide, is an extremely hygroscopic solid. When this salt is treated with ethyl sodioformylacetate in presence of potassium hydroxide, it is converted into 6-oxy-2-ethylthiol-1-methylpyrimidine,  $NMe \cdot \begin{smallmatrix} C(SET) : N \\ \diagup \quad \diagdown \\ CO - CH \end{smallmatrix} > CH$ , m. p.  $79-80^{\circ}$ , which forms stout prisms. This compound is also produced by the action of methyl iodide on 6-oxy-2-ethylthiolpyrimidine (Wheeler and Merriam, *loc. cit.*). 2:6-Dioxy-1-methylpyrimidine (1-methyluracil),  $NMe \cdot \begin{smallmatrix} CO \cdot NH \\ \diagup \quad \diagdown \\ CO \cdot CH \end{smallmatrix} > CH$ , m. p.  $174-175^{\circ}$ , crystallises in microscopic prisms, and when treated with a mixture of nitric and sulphuric acids is converted into 5-nitro-2:6-dioxy-1-methylpyrimidine (Behrend and Thurm, *Abstr.*, 1902, i, 832). The corresponding 5-bromo-derivative, m. p.  $228-229^{\circ}$ , forms transparent prisms.

2:6-Dioxy-1-ethylpyrimidine (1-ethyluracil),  $NEt \cdot \begin{smallmatrix} CO \cdot NH \\ \diagup \quad \diagdown \\ CO \cdot CH \end{smallmatrix} > CH$ , m. p.  $173-174^{\circ}$ , prepared by treating 6-oxy-2-ethylthiolpyrimidine with ethyl iodide in presence of potassium hydroxide and heating the product with strong hydrochloric acid, crystallises in prisms.

When 2-ethylthiol-1:4-dimethylpyrimidine, obtained by the condensation of  $\psi$ -methylethylthiocarbamide with ethyl acetoacetate, is

boiled with concentrated hydrochloric acid, 2:6-dioxy-1:4-dimethylpyrimidine (Behrend and Thurm, *loc. cit.*) is produced.

By the action of sodium ethoxide on a mixture of ethyl phenoxyacetate and ethyl formate, the sodium derivative of ethyl  $\beta$ -hydroxy- $\alpha$ -phenoxyacrylate,  $\text{ONa}\cdot\text{CH}\cdot\text{C}(\text{OPh})\cdot\text{CO}_2\text{Et}$ , is formed, which when treated with sulphuric acid yields the *ethyl* ester as a heavy oil. The *hydrazone* of ethyl formylphenoxyacetate,



m. p. 219—221° (decomp.), forms yellow prisms. 6-Oxy-5-phenoxy-2-ethylthiolpyrimidine,  $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{SEt})=\text{N} \\ \text{CO}\cdot\text{C}(\text{OPh}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 159°, obtained by condensing  $\psi$ -ethylthiocarbamide with the sodium derivative of ethyl  $\beta$ -hydroxy- $\alpha$ -phenoxyacrylate, crystallises in transparent prisms.

E. G.

**New Method of Preparation of Azoimide and Diazobenzene-imide [Phenylazoimide].** AUGUST DARAPSKY (*Ber.*, 1907, 40, 3033—3039. Compare Dimroth, this vol., i, 652).—The author has extended the study of the action of sodium hypochlorite and hypobromite on amides to amino-substances containing three or four nitrogen atoms in the chain in the hope of obtaining triazans or butylene derivatives. Biuret, however, gave hydrazine, and semicarbazide was completely decomposed with evolution of nitrogen in the cold. Hydrazodicarbonamide or azodicarbonamide are partly converted into triazencarbonamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{N}\cdot\text{N}\cdot\text{NH}_2$ , which was not isolated, but converted into sodium azoimide by oxidation and hydrolysis. The yield was about 9%.

Phenylsemicarbazide or phenylazocarbonamide give 53% and 64% yields of phenylazoimide accompanied by the formation of a small quantity of azobenzene. That phenyltriazene is an intermediate product in this reaction is proved by obtaining the compound by reducing phenylazoimide in ether at  $-20^\circ$  with stannous chloride, and is quantitatively oxidised again to phenylazoimide by hypobromite. The semicarbazides or azocarbonamides from *p*-methyl-, *p*-nitro-, and *p*-bromo-phenylhydrazine, and  $\beta$ -naphthylhydrazine all yield azoimides as the chief product of the reaction. Benzylsemicarbazide or benzoylsemicarbazide are not converted into azoimides, neither are they oxidised by permanganate to azocarbonamides. The conclusion is drawn that only such derivatives of hydrazinecarbonamides as are capable of being oxidised to azocarbonamides can be converted into azoimides by hypochlorite.

Benzoylhydrazine under the same conditions gives benzaldehydebenzoylhydrazone.

W. R.

**New Compound Obtained by the Action of Iodine on Benzaldehydephenylhydrazone in Pyridine Solution.** II. GIOVANNI ORTOLEVA (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 874—884. Compare Abstr., 1906, i, 715).—Various new derivatives of the compound  $\text{C}_{18}\text{H}_{14}\text{N}_3\text{I}$  (*loc. cit.*) are described, and its salt-like character confirmed.

The *nitrate*,  $\text{C}_{18}\text{H}_{18}\text{N}_3\cdot\text{HNO}_3$ , prepared by the action of nitric acid on the hydriodide, forms white needles, m. p. 214—215°. The

*platinichloride*,  $(C_{18}H_{13}N_3)_2 \cdot H_2PtCl_6$ , m. p. 238—239°; the *perbromide*,  $C_{18}H_{13}N_3 \cdot HBr \cdot Br_2$ , red needles, m. p. 161—162° or, when crystallised from alcohol, 147—148°, and the *picrate*,  $C_{18}H_{13}N_3 \cdot C_6H_3O_7N_3$ , m. p. 185—187°, were also prepared.

The base,  $C_{12}H_9N_3$ , obtained by oxidising the hydriodide,  $C_{12}H_9N_3 \cdot HI$ , with permanganate, yields the following derivatives. The *hydrochloride*,  $C_{12}H_9N_3 \cdot HCl$ , m. p. 181—182°; the *compound*  $C_{12}H_9N_3 \cdot 3H_2Cl_2 \cdot 2H_2O$ , m. p. indefinite; the *platinichloride*,  $(C_{12}H_9N_3)_2 \cdot H_2PtCl_6 \cdot \frac{1}{2}H_2O$ , which, when heated at 180—200°, yields the *platinosochloride*,  $(C_{12}H_9N_3)_2 \cdot PtCl_2$ ; the *picrate*,  $C_{12}H_9N_3 \cdot C_6H_3O_7N_3$ , m. p. 160—161°; the *ethiodide*,  $C_{12}H_9N_3 \cdot EtI$ , m. p. 189—190°, and the *compounds*  $C_{12}H_9N_3 \cdot 2BzCl$ , m. p. 183—186°, and  $C_{12}H_9N_3 \cdot AcCl$ , m. p. 183—185°.

Oxidation of the hydriodide,  $C_{12}H_9N_3 \cdot HI$ , with permanganate in acid solution yields: (1) an *acid*,  $C_{12}H_{10}O_2N_2$ , m. p. 114—115°, and (2) a substance, m. p. 143—145°, which gives a red coloration with ferric chloride.

T. H. P.

**Two New Classes of Metallic Salts of Imino-bases. Theory of Internally Complex Metallic Salts.** HEINRICH LEY and F. MÜLLER (*Ber.*, 1907, 40, 2950—2958. Compare this vol., i, 301).—The salts of diguanides have been investigated as being related to the acid imides, and, in order to ascertain which groups in the molecule of these compounds are necessary in order that the central hydrogen atom should still be replaceable by a metal, the 2:4:5-triphenyl-guanylamidide and 2:4:5-triphenylamidide have been prepared. These compounds are bases yielding hydrochlorides not hydrolysed in aqueous solution, and also stable abnormally coloured salts of heavy metals.

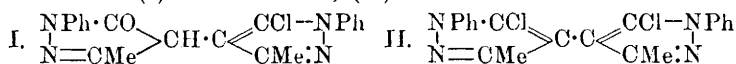
2:4:5-Triphenylguanylamidide, prepared by mixing a dry ethereal solution of benzamidine (1 mol.) with carbodiphenylimide (1 mol.), crystallises from alcohol in pale yellow needles, m. p. 142°. The *hydrochloride*, m. p. 252° (decomp.), is colourless, as is also the *sulphate*. The *cobalt* salt is deep yellow, that of *copper* is pale yellowish-grey, and the *nickel* salt is flesh-coloured. The base on hydrolysis gives diphenylguanidine; on warming the base with acetic anhydride, it is converted into a *triazine* compound,  $C_{22}H_{18}N_4$ , which crystallises in yellow leaflets, and, although forming a hydrochloride, does not form salts with metals. A *compound*,  $C_{33}H_{28}N_6$ , is formed as a by-product in the preparation of triphenylguanylamidide. It has m. p. 236°, is lemon-yellow in colour, and gives a hydrochloride, but no metallic salts. It possesses great stability, and is probably a cyclic compound.

2:4:5-Triphenyldiamidide,  $NH \cdot CPh \cdot NH \cdot CPh \cdot NPh$ , obtained by the interaction of benzamidine (2 mols.) with benzanilinoimino-chloride (1 mol.), forms pale yellow crystals, m. p. 152°. The *hydrochloride*, m. p. 250° (decomp.), is colourless. The *copper* salt is brown, the *nickel* and *cobalt* salts yellow.

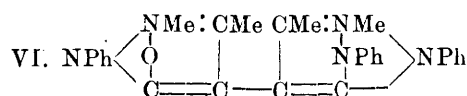
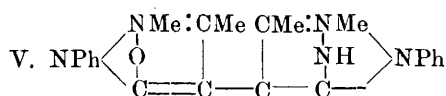
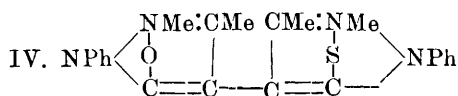
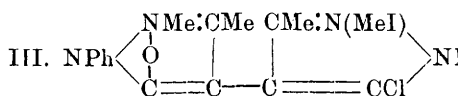
The authors discuss the nature of these salts from the point of view of Werner's theory.

W. R.

**Pyrynes from Bis-1-phenyl-3-methyl-5-pyrazolone.** AUGUST MICHAELIS, OTTO RADEMACHER, and ENOCH SCHMIEDEKAMPF (*Annalen*, 1907, **354**, 55—90. Compare Abstr., 1905, i, 476).—In continuation of the study of pyrynes, the preparation of such substances from a bispyrazolone offered some points of interest, since the presence of the two pyrazolone nuclei afforded the possibility of forming, on the one hand, bispyrynes and, on the other, mixed pyrynes. This has been accomplished as follows. Bis-1-phenyl-3-methyl-5-pyrazolone yields two *derivatives* when heated with phosphorus oxychloride in a sealed tube: (I) at 140—150°; (II) at 170°. The first of these is



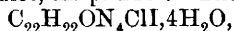
soluble in alkalis, and is converted by methyl iodide, or methyl sulphate and potassium iodide, into a *substance*, (III), which is a derivative of antipyrine and at the same time a 5-chloropyrazole methiodide. On treatment with potassium hydrogen sulphide, ammonia, or aniline, it yields the mixed pyrynes, *antithiopyrine*, (IV), *anti-iminopyrine*, (V), and *antianilopyrine*, (VI), respectively.



forms a dihydrochloride, but combines with only 1 mol. of methyl iodide, which is attached to the thiopyrine half of the molecule.

This *methiodide* loses methyl iodide when heated, forming *anti-ψ-thiopyrine*. Antianilopyrine yields a similar *anti-ψ-anilopyrine*.

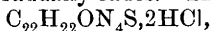
**5-Chloro-1 : 1'-diphenyl-3 : 3'-dimethyl-4' : 5'-dihydrobispyrazole-5-one**,  $\text{C}_3\text{N}_2\text{ClMePh} \cdot \text{C}_3\text{N}_2\text{HOMePh}$ , crystallises in white needles, m. p. 240°. The *methiodide*,



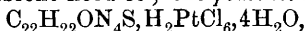
crystallises in leaflets, m. p. 203°, loses part of the water of crystallisation in a vacuum over sulphuric acid and the remainder at 115°, and yields bisantipyrine when heated with alkalis in alcoholic solution. The product, obtained on heating the 5-chlorodihydrobispyrazole-5'-one with methyl iodide, crystallises in colourless leaflets, containing  $4\text{H}_2\text{O}$ , m. p. 209°, and is a mixture of antipyrinyl-5-iodopyrazole and anti-

pyriny-5-chloropyrazole methiodides. The *methochloride* of anti-pyriny-5-chloropyrazole,  $C_{22}H_{22}ON_4Cl_2$ , crystallises in white needles, m. p.  $213^\circ$ , and forms two *platinichlorides*:  $(C_{22}H_{22}ON_4Cl_2)_2PtCl_4$ , yellow prisms, m. p.  $236^\circ$ , and  $C_{22}H_{22}ON_4Cl_2 \cdot HCl \cdot PtCl_4$ , a yellow, crystalline mass, decomposing without melting at high temperatures.

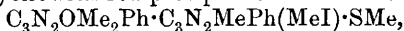
*Antithiopyrine*,  $C_{22}H_{22}ON_4S \cdot 2H_2O$ , separates from water in monoclinic crystals, from ether in needles, m. p.  $225^\circ$ , and gives with sulphurous acid an intense yellow, or with ferric chloride a reddish-brown, coloration which gradually fades. The *hydrochloride*,



crystallises in deliquescent needles; the *platinichloride*,

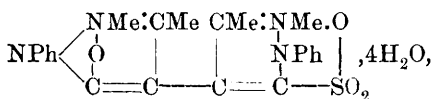


is obtained as a yellowish-red precipitate. The *methiodide*,



formed by the action of methyl iodide on antithiopyrine, crystallises in needles, m. p.  $192^\circ$ , and forms a dark red, crystalline *dibromide*,  $C_3N_2OMe_2Ph \cdot C_3N_2MePh(MeBr) \cdot SBr$ , m. p.  $189^\circ$  (decomp.), when treated with bromine in chloroform solution.

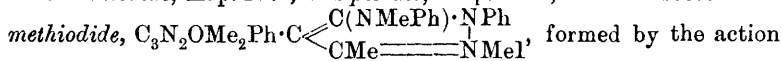
*Anti-ψ-thiopyrine* (5-methylthiol-1-phenyl-3-methyl-4-antipyriny-pyrazole), formed by distilling antithiopyrine under reduced pressure, is obtained in colourless crystals, m. p.  $168^\circ$ . *Antithiopyrine trioxide*



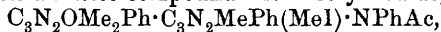
(annexed formula) is formed in stout crystals by the action of potassium sulphite on the methiodide, (III). It cannot be obtained by oxidation of

antithiopyrine, as this leads to the formation of resins.

*Antianilopyrine*,  $C_{28}H_{27}ON_5$ , m. p.  $215^\circ$ , forms yellow crystals, probably isomorphous with bisantipyrene, absorbs carbon dioxide from the air, has a strong alkaline reaction to litmus, and gives a reddish-yellow coloration with alcoholic ferric chloride; when dissolved in acids and precipitated by addition of alkalis, it yields a white precipitate, which becomes yellow only gradually and may be the ammonium hydroxide. The *hydrochloride*,  $C_{28}H_{27}ON_5 \cdot 2HCl$ , m. p.  $106^\circ$ , *platinichloride*,  $C_{28}H_{27}ON_5 \cdot H_2PtCl_6 \cdot 3H_2O$ , *aurichloride*, m. p.  $117^\circ$ , *mercurichloride*, m. p.  $157^\circ$ , and *picrate*, m. p.  $228^\circ$ , are described. The

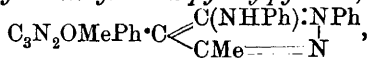


of methyl iodide on antianilopyrine at the ordinary temperature, could not be crystallised. The corresponding *methochloride* forms a *platinichloride*,  $C_{28}H_{27}ON_5 \cdot MeCl \cdot HCl \cdot PtCl_4 \cdot 2H_2O$ , crystallising in yellow needles. The *benziodide*,  $C_{28}H_{27}ON_5 \cdot CH_2PhI$ , forms colourless crystals, m. p.  $126^\circ$ . The *additive* compound with acetyl iodide,



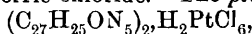
crystallises in colourless prisms, m. p.  $116^\circ$ .

5-Anilino-1-phenyl-3-methyl-4-antipyriny-pyrazole,



prepared by heating antianilopyrine hydrochloride, or a mixture of

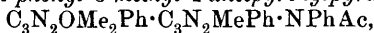
the base with ammonium chloride, or by the action of aniline at 180—200° on the mixed methiodide obtained from (I), crystallises in white leaflets, m. p. 240°, is neutral in alcoholic solution, and gives a yellow coloration with ferric chloride. The *platinichloride*,



forms yellowish-red crystals. When heated with methyl iodide at 100°, the base yields a salt from which antianilopyrine is obtained on treatment with sodium hydroxide.

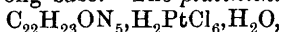
*Anti-ψ-anilopyrine* (5-methylanilino-1-phenyl-3-methyl-4-antipyrinylpyrazole,  $\text{C}_3\text{N}_2\text{OMe}_2\text{Ph} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{NMePh}$ , prepared by heating anti-anilopyrine methiodide, forms colourless crystals, m. p. 101°; the *platinichloride*,  $(\text{C}_{38}\text{H}_{27}\text{ON}_5)_2, \text{H}_2\text{PtCl}_6, 4\text{H}_2\text{O}$ , crystallises in small, yellowish-red needles.

5-Acetylanilino-1-phenyl-3-methyl-4-antipyrinylpyrazole,



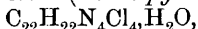
formed by heating the *additive* compound of acetyl iodide and anti-anilopyrine, crystallises in white leaflets, m. p. 238°.

*Anti-iminopyrine* crystallises in white leaflets, m. p. 259—260° (decomp.), and is a strong base. The *platinichloride*,



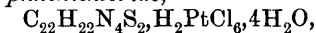
forms yellowish-red prisms. The *methiodide*, and *anti-ψ-iminopyrine*, obtained from it by heating, are oils. 5-Amino-1-phenyl-3-methyl-4-antipyrinylpyrazole,  $\text{C}_3\text{N}_2\text{OMe}_2\text{Ph} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{NH}_2$ , formed by heating the methiodide, (III), with ammonia at 250°, crystallises in white needles, m. p. 220°, and is neutral in aqueous or alcoholic solution. The *acetyl* derivative,  $\text{C}_{28}\text{H}_{28}\text{O}_2\text{N}_5$ , crystallises in colourless needles, m. p. 237°.

*Bis-5-chloro-1-phenyl-3-methylpyrazole*,  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_2$ , crystallises in white needles, m. p. 160°, and is soluble in concentrated hydrochloric acid. The *dimethiodide*,  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{Cl}_2\text{I}_2, 3\text{H}_2\text{O}$ , crystallises in leaflets, m. p. 205°, and loses  $2\text{H}_2\text{O}$  in a vacuum. When heated with methyl iodide, bischlorophenylmethylpyrazole yields a *product*, m. p. 210—215° (decomp.), consisting chiefly of bis-5-iodo-1-phenyl-3-methylpyrazole methiodide. The *methochloride* (*bisantipyrene chloride*),



m. p. 225°.

*Bistiopyrine* forms white crystals, m. p. 237°, is soluble in hydrochloric acid, and gives with ferric chloride a yellow coloration or with sulphurous acid a yellow, crystalline precipitate; the *platinichloride*,



was analysed. The *dimeth-*

*iodide*,  $\text{NPh} \cdot \text{C}(\text{SMe}) \text{NMeI} = \text{CMe} \text{C}(\text{SMe}) \cdot \text{NPh}$  separates from water in crystals containing  $2\text{H}_2\text{O}$ , m. p. 154°, or from alcohol in anhydrous, white prisms, m. p. 234°. The similarly constituted *additive* product with benzoyl chloride,  $\text{C}_{36}\text{H}_{32}\text{O}_2\text{N}_4\text{Cl}_2\text{S}_2$ , m. p. 134°. The *tetrabromide*,  $\text{NPh} \cdot \text{C}(\text{SBr}) \text{NMeBr} = \text{CMe} \text{C}(\text{SBr}) \cdot \text{NPh}$  forms a red, crystalline mass,

m. p. about 133°; the *tetrachloride* is deliquescent. *Bisthiopyrine trioxide*, formed by the action of chlorine on bisthiopyrine in aqueous or acetic acid solution, separates in stout crystals, and decomposes at high temperatures. *Bis-ψ-thiopyrine*,

$\text{SMe} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{SMe}$ , formed by heating bisthiopyrine methiodide at 200° under reduced pressure, distils as a viscid oil, and separates from alcohol in colourless crystals, m. p. 124°; it is oxidised by potassium permanganate in acetic acid solution, forming the *sulphone*,  $\text{C}_{22}\text{H}_{22}\text{O}_4\text{N}_4\text{S}_2$ , crystallising in white leaflets, m. p. 149°.

*Bisanilopyrine* crystallises in slightly yellow needles, m. p. 207°, and is a strong base. The *platinichloride*,  $\text{C}_{34}\text{H}_{32}\text{N}_6\text{H}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$ , *aurichloride*,  $\text{C}_{34}\text{H}_{32}\text{N}_6 \cdot 2\text{HAuCl}_4$ , m. p. 218°, *hydriodide*,  $\text{C}_{34}\text{H}_{32}\text{N}_6 \cdot 2\text{HI}$ , m. p. 328°, and *picrate*, m. p. 214°, are described. The *methiodide*,  $\text{C}_{36}\text{H}_{38}\text{N}_6\text{I}_2 \cdot 2\text{H}_2\text{O}$ , forms colourless crystals, m. p. 120° (decomp.).

*Bis-ψ-anilopyrine*,  $\text{NMePh} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{NMePh}$ , forms white crystals, m. p. 108°, and has a neutral reaction in alcoholic solution, but dissolves in acids. *Bis-5-anilino-1-phenyl-3-methylpyrazole*,

$\text{NHPh} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{NHPh}$ , prepared by heating bisanilopyrine hydrochloride or hydriodide, or by the action of aniline on bis-5-chloro-1-phenyl-3-methylpyrazole at 180—200°, crystallises in white needles, m. p. 315°, and is converted into bisanilopyrine hydriodide when heated with methyl iodide.

*Bisiminopyrine* crystallises in white leaflets, m. p. 250° (decomp.), has strong basic properties, and forms an oily *methiodide*. The *hydriodide*,  $\text{C}_{22}\text{H}_{24}\text{N}_6 \cdot 2\text{HI}$ , forms white crystals, m. p. 280°; the *picrate*,  $\text{C}_{22}\text{H}_{24}\text{N}_6 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , forms golden leaflets, m. p. 204°.

The *dibenzenesulphonyl* compound,  $\text{C}_{22}\text{H}_{22}\text{N}_6(\text{SO}_2\text{Ph})_2$ , m. p. 198°. The crystalline *platinichloride*,  $\text{C}_{22}\text{H}_{24}\text{N}_6\text{H}_2\text{PtCl}_6$ , is yellowish-red. *Bis-5-amino-1-phenyl-3-methylpyrazole*,  $\text{NH}_2 \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{NH}_2$ , formed by heating bisanti-pyrene chloride with ammonia at 250°, yields a *diacetyl* derivative crystallising in colourless needles, m. p. 272°. G. Y.

**Diazoamino compounds Derived from Purine Bases.** RICHARD BURIAN (*Zeitsch. physiol. Chem.*, 1907, 51, 425—437. Compare Abstr., 1904, i, 354).—A good yield of the diazobenzenesulphonyl derivative of adenine can be obtained only in the absence of an excess of alkali. The compound when prepared is also readily decomposed by alkalis. Full details for the preparation are given. It forms pale yellow, microscopic needles which decompose at 200° without melting. It is partially decomposed when boiled with water.

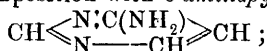


Guanine, xanthine, and theophylline react with diazobenzene-sulphonic acid even in the presence of an excess of alkali. Purine bases in which a methyl group is in the position 7, for example, caffeine and theobromine, do not react either in the presence or absence of excess of alkali.

Nucleic acids, although they contain guanine and adonine residues, do not condense with the diazosulphonic acid in the presence or absence of excess of alkali. The conclusion is drawn that guanine or adenine is attached at position 7 to the residue of the nucleic acid molecule and also that this union is effected by means of phosphorus.

J. J. S.

**Pyrimidine Derivatives from Purine Bases.** RICHARD BURIAN (*Zeitsch. physiol. Chem.*, 1907, 51, 438—456).—In order to determine whether some of the pyrimidine derivatives obtained by hydrolysing nucleic acids with moderately concentrated sulphuric acid may not be formed from purine bases by hydrolysis and reduction, experiments have been made by heating adenine and guanine with 30—40% sulphuric acid and dextrose or any other carbohydrate as a reducing agent. The results show that pyrimidine derivatives are produced under these conditions. From adenine, a product has been isolated which corresponds in composition with 6-aminopyrimidine,



it yields a *picrate*,  $\text{C}_4\text{H}_5\text{N}_3\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , which crystallises in pale yellow needles, softens at  $215^\circ$ , m. p.  $235\text{--}240^\circ$  (decomp.). The *platini-chloride*,  $(\text{C}_4\text{H}_5\text{N}_3)_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises in glistening, yellow prisms. A second product is 6-hydroxypyrimidine.

From guanine, Wheeler and Johnson's *isocytosine* or 2-amino-6-oxypyrimidine (Abstr., 1903, i, 526) has been obtained together with uracil, which is produced by the removal of the amino-group from the *isocytosine*.

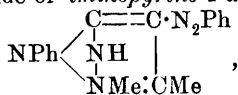
From 2 grams of guanine, 1.56 were recovered unaltered, and 0.234 gram was accounted for as *isocytosine*.

The results obtained account for the fact that in the estimation of purine bases a dilute sulphuric acid ( $\frac{1}{2}$  to 1%) should be used,

J. J. S.

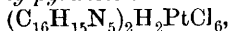
**5-Alkylamino-1-phenyl-3-methylpyrazole-4-azobenzene and 4:5-Diamino-1-phenyl-3-methylpyrazole.** AUGUST MICHAELIS and HANS KLOPSTOCK (*Annalen*, 1907, 354, 102—115).—It was shown previously that the chlorine atom of 5-chloro-1-phenyl-3-methylpyrazole-4-azobenzene is substituted readily by hydrogen, iodine, or the group SH (Michaelis, Abstr., 1905, i, 392). It is found now that whilst primary and secondary aliphatic amines, as also piperidine, react easily with this chloropyrazole, ammonia is almost without action even at high temperatures. On the other hand, the corresponding iodopyrazole reacts with alcoholic ammonia at  $200\text{--}210^\circ$ , forming 5-amino-1-phenyl-3-methylpyrazole-4-azobenzene (Michaelis and Danzfuss, Abstr., 1905, i, 476). With methyl iodide, this 5-amino-

pyrazole forms a *methiodide*,  $\begin{array}{c} \text{NPh} \cdot \text{C}(\text{NH}_2) \\ | \\ \text{NMe} \cdot \text{I} = \text{CMe} \end{array} > \text{C} \cdot \text{N} : \text{NPh}$ , which may be regarded as the hydriodide of *iminopyrine-4-azobenzene*,



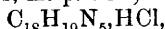
into which it is easily converted.

5-Amino-1-phenyl-3-methylpyrazole-4-azobenzene *platinichloride*,



forms a yellowish-red, sparingly soluble precipitate decomposing at  $199^\circ$ . The *methiodide* crystallises in scales, m. p.  $225^\circ$ ; the *methochloride* forms yellow leaflets, m. p.  $126^\circ$ , and when treated with aqueous potassium hydroxide yields *iminopyrine-4-azobenzene*; this crystallises in yellowish-red leaflets, m. p.  $161^\circ$ , and has strong basic properties. The *platinichloride*,  $(\text{C}_{17}\text{H}_{17}\text{N}_5)_2\text{H}_2\text{PtCl}_6$ , forms red needles, m. p.  $225^\circ$ ; the *mercurichloride*,  $\text{C}_{17}\text{H}_{17}\text{N}_5 \cdot \text{HCl} \cdot \text{HgCl}_2$ , m. p.  $201^\circ$ .

5-Ethylamino-1-phenyl-3-methylpyrazole-4-azobenzene,  $\text{C}_{18}\text{H}_{19}\text{N}_5$ , forms yellowish-red crystals, m. p.  $81^\circ$ ; the *hydrochloride*,



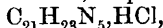
crystallises in red needles, m. p.  $99^\circ$ ; the *platinichloride*, yellowish-red crystals, m. p.  $184^\circ$ ; the *methiodide*, yellow scales, m. p.  $218^\circ$ . *Ethyliminopyrine-4-azobenzene*, formed from the preceding *methiodide*, yields a *platinichloride*,  $(\text{C}_{19}\text{H}_{22}\text{N}_5\text{Cl})_2\text{PtCl}_4$ , m. p.  $212^\circ$ .

5-Diethylamino-1-phenyl-3-methylpyrazole-4-azobenzene,  $\text{C}_{20}\text{H}_{23}\text{N}_5$ , forms yellowish-red crystals, m. p.  $82^\circ$ .

5-Piperidyl-1-phenyl-3-methylpyrazole-4-azobenzene,



crystallises in yellowish-red needles, m. p.  $112^\circ$ ; the *hydrochloride*,



red powder, m. p.  $142^\circ$ ; the *methiodide*, yellow needles.

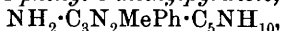
4 : 5-Diamino-1-phenyl-3-methylpyrazole,  $\text{C}_8\text{N}_2\text{MePh}(\text{NH}_2)_2$ , prepared by reduction with stannous chloride and hydrochloric acid of 5-amino-1-phenyl-3-methylpyrazole-4-azobenzene or the 4-azobenzenesulphonic acid,  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{N}_5\text{S}$ , m. p.  $255^\circ$ , or 4-isonitroso-5-imino-1-phenyl-3-methylpyrazolone (Walther, Abstr., 1897, i, 297), crystallises in needles, m. p.  $119^\circ$ , and reduces Fehling's and ammoniacal silver solutions in the cold; the *hydrochloride*,  $\text{C}_{10}\text{H}_{12}\text{N}_4 \cdot 2\text{HCl}$ , is more stable than the base on exposure to air.

1-Phenyl-3-methyl-4 : 5-aziminopyrazole,  $\text{N} \begin{array}{c} \text{NPh} \cdot \text{C} \cdot \text{NH} \\ | \quad | \\ \text{CMe} \cdot \text{C} - \text{N} \end{array} = \text{N}$ , formed

by the action of sodium nitrite on the diamino-base in acetic acid solution at  $0^\circ$ , crystallises in slightly yellow needles, m. p.  $190^\circ$

(decomp.). The *phenanthrazine* derivative,  $\text{N} \begin{array}{c} \text{NPh} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{C}_6\text{H}_4 \\ | \quad | \quad | \\ \text{CMe} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$ ,

prepared by the action of phenanthraquinone on the diamino-base in glacial acetic acid solution, crystallises in yellow needles, m. p.  $265^\circ$ , and forms a red solution in concentrated hydrochloric acid. 4 : 5-Di-acetyl-amino-1-phenyl-3-methylpyrazole,  $\text{C}_8\text{N}_2\text{MePh}(\text{NHAc})_2$ , m. p.  $233^\circ$ , is soluble in concentrated hydrochloric acid.

**4-Amino-5-piperidyl-1-phenyl-3-methylpyrazole,**

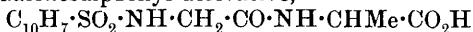
prepared by reduction of 5-piperidyl-1-phenyl-3-methylpyrazole-4-azobenzene with stannous chloride and hydrochloric acid, forms colourless crystals, m. p.  $87^\circ$ , and reduces Fehling's or slightly acid platinum tetrachloride solutions. The salts do not crystallise readily. The *acetyl* derivative,  $\text{NHAc} \cdot \text{C}_3\text{N}_2\text{MePh} \cdot \text{C}_5\text{NH}_{10}$ , crystallises in white needles, m. p.  $171^\circ$ , and is soluble in dilute acids; the *benzoyl* derivative,  $\text{C}_{22}\text{H}_{24}\text{ON}_4$ , forms white crystals, m. p.  $208^\circ$ . G. Y.

**Constitution of the Indole Group in Albumin. IV. Synthesis of Racemic Tryptophan.** ALEXANDER ELLINGER and CLAUDE FLAMAND (*Ber.*, 1907, 40, 3029—3033. Compare *Abstr.*, 1904, i, 639; 1905, i, 827; 1906, i, 696).—The azlactone, obtained from oxidising tryptophan or from indole-3-aldehyde (*loc. cit.*), crystallises with 1 mol. chloroform in glistening, dark orange prisms, m. p.  $220^\circ$ . When heated with excess of 1% sodium hydroxide, the lactone ring opens, and acidification of the solution precipitates *α*-benzoylamino-indolylacrylic acid,  $\text{C}_8\text{H}_6\text{N} \cdot \text{CH} : \text{C}(\text{NHBz}) \cdot \text{CO}_2\text{H}$ , which crystallises from alcohol in glistening prisms, m. p.  $232$ — $234^\circ$  (not sharp). Racemic tryptophan was prepared by reduction of the acrylic acid with sodium and alcohol, and the benzoyl group is hydrolysed on the addition of water. This substance behaves like the tryptophan, obtained from casein, towards naphthylcarbimide, naphthalene, and benzenesulphonyl chloride, and has the same m. p. and crystalline form. It is sweet, whereas the digestive tryptophan is almost tasteless, resembling racemic and *l*-leucine (compare E. Fischer, *Abstr.*, 1906, i, 72).

W. R.

**Formation of Polypeptides by the Hydrolysis of Proteins.**

EMIL FISCHER and EMIL ABDERHALDEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 30, 574—590. Compare *Abstr.*, 1906, i, 718).—Glycyl-*d*-alanine has been isolated from the products of the hydrolysis of silk-fibroin with hydrochloric acid; it is most readily obtained in the form of its  $\beta$ -naphthalenesulphonyl derivative,



(Fischer and Bergell, *Abstr.*, 1903, i, 24), m. p.  $155^\circ$  (corr.), which on hydrolysis yields  $\beta$ -naphthylsulphonylglycine and alanine.

A *tetrapeptide*,  $\text{C}_{16}\text{H}_{22}\text{O}_6\text{N}_4$ , has also been isolated from the hydrolytic products precipitated by phosphotungstic acid. This contains two glycine, one alanine, and one tyrosine residues; it has not been obtained in a crystalline form, dissolves readily in water, but is insoluble in absolute alcohol. It is not precipitated by the addition of concentrated sodium chloride solution except in the presence of a little nitric or acetic acid. When completely hydrolysed by boiling with 25% sulphuric acid, the products are glycine, alanine, and tyrosine. When partially hydrolysed with concentrated hydrochloric acid at  $16^\circ$ , glycyl-*d*-alanine anhydride and glycyl-*l*-tyrosine anhydride are formed.

Elastin with 70% sulphuric acid at  $36^\circ$  yields *d*-alanyl-*l*-leucine, and with fuming hydrochloric acid at the same temperature, *l*-leucylglycyl anhydride and *l*-leucyl-*d*-alanine anhydride. These anhydrides do not

crystallise so readily as the specimens prepared synthetically, and the possibility of isomerism is suggested.

The compounds crystallise readily after their aqueous solutions have been repeatedly evaporated, after boiling with quinoline, or after sublimation. Other compounds isolated from the hydrolytic products of elastin are a gelatinous *alanylproline anhydride*,  $C_6H_{12}O_2N_2 \cdot H_2O$ , and *glycylvaline anhydride*,  $C_7H_{12}O_2N_2$ , m. p. 245—250° (corr.).

The partial hydrolysis of diglycylglycine and of pentaglycylglycine has been studied. J. J. S.

**Amount of Oxygen in Horses' Oxyhæmoglobin.** M. PIETTRE and ANTONY VILA (*Compt. rend.*, 1907, 144, 1370—1372).—Crystals of oxyhæmoglobin contained 0.80 c.c. to 0.95 c.c. of oxygen per gram of dry matter. When dissolved in pure water, the substance gives up a much greater amount (1.4 c.c. to 1.7 c.c.).

The spectrum of solutions of oxyhæmoglobin reduced by the action of a vacuum and heat (45—50°) includes the bands  $\lambda = 634$ . The union of bands  $\alpha$  and  $\beta$  did not take place. N. H. J. M.

**Action of Hydrogen Peroxide on Hæmin.** JOHN A. GARDNER and G. A. BUCKMASTER (*Proc. physiol. Soc.*, 1907, xxxii—xxxiv.; *J. Physiol.*, 35).—When purified hæmin crystals are treated with dilute hydrogen peroxide, oxygen is evolved, and the solution shows traces of ferric chloride and free hydrochloric acid. With concentrated hydrogen peroxide, the crystals are eroded, and the chief products formed are carbon dioxide and oxalic acid; the chlorine and iron are all liberated, and about two thirds of the nitrogen is combined in the form of ammonium salts. Complex organic acids to the amount of 2—4% of the hæmin taken were also formed. These hæmatic acids were evidently identical with the oxidation products obtained by Kuster by other methods. W. D. H.

**Colouring Matter of Blood.** VII. LEO MARCHLEWSKI and ST. MOSTOWSKI (*Zeitsch. physiol. Chem.*, 1907, 51, 464—467. Compare Abstr., 1904, i, 463, 839; 1905, i, 399, 725; 1906, i, 779. Compare Kütscher, *Annalen*, 1906, 346, 9).—From the behaviour of hæmopyrrole towards sulphuric acid and diazobenzene chloride, the authors come to the conclusion that the base is chemically acted on by the sulphuric acid, probably polymerised. The base itself is probably homogeneous. The acid solution, obtained by shaking the ethereal solution of hæmopyrrole with sulphuric acid, yields, when neutralised with sodium carbonate, a product which also condenses with diazobenzene chloride. J. J. S.

**Nucleic Acids.** HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 51, 549).—Polemical against Burian. W. D. H.

**Nucleic Acids.** HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 52, 62).—By the oxidation of nucleic acid with nitric acid, the barium salt of a new acid,  $C_6H_{10}O_8$ , was obtained. This originates from the

carbohydrate group of the nucleic acid, and it is termed without prejudice, *episaccharic acid*. Its *quinine* salt,  $C_{20}H_{24}O_2N_2 \cdot C_6H_{10}O_8 \cdot 2H_2O$ , crystallises in long needles which are sparingly soluble in water.

W. D. H.

**Relation of Collagen and Gelatin.** A. D. EMMETT and WILLIAM J. GIES (*Proc. Amer. physiol. Soc.*, 1907, xi; *Amer. J. Physiol.*, 19).—If gelatin is continuously dried at  $130^\circ$  it is not, as Hofmeister stated, converted into collagen. The dried product is somewhat less soluble than the original gelatin, but it is digested by trypsin with equal readiness, whereas collagen is not affected. That gelatin is not a simple hydrate of collagen is shown by the fact that ammonia is liberated from collagen when the latter is converted into gelatin by boiling with water.

W. D. H.

**Action of Nitrous Acid on Gelatin.** JOHN SEEMANN (*Zeitsch. Biol.*, 1907, 49, 494—502).—Nitrous acid is a suitable reagent for studying the constitution of proteins; it acts as a deamidising reagent, and so part of the yield consists of hydroxy-acids free from the amino-group, and another part consists of the amino-acids in peptide linking. In the present research with gelatin, among other substances, hydrogen cyanide was obtained; this is regarded as probably derived from an intermediate nitroso-derivative of the guanidine residue of arginine. If leucine or asparagine are treated in the same way, no hydrogen cyanide was obtained, but guanidine carbonate and especially creatinine yielded it. From the deamidised portion, pure sulphur was crystallised out (1 gram from 1250 grams of gelatin). The ethereal extract contained no pyrotartaric acid, but oxalic acid was present; the old formula for cystein therefore probably needs revision, and the origin of the sulphur is obscure. The only volatile fatty acids which were identified are lactic and acetic, but others are present.

W. D. H.

**Deaminoglutin.** II. ZDENKO H. SKRAUP (*Monatsh.*, 1907, 28, 447—459).—The hydrolysis of deaminoglutin has been repeated on a large scale and the results previously obtained (*Abstr.*, 1906, i, 913) confirmed. In addition to glycine, histidine, and arginine, leucine, proline and alanine have been obtained by the hydrolysis of deaminoglutin, but not lysine. This latter compound is, however, present in the products produced by the hydrolysis of glutin, so that it is evident that lysine occupies an exposed position in the glutin molecule. The picrate, m. p.  $153-155^\circ$ , which is obtained from deaminoglutin in place of the lysine, is probably a mixture, since, on treatment with dilute sulphuric acid, there is obtained from it a compound, m. p.  $254^\circ$ , which is probably an aminohydroxyvaleric acid,  $C_5H_{11}O_3N$ , and another substance, m. p.  $217-218^\circ$ . From the analytical results, this substance is either an aminovaleric acid,  $C_5H_{11}O_2N$ , or an anhydride of aminohydroxyvaleric acid,  $C_5H_9O_2N$ , but the former is more probable, since it yields a well-defined, crystalline copper salt. These acids are not derived from the arginine, since the latter compound is obtained both from deaminoglutin and glutin to about the

same extent, so that it is probable that besides the arginine residue, there is present in gluten a diaminovaleric acid. W. H. G.

**Thioglutin.** WL. S. SADIKOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 411—422).—When collagen is heated with alkalis, the general properties of the gummy complex seem to be destroyed, but when an aqueous solution of gluten is heated with alkalis, in the presence of carbon disulphide, a sulphur derivative, *thioglutin*, is formed, which very readily undergoes both condensation and hydrolysis. It is combined with water in a colloidal state, which, when removed, causes the thioglutin to decompose. Thioglutin consists chiefly of a gelatinous substance combined with a base, such as sodium, calcium, &c., the calcium compound being the most gelatinous and stable. Thioglutin contains 3% to 4% of sulphur and 3.6% to 7.6% of calcium; it forms definite, unstable, very gelatinous *salts* with lead and tannin. A hot solution of thioglutin forms a gelatinous mass on cooling, which on gradual desiccation at the ordinary temperature, whether exposed to the atmosphere or not, becomes covered with a bright red crust, a condensation product not containing any gummy complex. In the presence of water, the colour is deepened, whilst different salts produce various shades of colour in this crust. On precipitation with alcohol and drying, thioglutin is converted into *thioglutan*, which itself readily decomposes, forming a soluble and an insoluble substance. By treating collagen with calcium sulphide, sulphur derivatives are obtained very similar to thioglutin, but not so strongly gelatinous. Z. K.

**Behaviour of Opsonin and Serum Proteins During Pressure Filtration.** WARRINGTON YORKE (*Bio-Chem. J.*, 1907, 2, 357—362).—Serum was filtered under pressure through a Pasteur-Chamberland filter; as filtration proceeded, less and less and finally no protein came through. Opsonins do not pass a filter of this kind and are non-dialysable through parchment paper. These facts, together with Tamar and Bispham's observation (*J. Exper. Med.*, Dec., 1906) that they are precipitable with euglobulin by half saturation with ammonium sulphate, are in favour of the protein-like nature of opsonins. W. D. H.

**Atoxyl.** ERNEST FOURNEAU (*J. Pharm. Chim.*, 1907, [vi], 25, 528—537).—Since the publication of the author's preliminary note on the subject (*ibid.*, 32), Ehrlich and Bertheim have suggested that atoxyl has the constitution  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH}) \cdot \text{ONa} \cdot 4\text{H}_2\text{O}$  (*Berl. klin. Woch.*, 1907, 682). The author has now compared the substance with the so-called arsenanilide, prepared by Béchamp in 1863, and finds that the two are identical. Atoxyl crystallises with  $5\text{H}_2\text{O}$  and loses  $3\text{H}_2\text{O}$  by efflorescence. The anhydrous substance is readily soluble in methyl alcohol. The reactions of its aqueous solution with solutions of various metallic salts and a detailed account of its therapeutic action are given in the original. T. A. H.

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## Organic Chemistry.

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**Equilibrium Isomerism on Heating Bromides of the Compositions  $C_nH_{2n+1}Br$  and  $C_nH_{2n}Br_2$ .** ALEXEI FAWORSKY (*Annalen*, 1907, 354, 325—389. Compare Abstr., 1895, i, 496; Ageewa, Abstr., 1905, i, 776).—Reversible, intramolecular transformations of isomerides, which take place under the influence of a catalyst such as potassium hydroxide, may be represented by the equation  $A + K \rightleftharpoons A' + K$ , in which A and A' are the isomerides and K is the catalyst. Consideration of the mechanism of these reactions led to the expectation that such transformations taking place in the absence of a catalyst would be found also to be reversible. Such cases have been found in the intramolecular transformations of the bromides  $C_nH_{2n+1}Br$  and  $C_nH_{2n}Br_2$ , which take place when these are heated.

According to Aronstein (Abstr., 1881, 567), *n*-propyl bromide dissociates at 280° into propylene and hydrogen bromide, which recombine, forming isopropyl bromide. It is found now that on five successive heatings for eight hours at 250°, the fraction, b. p. 69—70°, being removed after each heating, 200 grams of isopropyl bromide yield 40 grams of *n*-propyl bromide. Hence the transformation is reversible, as expressed by the equation  $CH_2Me \cdot CH_2Br = CHMe \cdot CH_2 + HBr = CHMe_2Br$ , and the addition of hydrogen bromide to propylene must take place in part contrary to Markownikoff's rule.

Similar, but more complicated, results are obtained with other bromides and dibromides. The discussion of the results leads to the conclusion that tautomerism and the reversible, intramolecular transformations of ordinary isomerides are analogous phenomena and may be included in one group, to which Schaum's term, equilibrium isomerism, is applied.

I. *Equilibrium Isomerism on heating isoButyl and tert.-Butyl Bromides.*—[With WAD. TOLSTOPJATOFF.]—Eltekoff found (*Ber.*, 1875, 8, 1244) that the transformation of isobutyl into *tert.*-butyl bromide, which takes place slowly at 145°, more rapidly at higher temperatures, reaches an equilibrium independently of the temperature when 20% of the isobromide remains unchanged, but later (*Inaug. Diss.*, Charkoff, 1884) considered that the transformation probably takes place completely. The experiments described in this paper show that the transformation is reversible, and that an equilibrium between the two isomerides is established when either bromide is heated at 210—220°; the main reaction is represented by the equilibrium equation:  $CMe_3Br \rightleftharpoons CMe_2 \cdot CH_2 + HBr \rightleftharpoons CHMe_2 \cdot CH_2Br$ . Part of the intermediately formed isobutylene reacts with isobutyl bromide,  $CMe_2 \cdot CH_2 + CMe_3Br = CMe_2 \cdot CH_2 \cdot CMe_2Br$ , forming isodibutyl bromide.

II. *Equilibrium Isomerism on heating Bromoisopentanes.*—[With E. FRITZMANN.]—Eltekoff (*loc. cit.*) found that isoamyl bromide is transformed at 256—260° into the *tert.*-bromide, which is found now to yield, at 220°, 15—20% of the *sec.*-bromide, 3—4% of the two pri-

mary amyl bromides, and 1—2% of higher brominated by-products, 75—80% remaining unchanged. The equilibrium is represented by the equation  $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Pr}^\beta \rightleftharpoons \text{CH}_2\cdot\text{CHPr}^\beta + \text{HBr} \rightleftharpoons \text{CHBrMePr}^\beta \rightleftharpoons \text{CHMe}\cdot\text{CMe}_2 + \text{HBr} \rightleftharpoons \text{CBrMe}_2\text{Et} \rightleftharpoons \text{CH}_2\cdot\text{CMeEt} + \text{HBr} \rightleftharpoons \text{CH}_2\text{Br}\cdot\text{CHMeEt}$ .

The reactions take place in part, not only contrary to Markownikoff's, but also to Saytzeff's, rule that on formation of a hydrogen haloid from an alkyl haloid the hydrogen atom is split off from the less hydrogenated carbon atom.

III. *Equilibrium Isomerism on heating Ethylene and Ethylidene Dibromides*.—[With N. SOKOWNIN and ŽINEWSKY.]—The equilibrium mixture of ethylene and ethylidene dibromides, obtained on heating either isomeride, contains chiefly ethylene dibromide. Thus 40 grams of ethylene dibromide, b. p. 130—131°, when heated at 300—315°, yields 3·5 grams, b. p. 106·5—110·5°; ethylidene dibromide has b. p. 108°. Ethyl bromide and tribromoethane, formed according to the equations  $\text{C}_2\text{H}_4\text{Br}_2 + \text{HBr} \rightleftharpoons \text{C}_2\text{H}_5\text{Br} + \text{Br}_2$  and  $\text{C}_2\text{H}_4\text{Br}_2 + \text{Br}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{Br}_3 + \text{HBr}$ , are found as by-products. The ethylidene dibromide, formed from its isomeride, is identified by conversion into the *dibenzoate*,  $\text{CHMe}(\text{OBz})_2$ , which crystallises in colourless prisms, m. p. 72°. A mixture of this with ethylene dibenzoate, m. p. 71·5°, formed from ethylene dibromide, had m. p. 51°.

IV. *Equilibrium Isomerism on heating Dibromopropanes*.—[With N. SOKOWNIN.]—Propylene dibromide remains almost unchanged at 200—205°, but at 240—250° is transformed to the extent of 2—3% into trimethylene dibromide. This, on the other hand, when heated at 240—250°, yields an equilibrium mixture consisting chiefly of propylene dibromide together with trimethylene dibromide, *n*- and *iso*-propyl bromides, and tribromopropane, whilst dibromoacetol at 220—230° is transformed almost entirely into propylene dibromide together with only traces of trimethylene dibromide. Small amounts of dibromoacetol, formed when propylene dibromide is heated at 225—230°, are identified by conversion into the *dibenzoate*. The presence of the unknown propylidene dibromide in these equilibrium mixtures could not be determined.

V. *Equilibrium Isomerism on heating Dibromoisobutanes*.—[With N. SOKOWNIN.]—When heated at 205—220°, *isobutylene* dibromide yields chiefly  $\beta$ -methyltrimethylene dibromide together with small amounts of *iso*- and *tert*-butyl bromides and tribromoisobutane.

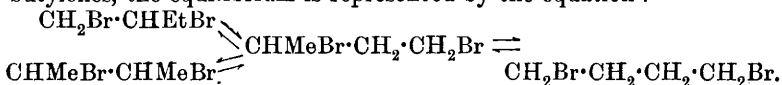
$\beta$ -Methyltrimethylene dibromide,  $\text{CHMe}(\text{CH}_2\text{Br})_2$ , b. p. 177·5—178°/765 mm.,  $D_0^\circ$  1·8515,  $D_{20}^\circ$  1·8207, is reduced by zinc dust and alcohol at 60—93°, forming methylcyclopropane together with traces of *isobutylene*, and when heated with silver acetate forms a *diacetate*, b. p. 211—214°/770 mm., which, on hydrolysis, yields  $\beta$ -methyltrimethylene glycol,  $\text{C}_4\text{H}_{10}\text{O}_2$ , b. p. 110—111°/14·5 mm. or 214—214·5°/771 mm.,  $D_0^\circ$  1·0297. This, on oxidation with potassium permanganate, forms methylmalonic acid.

When heated at 210—225°,  $\beta$ -methyltrimethylene dibromide is transformed to the extent of more than 50% into *isobutylene* dibromide. The presence of *isobutylidene* dibromide in the equilibrium mixtures has not been established; in any case, it would be present only in traces.

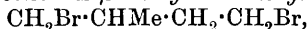


VI. *Equilibrium Isomerism on heating Dibromo-n-butanes.*—[With N. SOKOWNIN.]—When heated at 215—220°, 114 grams of  $\alpha\beta$ -dibromo-*n*-butane, b. p. 99—99.5°/100 mm. or 165—166°/760 mm., yields 6.5 grams of a fraction, b. p. 59—62.5°/25 mm. or 158—161°/759 mm., which consists, at least for the most part, of  $\beta\gamma$ -dibromo-*n*-butane, as on successive treatment with sodium ethoxide and bromine it forms  $\beta\beta\gamma\gamma$ -tetrabromobutane.

When heated at 220—230°, 280 grams of  $\beta\gamma$ -dibromo-*n*-butane, containing small amounts of the  $\alpha\beta$ -isomeride formed from *isobutyl* alcohol (Abstr., 1890, 1218), yields 40 grams of  $\alpha\gamma$ -dibromo-*n*-butane, b. p. 173.5—176.5°/767 mm. (Demjanoff, Abstr., 1895, i, 161), and 10 grams of  $\alpha\delta$ -dibromo-*n*-butane (Hamonet, Abstr., 1905, i, 403). Omitting the immediately formed hydrogen bromide and isomeric butylenes, the equilibrium is represented by the equation :



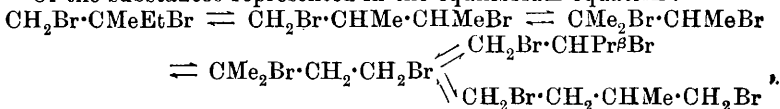
VII. *Equilibrium Isomerism on heating Dibromoisopentanes.*—[With L. KUTSCHEROFF.]—After being heated at 180—185°, 1850 grams of  $\beta$ -methyl- $\Delta^2$ -butylene dibromide, b. p. 47.5—48°/10 mm. (Ipatieff, Abstr., 1896, i, 401), yields three fractions. The fraction, b. p. 61—65°/10 mm., 550 grams, contains  $\beta\delta$ -dibromo- $\beta$ -methyl-*n*-butane, which, on hydrolysis with potassium carbonate, yields  $\alpha\alpha$ -dimethyltrimethylene glycol (Kondakoff, Abstr., 1893, i, 541) together with traces of *isopropylethylene* dibromide. The fraction, b. p. 68—70°/10 mm., 115 grams, contains  $\beta\delta$ -dibromo- $\beta$ -methyl-*n*-butane together with smaller amounts of *isopropylethylene* and  $\beta$ -methyltetramethylene dibromides. The fraction, b. p. 80—83°/11.5 mm., 44 grams, contains  $\beta$ -methyltetramethylene dibromide,



D<sub>0</sub> 1.7491, D<sub>0</sub> 1.7225, which forms a diacetate, C<sub>5</sub>H<sub>10</sub>(OAc)<sub>2</sub>, b. p. 113°/12 mm. This, on hydrolysis, forms  $\beta$ -methyltetramethylene glycol, C<sub>5</sub>H<sub>12</sub>O<sub>2</sub>, b. p. 131—133°/18 mm., which, on oxidation with potassium permanganate, yields methylsuccinic acid. Ethyltrimethylene dibromide is not present.

The equilibrium mixture, obtained by heating  $\beta\delta$ -dibromo- $\beta$ -methyl-*n*-butane at 180—185°, contains chiefly trimethylethylene dibromide and small amounts of  $\alpha\beta$ -dibromo- $\beta$ -methyl-*n*-butane, CH<sub>2</sub>Br·CMeEtBr, b. p. 63—65°/18 mm.; when heated with water and lead dioxide, distilled, and treated with moist silver oxide, this yields methyl *isopropyl* ketone and silver *isovalerate*, C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>Ag, which must be derived from  $\alpha\alpha$ -methylethylethylene.

Of the substances represented in the equilibrium equation :

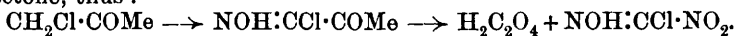


only  $\alpha\gamma$ -dibromo- $\beta$ -methyl-*n*-butane has not been isolated.

Primary and secondary monobromo- and tribromo-*isopentanes* are shown to be present in the fractions, having the lowest boiling points,

obtained from the equilibrium mixture formed by heating  $\beta$ -methyl- $\Delta^{\beta}$ -butylene dibromide. G. Y.

**Chloromethylnitrolic Acid.** GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1907, 42, 780—788).—It was stated by Glutz (*J. pr. Chem.*, 1870, 1, 141) and by Barbaglia (this Journ., 1873, 877) that the action of concentrated nitric acid on chloroacetone yields a compound,  $C_3H_4O_2NCl$ , which was afterwards shown to be chloroisnitrosoacetone. But Tcherniac (Abstr., 1892, 1425) demonstrated that the compound used by Barbaglia and probably also by Glutz was not chloroacetone, but a mixture of dichloroacetone and acetone. The author finds that the interaction of true chloroacetone and concentrated nitric acid yields chloromethylnitrolic and oxalic acids. The reaction proceeds with intermediate formation of chloroisnitrosoacetone, thus:



*Chloromethylnitrolic acid*,  $NOH \cdot CCl \cdot NO_2$ , crystallises from chloroform in flattened needles exhibiting a faint yellow reflection, m. p.  $101^{\circ}$  (decomp.). It can be kept unchanged for some time in sealed vessels, but in the air it decomposes rapidly with evolution of nitrous fumes. It has the normal molecular weight in freezing acetic acid and dissolves readily in ether and, to a moderate extent, in chloroform or carbon tetrachloride; it dissolves also in benzene, but decomposes when the solution is heated. It is acted on by water, undergoing limited decomposition according to the equation:  $NOH \cdot CCl \cdot NO_2 = CO_2 + HCl + N_2O$ . Its salts are very unstable, and in presence of water undergo quantitative decomposition, yielding nitrous oxide together with the carbonate and chloride of the metal. This decomposition is similar to that occurring with nitrolic acids in presence of water (compare Graul and Hantzsch, Abstr., 1899, i, 187). In presence of acids, chloromethylnitrolic acid is moderately stable.

T. H. P.

**Synthesis of Secondary *iso*Amyl Alcohol.** LOUIS HENRY (*Compt. rend.*, 1907, 145, 21—25).—By the action of magnesium methyl bromide in ethereal solution on *isobutylene oxide*, neither  $\gamma\gamma$ -dimethylpropyl alcohol nor  $\beta$ -methylbutane- $\beta$ -ol is formed, but the product consists of  $\beta$ -methylbutane- $\gamma$ -ol, also formed by the action of magnesium methyl bromide on *isobutaldehyde*, which is isomeric with *isobutylene oxide*. This unlooked-for result is probably due to the preliminary transformation of *isobutylene oxide* into *isobutaldehyde*, since  $\gamma\gamma$ -dimethylpropyl alcohol, a direct product from the oxide, is known to change into the tertiary  $\beta$ -methylbutane- $\beta$ -ol, but not into the secondary  $\beta$ -methylbutane- $\gamma$ -ol.

The syntheses of the latter alcohol by the action of zinc methyl on bromoacetyl bromide (Winogradoff, Abstr., 1878, 485) and on chloroacetyl chloride (Bogomotez, *Annalen*, 1881, 209, 70) are probably to be explained by the reaction of the zinc methyl with the  $\cdot COBr$  and  $\cdot COCl$  groups, forming the compounds  $CH_2Br \cdot CMe_2 \cdot OZnMe$  and  $CH_2Cl \cdot CMe_2 \cdot OZnMe$ , which by splitting off  $MeZnCl$  or  $MeZnBr$

form *isobutylene oxide*, the latter then reacting with zinc methyl as with magnesium methyl bromide (compare this vol., i, 670).

Magnesium methyl bromide in ethereal solution reacts with chloroacetone giving the compound  $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OMgBr}$ , which, on heating in ethereal solution, forms magnesium chlorobromide and *isobutylene oxide*, the latter then reacting with magnesium methyl bromide in the usual way.

By the action of magnesium methyl bromide (3 mols.) on chloroacetyl chloride (1 mol.), whilst the chief product is *isobutylene chlorohydrin*,  $\text{CH}_2\cdot\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$ , a very appreciable quantity of  $\beta$ -methylbutane- $\gamma$ -ol is formed. E. H.

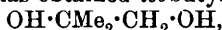
**Cetyl Alcohol from the Fat of Dermoid Cysts.** FRANZ AMESDER (*Zeitsch. physiol. Chem.*, 1907, 52, 121—128. Compare Ludwig, *Abstr.*, 1897, ii, 336).—The compound obtained from the fat of dermoid cysts and described as cetyl alcohol is shown to be an *eicosyl alcohol*,  $\text{C}_{20}\text{H}_{42}\text{O}$ ; it melts at  $70^\circ$  and yields an *acetate*, m. p.  $44^\circ$ , b. p.  $220^\circ/3$  mm. The acetate when hydrolysed yields 17.3% of acetic acid, and the alcohol when oxidised yields arachidic acid.

J. J. S.

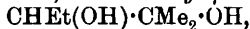
**Structural Stability of Ethylene Oxide.** LOUIS HENRY (*Compt. rend.*, 1907, 145, 154—156).—When treated with magnesium methyl bromide, *isobutylene oxide*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CMe}_2 \end{array} > \text{O}$ , yields the secondary *isoamyl alcohol*,  $\text{CHMe}_2\cdot\text{CHMe}\cdot\text{OH}$ , but ethylene oxide gives the primary *n*-butyl alcohol. Hence, contact with magnesium ethyl bromide does not cause ethylene oxide to react as if it had the isomeric constitution  $\text{CHMe}\cdot\text{O}$ . This is due to the stability conferred upon polycarbon nuclei and carbon molecules, in general, by abundance of hydrogen.

T. H. P.

**Hydrolysis of the Ethylenic Oxides by Sulphuric Acid.** LOUIS HENRY (*Compt. rend.*, 1907, 144, 1404—1406).—The method of preparing glycerol  $\alpha$ -chlorohydrin by the hydrolysis of epichlorohydrin by sulphuric acid is applicable to all the ethylenic oxides containing the group  $\begin{array}{c} :\text{C} \\ | \\ :\text{C} \end{array} > \text{O}$ . Since the latter can be readily prepared from the monochlorohydrins containing the group  $:\text{C}(\text{OH})\cdot\text{CCl}:$ , which are obtained by the application of Grignard's reaction to chloro-ketones containing the group  $\cdot\text{CO}\cdot\text{CCl}:$ , or to esters of  $\alpha$ -chlorofatty acids, the method is a convenient one for preparing the  $\alpha$ -glycols. In this way, the author has obtained *isobutylene glycol*,



$\beta$ -ethylbutylene- $\alpha\beta$ -glycol,  $\text{CEt}_2(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , a crystalline solid, m. p.  $46^\circ$ , b. p.  $200\text{--}202^\circ/756$  mm.,  $\beta$ -methylbutylene- $\alpha\beta$ -glycol,  $\text{CMeEt}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , a liquid, b. p.  $190^\circ/756$  mm.,  $\beta$ -isoamylene glycol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMe}\cdot\text{OH}$ , and  $\alpha$ -methyl- $\beta$ -amylene glycol,



a liquid, b. p.  $184\text{--}185^\circ$ , prepared from ethyl  $\alpha$ -chlorobutyrate. The

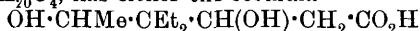


The acid,  $C_9H_{18}O_3$ , is probably identical with that obtained by Kohn (*loc. cit.*), who assigned to it the formula  $C_9H_{16}O_3$ .

The acid,  $C_6H_{12}O_3$ , is undoubtedly  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid, since it gives a barium salt,  $(C_6H_{11}O_3)_2Ba$ , and yields diethyl ketone, carbon dioxide, and acetic and propionic acids on oxidation.

The acid,  $C_8H_{14}O_3$ , is probably diethylacetoacetic acid, since it gives a brown turbidity with ferric chloride and is decomposed by dilute sulphuric acid into  $\alpha$ -ethylbutyric and acetic acids.

The acid,  $C_{10}H_{20}O_4$ , has either the formula



or  $OH \cdot CHMe \cdot C(OH)(CH_2) \cdot CH_2 \cdot CO_2H$ , since it gives a silver salt,  $C_{10}H_{19}O_4Ag$ , and yields diethyl ketone and malonic acid on oxidation. When heated alone, it decomposes into diethyl ketone, acetic acid, and carbon dioxide.

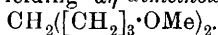
The alcohol,  $C_{10}H_{22}O$ , is a liquid, b. p.  $205^\circ$ . It does not combine with bromine, and gives the iodoform reaction.

The saturated hydrocarbon,  $C_{10}H_{20}$ , is a liquid, b. p.  $198^\circ$ .

W. H. G.

**Asymmetric Derivatives of Hexane- $\alpha\zeta$ -diol; Heptamethylene Glycol.** R. DIONNEAU (*Compt. rend.*, 1907, 145, 127—129. Compare Abstr., 1906, i, 134).—Bromo-ethers of hexane- $\alpha\zeta$ -diol are obtained more easily from the dibromo- than from the dialkyloxy-compounds.

$\zeta$ -Bromo- $\alpha$ -methoxyhexane,  $CH_3Br \cdot [CH_2]_4 \cdot CH_2 \cdot OMe$ , formed together with  $\alpha\zeta$ -dimethoxyhexane by the action of sodium ethoxide on  $\alpha\zeta$ -dibromohexane, is obtained in a 75% yield as a colourless liquid, b. p.  $112^\circ/35$  mm.,  $D^{21}_4$  1.194, having a slight fruity odour. This forms the magnesium derivative,  $MgBr \cdot CH_2 \cdot [CH_2]_4 \cdot CH_2 \cdot OMe$ , which reacts with bromomethoxymethane yielding  $\alpha\eta$ -dimethoxyheptane,



$\alpha\eta$ -Dibromoheptane, b. p.  $156^\circ/35$  mm., is prepared by heating the dimethoxyheptane with hydrobromic acid at  $100^\circ$ , and reacts with sodium phenoxide, forming diphenoxyheptane, m. p.  $53^\circ$ .  $\alpha\eta$ -Diacetoxyheptane, formed by the action of silver acetate on the dibromoheptane, is a colourless liquid, b. p.  $270^\circ$ ,  $D^{15}_4$  1.01, and when hydrolysed yields heptane- $\alpha\eta$ -diol (heptamethylene glycol), which is obtained in crystals, m. p.  $19^\circ$ , b. p.  $172^\circ/35$  mm. or  $259^\circ/760$  mm., and deliquesces on exposure to air.

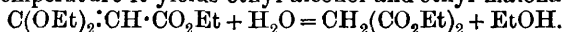
G. Y.

**Direct Hydrogenation of the Anhydrides of Aliphatic Acids.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, 145, 18—21).—When the vapour of acetic anhydride mixed with excess of hydrogen is passed over reduced nickel heated at  $180^\circ$ , there are formed (1) a small quantity of acetaldehyde; (2) ethyl acetate; (3) ethyl alcohol, and (4) acetic acid. The first reaction probably consists in the splitting up of the acetic anhydride molecule, thus:  $(COMe)_2O + H_2 = CH_3 \cdot CHO + CH_3 \cdot CO_2H$ . The aldehyde is further hydrogenated to ethyl alcohol, part of which esterifies some of the acetic acid, the water so liberated acting on some of the unaltered acetic anhydride. The first reaction cannot be the direct hydrogenation of

acetic anhydride to ethyl acetate, thus :  $(\text{COMe})_2\text{O} + 2\text{H}_2 = \text{CH}_3\cdot\text{CO}_2\text{Et} + \text{H}_2\text{O}$  (compare Godchot, *Bull. Soc. chim.*, 1907, [iv], 1, 243), followed by decomposition into acetaldehyde and ethyl alcohol, since ethyl acetate is not hydrogenated at  $180^\circ$ . The nickel is not attacked by the acetic acid produced. Similarly, with propionic, methylpropionic, butyric, and methylbutyric anhydrides the main reaction is a decomposition into acid and aldehyde, and this is followed by hydrogenation of the aldehyde and formation of the ester. The proportion of the latter diminishes, whilst that of the aldehyde increases, with the carbon-content of the anhydride. The reaction is the same when reduced copper at  $200\text{--}210^\circ$  is substituted for the nickel, but copper being much less active, the principal products are the aldehyde and acid (which attacks copper much more rapidly than nickel). E. H.

**New Derivative of Molybdenum Peroxide.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 963—966. Compare this vol., ii, 54).—When barium chloride solution is added to a solution of the compound  $\text{MoO}_3(\text{NH}_4)_2\text{C}_2\text{O}_4$  and the crystalline precipitate formed treated with hydrogen peroxide, it yields the compound  $\text{BaC}_2\text{O}_4\cdot\text{MoO}_4\cdot 2\frac{1}{2}\text{H}_2\text{O}$ , which separates from aqueous alcohol in cream-yellow flocks. T. H. P.

**Attempts to Prepare Esters of Ortho-Acids.** HANS REITER and A. WEINDEL (*Ber.*, 1907, 40, 3358—3361. Compare this vol., i, 677).—Attempts have been made to prepare the semi-ortho-ester of malonic acid,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})_2$ , by the action of alcohol at the ordinary temperature on the hydrochloride of the iminoether of ethyl cyanoacetate (Pinner and Oppenheimer, *Abstr.*, 1895, i, 266). The product actually obtained by fractional distillation under reduced pressure, after the removal of ammonium chloride, contains a molecule of alcohol less than the expected ester, and is probably *ethyl  $\beta$ -diethoxyacrylate*,  $\text{C}(\text{OEt})_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ . It is a colourless, refractive liquid, b. p.  $127\text{--}8\text{--}128\text{--}2^\circ/12\text{ mm.}$ ,  $D^{15}_4$  1.035. With an excess of bromine in chloroform solution, it yields ethyl dibromomalonate, and with water at the ordinary temperature it yields ethyl alcohol and ethyl malonate:



J. J. S.

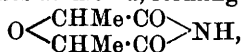
**Intermediate Products in Chemical Reactions.** JULIUS TAFEL (*Ber.*, 1907, 40, 3318—3321).—Polemical. A reply to Wohl's contention that intermediate products exist in transformations such as that of fumaric into maleic acid (this vol., i, 583). W. R.

**Diglycollic Acid and its Homologues.** ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1907, 145, 70—73. Compare this vol., i, 471).—By the action of ethyl chloroacetate on the sodium derivative of ethyl glycolate, *diethyl diglycolate*,  $\text{O}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , b. p.  $129\text{--}130^\circ/20\text{ mm.}$ , is formed, and by saponification gives Heintz's diglycollic acid (*Annalen*, 1867, 144, 91). The interaction of ethyl  $\alpha$ -bromopropionate with the sodium derivative of ethyl glycolate, or ethyl chloroacetate with the sodium derivative of ethyl lactate, gives

*ethyl methyl diglycollate*,  $\text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , a liquid insoluble in water, b. p.  $122-125^\circ/20$  mm., which, by the method previously described, yields the *acid* in crystals, m. p.  $30^\circ$ . When the latter is heated with acetyl chloride, it loses water, forming *methyl diglycollic anhydride*,  $\text{O}\langle\begin{smallmatrix} \text{CHMe}\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}\rangle\text{O}$ , a syrupy liquid, b. p.  $122-125^\circ/25$  mm.,  $D_{20}^{20} 1.2729$ , which in contact with water regenerates the acid.

By the prolonged action of concentrated aqueous ammonia on ethyl methyl diglycollate, the *diamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , is formed in small prisms, m. p.  $126^\circ$ . By heating the latter above its melting point, or by treating a benzene solution of the anhydride with dry ammonia, a substance is formed which seems to be the corresponding *imide*.

When ethyl dilactylate is submitted to the action of cold concentrated aqueous ammonia, it is transformed into *dilactylic diamide*,  $\text{O}(\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2)_2$ , forming thin plates, m. p.  $156^\circ$ ; when heated at  $160-170^\circ$ , the latter loses ammonia, forming the *imide*,



which crystallises in large, colourless prisms, m. p.  $122^\circ$ . E. H.

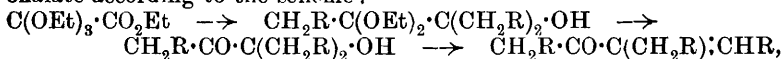
**Preparation of Ketone Acetals.** ALEXANDER E. ARBUSOFF (*Ber.*, 1907, 40, 3301—3304. Compare Reitter and Hess, this vol., i, 677).—The author concludes that (1) chemically pure ethyl orthoformate does not react with pure ketones in ether, free from water and alcohol, or by themselves (compare Claisen, *Abstr.*, 1896, i, 463; 1897, i, 188). (2) In the presence, however, of primary alcohols, they react forming ketone acetals and ethyl formate. (3) The alcohol takes therefore an active part in the interaction. (4) Ethyl orthoformate reacts with ketones in the presence of mineral acid, which acts as a catalyst. (5) The reaction proceeds most easily with fatty ketones, less easily with aromatic, and least readily with cyclic, ketones. The examples given in the paper are acetone acetal, acetophenone acetal, and *chloroacetone acetal*; the latter has b. p.  $162-163^\circ/760$  mm. and  $57^\circ/12$  mm.,  $D_{20}^{20} 1.0002$ . W. R.

**Syntheses by Means of Mixed Organo-metallic Derivatives of Zinc.**  $\alpha\beta$ -Acyclic Unsaturated Ketones. EDMOND E. BLAISE and M. MAIRE (*Compt. rend.*, 1907, 145, 73—75).—The  $\beta$ -hydroxy-aliphatic acids are easily prepared by condensing the esters of  $\alpha$ -halogen-aliphatic acids with aldehydes or ketones in the presence of zinc. When these contain a primary or secondary alcohol group, they form acetyl compounds, which are transformed by thionyl chloride into the acid chlorides. The latter react with the mixed organo-metallic derivatives of zinc to form  $\beta$ -acetoxyketones, which on saponification are transformed into the  $\alpha\beta$ -unsaturated ketones in theoretical yield,  $\text{OH}\cdot\text{CHR}\cdot\text{CHR}'\cdot\text{CO}_2\text{H} \rightarrow \text{OAc}\cdot\text{CHR}\cdot\text{CHR}'\cdot\text{COCl} \rightarrow \text{OAc}\cdot\text{CHR}\cdot\text{CHR}'\cdot\text{COR}'' \rightarrow \text{R}\cdot\text{CH}:\text{CR}'\cdot\text{COR}''$ .

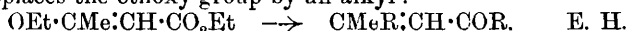
When the  $\beta$ -hydroxy-acid contains a tertiary alcohol group, attempted acetylation results in the dehydration of the acid, but the chloride of the unsaturated acid produced reacts with the organo-

metallic derivative to form the corresponding unsaturated ketone (in good yield), except in cases where the fundamental chain of the acid is insufficiently substituted. In the latter instances, the  $\cdot\text{COCl}$  group is transformed into the tertiary alcohol group, which is further changed by the acid chloride present into an ester,  $\text{CH}_2\cdot\text{CEt}\cdot\text{COCl} \rightarrow \text{CH}_2\cdot\text{CEt}\cdot\text{CR}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CEt}\cdot\text{CH}_2$ . The above reactions give satisfactory results in a large number of cases, but the authors consider it probable that the acetoxyketones have not the normal constitution.

Magnesium organo-metallic derivatives react with ethyl semi-ortho-oxalate according to the scheme:



but a large excess (5 mols.) of the organo-magnesium compound is required, and the method only gives ketones of a certain type. With ethyl  $\beta$ -ethoxycrotonate, organo-magnesium compounds do not react in the normal manner, but 1 molecule of the magnesium compound transforms the esteric group into a ketonic group, whilst a second molecule replaces the ethoxy-group by an alkyl:



**Carbohydrate contained in Elm Galls,** NAPOLEONE PASSERINI (*Gazzetta*, 1907, 37, i, 386—391).—Fresh elm galls, produced by *Schizoneura ulmi*, contain a colourless or brown, faintly alkaline liquid, having  $D^{21}_D$  1.06553 and  $[\alpha]^{21}_D +46.4^\circ$ . Analysis of one sample gave 84.8% water, 14.54% organic and volatile substances, and 0.66% ash. The amount of solid matter present is 14—20%, consisting principally of a gummy carbohydrate,  $\text{C}_6\text{H}_{10}\text{O}_5$  (?), which is precipitated by alcohol, softens at  $230-240^\circ$  and swells up at  $250-255^\circ$ , and dissolves sparingly in 98% alcohol, ether, or chloroform;  $[\alpha]^{20}_D +191.8$ . With water it forms pseudo-solutions, and with nitric acid it yields tartaric and oxalic acids. It probably belongs to the dextrin group, but differs from ordinary dextrin in being precipitable by basic lead acetate solution. Its rotatory power and iodine reaction resemble those of Musculus and Gruber's achroodextrin  $\beta$ . T. H. P.

**Saccharification of Soluble Starch by Extract of Barley.** AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1907, 145, 80—82).—Extracts of barley convert the most resistant dextrans into maltose; the change is, however, much slower than with malt extract. When the temperature is raised to  $45^\circ$ , the action is incomplete, and a residue of a stable dextrin remains. N. H. J. M.

**Colour Reactions of Lignocellulose.** CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Ber.*, 1907, 40, 3119—3126. Compare *Trans.*, 1899, 75, 752).—The reactions of phloroglucinol in presence of hydrochloric acid and of dimethyl-*p*-phenylenediamine with certain reactive groups in lignocellulose have been found of value in the localisation of these in the molecule. Phloroglucinol reacts mainly and quantitatively with the lignone complex, but independently of this, in the colour reaction with that part of the molecule which yields furfuraldehyde on treatment with hydrochloric acid; bases,



on the other hand, react only with the latter part of the lignocellulose molecule.

The maximum absorption of phloroglucinol by lignocelluloses is determined with the aid of a volumetric method founded on the reaction of furfuraldehyde with phloroglucinol; paper made from wood shavings is a sensitive indicator, giving a coloration with phloroglucinol in 1:30,000 solution. The following maximum absorptions of phloroglucinol are given in percentages of the fibres: pine-wood, 6.71, 6.63; jute, 4.23, 4.20, 4.34; wood cellulose (sulphite), 0.75; esparto-cellulose, 0.50; cotton-wool cellulose, 0.20; hydrocellulose, formed by treatment of cotton-wool with hydrochloric acid, 0.42; hydrolignocellulose from jute, 4.45. These results give a method for the estimation of pine-wood fibres which is free from the errors of the colorimetric method. The constitution of the lignone complex of jute is not altered on chlorination or acetylation, as the maximum absorption remains almost unchanged. The increase over the normal maximum absorption of cotton-wool and jute after treatment with hydrochloric acid has no relation to the amount of furfuraldehyde formed (compare Schwalbe, this vol., i, 390).

The intensity of the coloration obtained with pine-wood sawdust and dimethyl-*p*-phenylenediamine hydrochloride in sodium acetate solution increases with the amount of base present, as does also the percentage of base absorbed and not removed by washing with water. The action of phenylhydrazine on lignocelluloses is of the same nature; the phenylhydrazones formed give colour reactions only on prolonged treatment with phloroglucinol and hydrochloric acid, hence the phenylhydrazine must react with the groups which give the coloration with the phenol. In their stability, the phenylhydrazones lie between the derivatives of lignocellulose with mono- and di-amines, which are readily hydrolysed by acids or alkalis, and the compounds with phloroglucinol, which remain unchanged in boiling dilute alkalis.

Lignocelluloses react with hydroxylamine, undergoing a change of colour, which, in general, consists of a partial bleaching; the products give colorations on prolonged treatment with phloroglucinol and hydrochloric acid, but not with aniline or diamines. G. Y.

**Cobaltinitrites.** KARL A. HOFMANN and O. BURGER (*Ber.*, 1907, 40, 3298—3301).—The surprising stability of the cobaltinitrites would suggest that these salts do not possess the nitrite constitution. If potassium cobaltinitrite is warmed with chloroplatinic acid in alcohol, ethyl nitrite is gradually evolved, but not nitroethane; but this is not conclusive, as it might be a secondary result due to nitrous acid. Also, if the silver salt, obtained by the interaction of ethylammonium cobaltinitrite and silver nitrate, is treated with ethyl iodide, there is a good yield of ethyl nitrite, but nitroethane cannot be detected, from which it may be concluded that the salt has the normal nitrite structure. Ammonium cobaltinitrite (Rosenheim and Koppel, *Abstr.*, 1898, ii, 430), of which the method of preparation is given, when heated evolves 20.39% of its nitrogen in the free state, 6.63% as nitric oxide, and the remainder as nitrate. The nitrogen % corresponds nearly with that required for the decomposition of the 3 mols. of ammonium nitrite.

*Ethylammonium cobaltinitrite*,  $\text{Co}(\text{NO}_2)_6 \cdot (\text{NH}_3\text{Et})_3$ , obtained by passing nitrous fumes into an ice-cooled mixture of cobalt carbonate, water, and ethylamine, crystallises in hexagonal, orange plates, decomp. at  $131^\circ$ . Heated at  $145^\circ$ , ethylamine is not evolved, but 18.63–18.87% N and 5.6–6.8% N in the form of nitric oxide is obtained. This % of free nitrogen corresponds again with 3 mols. of ethylammonium nitrite of normal constitution. W. R.

**Action of Zinc Ethyl on Nitrosyl Chloride.** IWAN BEWAD (*J. pr. Chem.*, 1907, [ii], 76, 62–64. Compare Abstr., 1900, i, 629).—As the nitrosyl group,  $\text{:NO}$ , of nitrous esters reacts with zinc alkyls in the same manner as does the carbonyl group of such substances as aldehydes or formic esters, it was to be expected that the nitrosyl group of nitrosyl chloride would react with zinc alkyls in the same manner as the carbonyl group of phosgen or of the chloro-anhydrides of carboxylic acids. This has been found to be the case with nitrosyl chloride and zinc ethyl, which react in cooled ethereal solution; treatment of the product with ice-water leading to the formation of  $\beta$ -diethylhydroxylamine in a 44% yield, together with small amounts of ethyl alcohol and ethyl iodide. G. Y.

**Preparation of Primary Amino-alcohols.** HENRI GAULT (*Compt. rend.*, 1907, 145, 126–127. Compare Bouveault and Blanc, Abstr., 1905, i, 12).—Primary alcohols containing a secondary or tertiary amino-group are obtained by reduction of the corresponding ethyl esters by means of sodium and alcohol. The following alcohols were obtained in this manner in the percentage yields quoted.

$\beta$ -Diethylaminoethyl alcohol, 50%;  $\beta$ -benzylaminoethyl alcohol, 20%;  $\beta$ -anilinoethyl alcohol, 40–50%;  $\beta$ -methylanilinoethyl alcohol, 30%, together with considerable amounts of methylaniline;  $\gamma$ -diethylaminopropyl alcohol, 40%, together with diethylamine.

Alcohols are not obtained in this manner from ethyl *m*- and *p*-toluidinoacetates, probably in consequence of the formation of insoluble, unreducible sodium derivatives. On treatment with sodium and alcohol, glycine ethyl ester is decomposed into ammonia and acetic acid and does not yield even traces of the amino-alcohol.

G. Y.

**Preparation of Aliphatic Thiocyanates, Nitriles, and Nitro-compounds.** PAUL WALDEN (*Ber.*, 1907, 40, 3214–3217).—Methyl thiocyanate is obtained in 80–81% yield when methyl sulphate is added slowly and with vigorous shaking to a concentrated aqueous solution of potassium thiocyanate in quantities determined by the equation:  $\text{Me}_2\text{SO}_4 + \text{KSCN} = \text{KMeSO}_4 + \text{MeSCN}$ . An 87% yield of ethyl thiocyanate is obtained in a similar manner.

For the preparation of acetonitrile, 1 mol. (65 grams) of potassium cyanide is dissolved in 50–60 grams of water, and 1 mol. of methyl sulphate added in three portions to the solution, which is shaken vigorously and cooled in ice. After the distillation of the nitrile, a second mol. of potassium cyanide is added to the residual liquor, which is then carefully heated in a reflux apparatus; by distillation from

a water bath, a further quantity of the nitrile is obtained, the total yield being theoretical. Propionitrile is obtained in a similar manner.

Nitromethane is obtained in 50—57% yield when methyl sulphate (1 mol.) is added to a concentrated aqueous solution of potassium or sodium nitrite (1 mol.), the mixture being shaken and kept cold; when the reaction slackens, a second mol. of the nitrite is added. The mixture is then distilled finally under reduced pressure. Ethyl sulphate reacts in a similar manner, but less energetically than the methyl ester.  
C. S.

**Direct Oxidation of Toluene by Catalysis.** PAUL WOOG (*Compt rend.*, 1907, 145, 124—126).—Coquillon (this Journ., 1873, 1214) found that toluene, when mixed with air and passed over a red-hot spiral of platinum or palladium, is oxidised to benzaldehyde and benzoic acid. The present paper is an extension of this investigation to the direct oxidation of toluene under the influence of various catalysts.

When mixed with air and passed over meerschaum, which has been impregnated with a platinum salt and reduced, toluene vapour is oxidised to carbon dioxide and water, with development of sufficient heat to raise the mass to incandescence. The reaction does not take place if the tube containing the meerschaum is maintained below the b. p. of toluene. Benzaldehyde is formed when the mixture of toluene and air is passed over pumice impregnated with ferric oxide; the best yields are obtained by heating the toluene at 90° and the catalyst at 280°. Under similar conditions, benzaldehyde is formed in presence of nickel oxide at 150°, at 230° phenolic products are obtained, whilst if the tube is heated at 270°, the oxide becomes incandescent. With copper oxide as the catalyst, small amounts of benzaldehyde are formed at 180—260°, but the greater part of the toluene is completely oxidised; incandescence is observed at 250°. With manganese dioxide, the oxidation is complete; the catalyst becomes incandescent at 250°. In presence of coke, toluene is oxidised at 200°, yielding small amounts of benzaldehyde together with larger quantities of benzoic acid, which is formed abundantly at 370°. The coke does not become incandescent.  
G. Y.

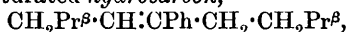
**Condensations under the Influence of Sodium.** PAUL SCHORIGIN (*Ber.*, 1907, 40, 3111—3118).—Since in the Wurtz synthesis of hydrocarbons, two positive groups combine in consequence of the elimination of halogen by sodium, and, on the other hand, two negative benzoyl groups unite to form benzil in Klinger's synthesis of this substance by the action of sodium amalgam on benzoyl chloride (*Abstr.*, 1883, 920), it was to be expected that the action of sodium on a mixture of an alkyl haloid,  $RX$ , and benzoyl chloride would lead to the formation of a ketone,  $R \cdot C(Ph)_2$ , rather than to that of the hydrocarbon,  $R \cdot R$ , and benzil. The interaction of isobutyl bromide, benzoyl chloride, and sodium in benzene solution is found to be more complicated, the product obtained on distillation of the reaction mixture being  $\delta$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta\gamma$ -heptene, which is considered to be formed in the four stages: (1)  $C_4H_9Br + C(Ph)_2Cl + 2Na =$

$\text{NaCl} + \text{NaBr} + \text{COPh}\cdot\text{C}_4\text{H}_9$ ; (2)  $\text{COPh}\cdot\text{C}_4\text{H}_9 + \text{C}_4\text{H}_9\text{Br} + 2\text{Na} = \text{NaBr} + \text{ONa}\cdot\text{CPh}(\text{C}_4\text{H}_9)_2$ ; (3)  $\text{ONa}\cdot\text{CPh}(\text{C}_4\text{H}_9)_2 + \text{COPhCl} = \text{NaCl} + \text{COPh}\cdot\text{O}\cdot\text{CPh}(\text{C}_4\text{H}_9)_2$ , and (4)  $\text{COPh}\cdot\text{O}\cdot\text{CPh}(\text{C}_4\text{H}_9)_2 = \text{CH}_2\text{Pr}^\beta\cdot\text{CPh}\cdot\text{CHPr}^\beta + \text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$ .

The intermediate formation of the sodium derivative of the tertiary alcohol is the more probable, since phenyldiisoamylcarbinol is formed by the action of isoamyl bromide on ethyl benzoate in presence of sodium. The fourth stage takes place during the distillation of the reaction mixture (compare Krafft, Abstr., 1884, 571). The unsaturated hydrocarbon may be formed, however, at least partially, by direct loss of water from the tertiary alcohol, since phenyldiisoamylcarbinol decomposes partially in this manner when distilled in a vacuum. Attempts to prepare phenyldiisobutylcarbinol by Grignard's reaction led to the formation of phenylisobutylcarbinol, probably in consequence of reduction of the ketone formed in the first stage by the second mol. of magnesium isobutyl bromide.

$\delta$ -Phenyl- $\beta$ -dimethyl- $\Delta$ -heptene,  $\text{CHPr}^\beta\cdot\text{CPh}\cdot\text{CH}_2\text{Pr}^\beta$ , is a colourless oil, b. p.  $110$ — $112^\circ/10$  mm. or  $124$ — $126^\circ/20$  mm.,  $D_4^{16.5}$   $0.8731$  (corr.),  $n_D^{25}$   $1.49762$ , and forms an additive compound with bromine.

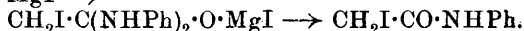
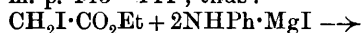
Phenyldiisoamylcarbinol,  $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_{11})_2$ , formed by the action of sodium on a mixture of isoamyl bromide and ethyl benzoate in ethereal solution, or of magnesium isoamyl bromide on methyl benzoate, is a colourless, viscid oil, b. p.  $163$ — $165^\circ/14$  mm. (corr.),  $D_4^0$   $0.9349$ — $0.9365$  (corr.),  $D_4^{17}$   $0.9210$ — $0.9213$  (corr.),  $n_D^{24.5}$   $1.49373$ ,  $n_D^{27}$   $1.49288$ ; on repeated distillation in a vacuum, it is decomposed almost entirely into water and the unsaturated hydrocarbon,



which is formed also by heating phenyldiisoamylcarbinol with acetic anhydride. It is obtained as a mobile, colourless liquid, b. p.  $153$ — $155^\circ/18$  mm.,  $D_4^0$   $0.8859$  (corr.),  $D_4^{26}$   $0.8666$  (corr.),  $n_D^{26.5}$   $1.49913$ , and forms an additive compound with bromine.

Phenylisobutylcarbinol, formed by the action of magnesium isobutyl bromide on methyl benzoate or benzoyl chloride, has the properties described by Klages (Abstr., 1904, i, 567). G. Y.

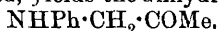
**Action of Some Esters of  $\alpha$ -Iodo-fatty Acids on Magnesium Aniline and *o*-Toluidine Iodides.** F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1907, 144, 1437—1438. Compare Bodroux, Abstr., 1905, i, 585, 643).—When ethyl iodoacetate is allowed to act on magnesium aniline iodide in presence of sufficient ether to keep the latter in solution, a similar reaction to that observed with the toluidine compound occurs, iodoacetanilide being formed in white needles, m. p.  $143$ — $144^\circ$ , thus:



By the action of ethyl  $\alpha$ -iodopropionate and  $\alpha$ -iodobutyrate on magnesium aniline iodide and magnesium *o*-toluidine iodide, the authors have obtained  $\alpha$ -iodopropionanilide,  $\text{CHMeI}\cdot\text{CO}\cdot\text{NHPh}$ , m. p.  $135$ — $136^\circ$ ;  $\alpha$ -iodopropion-*o*-toluidide,  $\text{CHMeI}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p.  $148^\circ$ ;  $\alpha$ -iodobutyranilide,  $\text{CH}_2\text{Me}\cdot\text{CHI}\cdot\text{CO}\cdot\text{NHPh}$ , m. p.  $126$ — $127^\circ$ , and  $\alpha$ -iodobutyryl-*o*-toluidide,  $\text{CH}_2\text{Me}\cdot\text{CHI}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p.

138—139°, all of which crystallise in white needles, which slowly become yellow in the light. E. H.

**Action of Halogen Derivatives of Acetone on Some Aromatic Amines.** A. RICHARD (*Compt. rend.*, 1907, 145, 129—131).—Vladesco found that methyl  $\alpha$ -chloroethyl ketone reacts with aniline and methylaniline, forming 2:3-dimethyl- and 1:2:3-trimethylindole respectively (Abstr., 1892, 810). The author has confirmed these results and has obtained 2:3:5-trimethylindole by the action of methyl  $\alpha$ -chloro- or  $\alpha$ -bromo-ethyl ketone on *p*-toluidine. The action of chloro- or bromo-acetone on aniline leads, on the other hand, to the formation of a *hydrate* of anilinoacetone, which, when boiled in aqueous solution and dried, yields the anhydrous compound



The three *toluidinoacetones* are prepared in the same manner.

G. Y.

**Partial Reduction of 2:6- and 2:4-Dinitrotoluenes by Electrolytic Methods.** KURT BRAND and H. ZÖLLER (*Ber.*, 1907, 40, 3324—3334. Compare Abstr., 1906, i, 80).—2:2'-Dinitro-6:6'-azoxytoluene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2\text{O} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$ , is obtained when 2:6-dinitrotoluene is reduced electrolytically in faintly alkaline solution, using a dilute alcoholic solution of sodium acetate mixed with ethyl acetate as the cathode liquid, and hot saturated sodium carbonate as the anode liquid. It crystallises from benzene in glistening, yellow needles, m. p. 187°. When heated for three to four hours on the water-bath with concentrated sulphuric acid, the azoxy-compound is transformed into 2:2'-dinitro-3-hydroxy-6:6'-azotoluene,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}(\text{NO}_2) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$ , which crystallises from alcohol in slender, yellow needles, m. p. 222°. The sodium salt crystallises in red needles, and also the *acetyl* derivative,  $\text{C}_{16}\text{H}_{15}\text{O}_6\text{N}_4$ , m. p. 161°.

2:2'-Dinitro-4:4'-azoxytoluene, m. p. 164° (compare Weyprecht, *Inaug. Diss. Giessen*, 1902), is produced by the reduction of 2:4-dinitrotoluene under similar conditions. Its constitution follows from its synthesis from 2-nitro-4-hydroxylaminotoluene and 2-nitro-4-nitrosotoluene in alkaline solution.

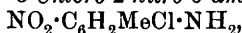
When 2:6- and 2:4-dinitrotoluenes are reduced in strongly acid solution in the presence of cupric chloride, using lead as the anode and copper or nickel gauze as cathode, the products are respectively 2-nitro-6-aminotoluene and 2-nitro-4-aminotoluene.

A 50—60% yield of pure 2-nitro-6-hydroxylaminotoluene,



is formed when 2:6-dinitrotoluene is reduced in the presence of sodium acetate, acetic acid, and alcohol, using as cathode a lead coil through which cold water is passed, so that the temperature remains at 40—50°; voltage 14. The product is isolated by the addition of ice, and may be crystallised from benzene. It forms glistening, yellow crystals, m. p. 115°. With sodium hydroxide solution, it yields mainly 2:2'-dinitro-6:6'-azoxytoluene. When heated, it loses water, yielding dinitroazotoluene, and when oxidised

with ferric chloride and sodium acetate in aqueous alcoholic solution it yields *2-nitro-6-nitrosotoluene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}$ , which crystallises from benzene in colourless needles, melting at  $117^\circ$  to a green liquid. Concentrated sulphuric acid converts the hydroxylamino-compound into *2-nitro-6-amino-3-hydroxytoluene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{OH}) \cdot \text{NH}_2$ , which crystallises from alcohol in compact, reddish-brown needles, m. p.  $201^\circ$ . The *diacetyl* derivative,  $\text{C}_{11}\text{H}_{12}\text{O}_5\text{N}_2$ , crystallises in colourless needles, m. p.  $127$ — $128^\circ$ . The formation of a diacetyl derivative indicates that the hydroxyl group is in the para-position with respect to the amino-group, since if it were in the ortho-position, acetic anhydride would cause the elimination of water and the formation of a methylbenzoxazole derivative. *3-Chloro-2-nitro-6-aminotoluene*,

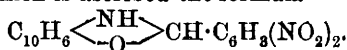


obtained by heating the hydroxylamino-compound with concentrated hydrochloric acid, crystallises from light petroleum in yellow needles, m. p.  $96^\circ$ . Its *acetyl* derivative has m. p.  $158$ — $160^\circ$ . In the formation of the 3-chloro-derivative a small amount of the isomeric 5-chloro-2-nitro-6-aminotoluene appears to be formed. The position of the chlorine in the 3-chloro-derivative has been established by removal of the amino-group and oxidation of the chloronitrotoluene to 3-chloro-2-nitrobenzoic acid, m. p.  $235^\circ$ .

*2-Nitro-4-hydroxylaminotoluene*,  $\text{C}_7\text{H}_8\text{O}_3\text{N}_2$ , obtained by the reduction of 2:4-dinitrotoluene in nearly neutral solution, separates from benzene in compact, yellow crystals, m. p.  $99^\circ$ . When oxidised, it yields *2-nitro-4-nitrosotoluene*,  $\text{C}_7\text{H}_7\text{O}_3\text{N}_2$ , in the form of colourless needles, melting at  $87^\circ$  to a green liquid, and when heated with concentrated hydrochloric acid it forms *3-chloro-2-nitro-4-aminotoluene*,  $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{Cl}$ , as pale yellow needles, m. p.  $63^\circ$ ; the *acetyl* derivative has m. p.  $123$ — $124^\circ$ . The position of the chlorine has been established by removal of the amino-group and subsequent oxidation to 3-chloro-2-nitrobenzoic acid. *5-Chloro-2-nitro-4-aminotoluene*, obtained as a by-product in the preparation of the 3-chloro-derivative, has m. p.  $131^\circ$  (Claus and Davidsen, Abstr., 1892, 172, gave  $129.5^\circ$ ).

J. J. S.

**New Derivatives of 2:4-Dinitrobenzaldehyde.** FRANZ SACHS and WLADIMIR BRUNETTI (*Ber.*, 1907, 40, 3230—3235).—The 2:4-dinitrobenzylidenaminonaphthols are sparingly soluble, crystalline compounds, and are obtained by the interaction of their components in acetic acid solution. They resemble one another in their behaviour towards mineral acids, solubility in alkali hydroxides, and colour reactions with alcoholic alkalis, with the exception of 2:4-dinitrobenzylidene-1-amino- $\beta$ -naphthol, m. p.  $201$ — $202^\circ$ , which does not possess these properties and to which is ascribed the formula



2:4-Dinitrobenzylidene- $\alpha$ -naphthylamine, m. p.  $201$ — $203^\circ$ , forms slender, orange, monoclinic prisms, and the corresponding derivative of  $\beta$ -naphthylamine, m. p.  $197$ — $199^\circ$ , yellow, microcrystalline needles.

2':4'-Dinitrobenzylidene-7-amino- $\beta$ -naphthol, m. p.  $189^\circ$  (decomp.), separates from acetone in yellow needles, which darken by exposure to

light; the solution in alcoholic alkalis is dark red. The *methyl ether* has m. p. 206—207°.

2':4'-*Dinitrobenzylidene-4-amino- $\alpha$ -naphthol*, m. p. 216° (decomp.), forms reddish-brown needles and develops an intense blue coloration with alcoholic alkalis. The *acetate*, m. p. 210°, forms yellow, hexagonal prisms.

2':4'-*Dinitrobenzylidene-3-amino- $\beta$ -naphthol*, m. p. 204° (decomp.), forms yellow needles and gives a reddish-brown coloration with alcoholic potassium hydroxide; the *benzoate* has m. p. 243° (decomp.).

2':4'-*Dinitrobenzylidene-5-amino- $\beta$ -naphthol*, m. p. 201° (decomp.), yields a dark red coloration with alcoholic alkalis. 2':4'-*Dinitrobenzylidene-5-amino- $\alpha$ -naphthol* has m. p. 219° (decomp.), and alcoholic alkalis develop a dark violet, whilst the corresponding *derivative of 8-amino- $\beta$ -naphthol*, m. p. 216° (decomp.), yields a pure violet, coloration.

C. S.

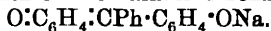
**Derivatives of Triphenylcarbinol.** ADOLF VON BAEYER [and, in part, ALFONS VON BENTHEIM and CARL DIEHL] (*Annalen*, 1907, 354, 152—204).—A systematic investigation of the derivatives of triphenylcarbinol has been undertaken with the object of explaining the many obscure points met with in the study of triphenylcarbinol (Abstr., 1902, i, 380, 769; 1903, i, 811; 1904, i, 308, 786, 898; 1905, i, 281, 358). The present paper deals with derivatives of triphenylcarbinol containing not more than one hydroxyl or amino-group in each benzene nucleus. Such substances the author terms unitary derivatives, whilst binary and ternary derivatives are such as contain two and three substituting groups respectively in at least one of the benzene nuclei.

It was shown previously (Baeyer and Löhr, Abstr., 1890, 1141; Baeyer and Villiger, Abstr., 1904, i, 308, 786) that whilst *p*-amino-triphenylcarbinol forms a dye salt, this is only orange in colour and cannot be reckoned as a true aniline dye. In agreement with this, Bistrzycki and Herbst (Abstr., 1903, i, 639) found that diphenylquinomethane, which the present author has termed fuchsone, formed by the elimination of water from *p*-hydroxytriphenylcarbinol, has the same orange colour. On the other hand, Pechmann stated (Abstr., 1881, 96) that *p*-hydroxydiphenylphthalide forms a violet solution in alkalis. This was considered (Abstr., 1905, i, 281) to point to a chromophoric action of the lactone grouping, but it is found now that the violet colour observed by Pechmann was caused by the presence of phenolphthalein and that pure *p*-hydroxydiphenylphthalide is colourless in alkaline solution. If boiled in sodium carbonate solution, *p*-hydroxydiphenylphthalide becomes yellow, which must be ascribed to the formation of the sodium fuchsoncarboxylate,  $\text{O}:\text{C}_6\text{H}_4:\text{CPh}\cdot\text{C}_6\text{H}_4:\text{CO}_2\text{Na}$ , since the solution becomes again colourless on addition of an alkali.

Excluding, as is done in this paper, any consideration of the acid salts of the phenolic derivatives, there are only two coloured mono-hydroxy- and monoamino-triphenylcarbinols: fuchsone,  $\text{CPh}_2:\text{C}_6\text{H}_4:\text{O}$ , and fuchsonium chloride,  $\text{CPh}_2:\text{C}_6\text{H}_4:\text{NH}_2\text{Cl}$ . Fuchsones are formed from unitary dihydroxy- and diamino-triphenylcarbinols only if at least one of the substituting groups is in the *p*-position. In the case of the dihydroxy-compounds, the formation of the fuchsone

takes place with varying ease according to the position of the second substituting group; *p*-hydroxyfuchson (benzaurin) is formed immediately as a yellow precipitate on addition of acetic acid to the colourless alkaline solution of 4:4'-dihydroxytriphenylcarbinol, whereas the 2:4'- and 3:4'-derivatives yield white precipitates, which are transformed into the yellow *o*- and *m*-hydroxyfuchsones only when warmed or treated with a mineral acid. These fuchsones have corresponding stabilities, benzaurin forming a violet alkaline solution which becomes colourless only on addition of a large excess of alkali, whilst the bluish-red and blood-red alkaline solutions of the *o*- and *m*-hydroxyfuchsones respectively are readily decolorised. Although the quinone groupings of these substances differ only in degree and not fundamentally, only benzaurin gives a characteristic absorption spectrum.

The unitary dihydroxydiphenylphthalide is phenolphthalein, the violet solution of which in aqueous sodium carbonate must contain the disodium salt,  $\text{O}:\text{C}_6\text{H}_4:\text{C}(\text{C}_6\text{H}_4\cdot\text{ONa})\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$ , since its absorption spectrum is identical with that of alkaline benzaurin,



Further proof that the lactone grouping of the phthaleins is not chromophoric is found in the colourless alkaline solution of 3:3'-dihydroxyditolylphthalide.

Of the six possible unitary tetramethyldiaminotriphenylcarbinols, only the 4:4'-compound yields a dye, malachite-green, when treated with cold dilute hydrochloric acid. The 3:4'-compound forms an orange fuchsonium chloride with cold or hot dilute or concentrated hydrochloric acid, whilst the 2:4'-compound forms a yellow fuchsonium chloride only with the concentrated or hot dilute acid, remaining colourless when treated with the cold dilute acid; the *o*-amino-group acts as an antiauxochrome. The absorption spectrum of Doebner's violet, the parent substance of malachite-green, is identical with that of alkaline benzaurin; these substances must have corresponding constitutions, although, according to the usual formulæ, the salt formation takes place at different parts of the molecules:  $\text{ONa}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}:\text{C}_6\text{H}_4:\text{O}$ ,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}:\text{C}_6\text{H}_4:\text{NH}_2\text{Cl}$ .

Of the ten possible unitary trihydroxytriphenylcarbinols, only the 4:4':4''-form, which changes spontaneously into the 4:4'-dihydroxyfuchson, aurin, is known. Aurin forms a violet solution in alkalis, becoming decolorised on addition of an excess of the alkali; the spectrum of the violet solution resembles that of benzaurin, the absorption bands being displaced slightly towards the violet.

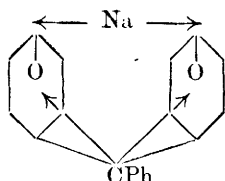
Of the ten possible forms of unitary triaminotriphenylcarbinols, seven have been prepared in various degrees of methylation. Dyes, pararosaniline and *o*-aminomalachite-green, are obtained from the 4:4':4''- and 2:4':4''-forms; the 2:3':4''-compound forms a yellow fuchsonium chloride with hot dilute hydrochloric acid, but is colourless in cold dilute, and almost so in concentrated, acid, whilst the 2:2':4''-compound is coloured only very slightly by the concentrated, or hot dilute acid. The compounds which do not contain a para-substituting group do not form coloured hydrochlorides.

As the absorption spectrum of pararosaniline is identical with that of alkaline aurin, the constitutions of these two substances must

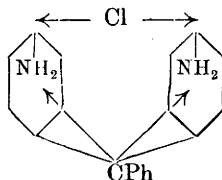


resemble one another in the same manner as those of Doebner's violet and alkaline benaurin.

The cause of the colour of the aniline and aurin dyes is discussed and considered to be an oscillation between two forms expressed by the schemes :



Sodium benaurin.



Doebner's violet.

*o*-Hydroxytriphenylcarbinol,  $C_{19}H_{16}O_2$ , prepared by Grignard's reaction from *o*-methoxybenzoic acid and bromobenzene, crystallises in colourless, rectangular plates or prisms, m. p.  $140.5^\circ$ , gives with concentrated sulphuric acid in glacial acetic acid solution a cherry-red coloration which disappears on addition of water, forms a sparingly soluble, crystalline sodium salt, yields 9-phenylxanthen when distilled in a vacuum, and is reduced by zinc dust in boiling glacial acetic acid solution, forming *o*-hydroxytriphenylmethane,  $C_{19}H_{16}O$ , which crystallises from a mixture of benzene and light petroleum in colourless spears, m. p.  $124^\circ$ , or from alcohol in needles, m. p.  $76^\circ$ , containing alcohol of crystallisation.

*Diphenyl-o-anisylcarbinol*,  $C_{20}H_{18}O_2$ , prepared by Grignard's reaction from methyl salicylate and bromobenzene, crystallises in colourless, rhombic plates, m. p.  $128-129^\circ$ , gives an intense cherry-red coloration with sulphuric and glacial acetic acids, differs from the para-compound in remaining unchanged when heated with glacial acetic acid and dilute sulphuric acids, and on treatment with hydrogen chloride in ethereal solution yields the *carbinyl chloride*,  $C_{20}H_{17}OCl$ , which crystallises in needles, m. p.  $126^\circ$  (decomp.), and is reconverted into the carbinol on exposure to air. The *anilide*, formed by the action of aniline on the carbinyl chloride in ethereal solution, crystallises in hard cubes, m. p.  $151^\circ$ . *Diphenyl-o-anisylmethane*,  $C_{20}H_{18}O$ , formed by heating the carbinol with zinc dust and glacial acetic acid, crystallises in colourless rhombohedra, m. p.  $114^\circ$ .

*m*-Hydroxytriphenylcarbinol crystallises in prisms, m. p.  $147-148^\circ$ , gives a transient, brownish-red coloration with sulphuric and glacial acetic acids, and is decomposed when boiled with concentrated hydrochloric acid. *Diphenyl-m-anisylcarbinol* separates from ether in large, regular crystals, m. p.  $88^\circ$ . *m*-Hydroxytriphenylmethane forms colourless prisms, m. p.  $106^\circ$ .

*o*-Hydroxydiphenylphthalide,  $C_{20}H_{14}O_3$ , formed by fusing *o*-benzoylbenzoic acid with phenol and treatment of the product with concentrated sulphuric acid, crystallises in prisms, m. p.  $167^\circ$ .

*2-Hydroxy-5-methyldiphenylphthalide* (*o*-hydroxyphenyltolylphthalide),  $C_{21}H_{16}O_3$ , prepared by the action of concentrated sulphuric acid on a mixture of *p*-cresol and *o*-benzoylbenzoic acid (compare Drewsen, Abstr., 1882, 1098; Meyer and Hoffmeyer, Abstr., 1892, 970), forms colourless prisms, m. p.  $226^\circ$ , gives an emerald-green coloration with con-

concentrated sulphuric acid, and dissolves in moderately concentrated alkalis on heating; on cooling, the *alkali* salt crystallises in small needles.

*m*-Dimethylaminotriphenylcarbinol,  $C_{21}H_{21}ON$ , prepared by Grignard's reaction from methyl *m*-dimethylaminobenzoate and bromobenzene, crystallises in colourless plates, m. p.  $110^\circ$ , gives a slight yellow coloration with fuming hydrochloric acid, and dissolves in concentrated sulphuric acid, forming a colourless solution; the *hydrochloride*,  $C_{21}H_{21}ON \cdot HCl$ , crystallises in colourless leaflets, m. p.  $181^\circ$  (decomp.). The *hydrochloride* of the *carbinyl chloride*,  $C_{21}H_{20}NCl \cdot HCl$ , m. p.  $154^\circ$  (decomp.), is converted into the hydrochloride of the carbinol by the action of moist air, and yields hydrogen chloride and a brown, amorphous mass when heated in a current of hydrogen. The *methyl ether*,  $C_{22}H_{23}ON$ , prepared by the action of sodium methoxide on the carbinyl chloride hydrochloride, crystallises in rhombic plates and prisms, m. p.  $81^\circ$ .

2 : 4'-Dihydroxytriphenylcarbinol,  $C_{19}H_{16}O_3$ , formed from 2 : 4'-dihydroxybenzophenone, m. p.  $150$ — $151^\circ$  ( $143$ — $144^\circ$ : Michael, Abstr., 1884, 311), and bromobenzene by Grignard's reaction, crystallises in colourless prisms, m. p.  $143^\circ$  (decomp.), dissolves to a colourless solution in alkalis, is precipitated unchanged by acetic acid, and gives a blood-red coloration with concentrated sulphuric acid. *o*-Hydroxyfuchson,  $C_{10}H_{14}O_2$ , formed from the dihydroxycarbinol at  $150^\circ$ , crystallises in orange prisms, m. p.  $204$ — $205^\circ$ , forms bluish-red alkaline solutions which rapidly become colourless in consequence of the formation of the carbinol, and with sulphuric acid gives the same coloration as the carbinol.

3 : 4'-Diaminobenzophenone has m. p.  $131$ — $132^\circ$  ( $121$ — $122^\circ$ : Gattermann and Rüd, Abstr., 1894, i, 599). 3 : 4'-Dihydroxybenzophenone has m. p.  $205$ — $206^\circ$  ( $200^\circ$ : Gattermann and Rüd, *loc. cit.*).

3 : 4'-Dihydroxytriphenylcarbinol, m. p.  $155$ — $160^\circ$  (decomp.), formed from 3 : 4'-dihydroxybenzophenone and bromobenzene by Grignard's reaction, was not purified. It gives an orange-red coloration with sulphuric acid, and when heated at  $150^\circ$  yields *m*-hydroxyfuchson,  $C_{19}H_{14}O_2$ , which crystallises from acetone in orange prisms, m. p.  $183^\circ$ , or from chloroform in crystals, m. p.  $105$ — $110^\circ$  (decomp.), containing chloroform, and behaves towards alkalis and concentrated sulphuric acid in the same manner as the *o*-compound.

Phenyl-di-*o*-anisylcarbinol,  $C_{21}H_{20}O_3$ , formed from *o*-iodoanisole and methyl benzoate, crystallises in rhombic plates, m. p.  $115^\circ$ , gives a brownish-violet coloration with sulphuric and glacial acetic acids, and forms a yellow solution when heated with glacial acetic acid. Phenyl-di-*o*-anisylmethane,  $C_{21}H_{20}O_2$ , crystallises in colourless prisms, m. p.  $106^\circ$ , and has an odour resembling that of guaiacol.

3 : 3'-Dihydroxytriphenylcarbinol,  $C_{19}H_{16}O_3 \cdot C_2H_6O$ , m. p. below  $100^\circ$  (decomp.), formed from 3 : 3'-dihydroxybenzophenone, m. p.  $170^\circ$  ( $162$ — $164^\circ$ : Gattermann and Rüd, *loc. cit.*) and bromobenzene, gives a Bordeaux-red coloration with concentrated sulphuric acid.

Phenyl-di-*m*-anisylcarbinol,  $C_{20}H_{21}O_3$ , from *m*-iodoanisole and methyl benzoate, crystallises in rhombic leaflets, m. p.  $82$ — $83^\circ$ , and gives a Bordeaux-red coloration with sulphuric acid in glacial acetic acid solution.

Di-*m*-nitroditolylphthalide, m. p.  $157$ — $158^\circ$  ( $132^\circ$ : Limpricht,

Abstr., 1898, i, 323), yields 3 : 3'-diaminoditolylphthalide, m. p. 197° (192° : Limpricht, *loc. cit.*), which, when treated with amyl nitrite in concentrated sulphuric acid solution, yields a crystalline *diazosulphate*, which decomposes suddenly when heated. Di-*m*-hydroxyditolylphthalide,  $C_{12}H_{18}O_4$ , formed by heating the *diazosulphate* with water at 60°, crystallises in colourless prisms, m. p. 206°, and is colourless in alkaline solution.

*m*-Dimethylaminobenzophenone,  $C_{15}H_{15}ON$ , formed by the action of methyl sulphate and sodium hydroxide on *m*-aminobenzophenone, is isolated in the form of its *methiodide*,  $C_{16}H_{18}ONI$ , which crystallises in slender needles, and when heated at 205° loses methyl iodide and yields the *base*, crystallising in slightly yellow plates, m. p. 47°. *m*-Dimethylaminobenzhydrol,  $C_{15}H_{17}ON$ , prepared by reduction of the ketone with sodium amalgam in alcoholic solution, crystallises in colourless needles, m. p. 102°.

*p*-Dimethylaminobenzophenone (Doebner and Weiss, Abstr., 1882, 176) is obtained in good yields by the action of methyl sulphate on *p*-aminobenzophenone.

3 : 4'-Tetramethyldiaminobenzophenone,  $C_{17}H_{20}ON_2$ , prepared by heating 3 : 4'-diaminobenzophenone with methyl alcohol at 140—145°, separates from alcohol or ether in brownish-yellow crystals, m. p. 77—78.5°; the *hydrochloride* crystallises in colourless needles, m. p. 278—280° (decomp.); the *platinichloride*,  $C_{17}H_{20}ON_2 \cdot H_2PtCl_6 \cdot H_2O$ , forms golden plates, darkens at 100°, and decomposes at 200°. 3 : 4'-Tetramethyldiaminobenzhydrol,  $C_{17}H_{22}ON_2$ , prepared by reduction of the ketone with sodium amalgam, crystallises in colourless needles, m. p. 100—101°, gives with concentrated sulphuric acid a yellow, or with hot glacial acetic acid a yellowish-green, coloration, and forms colourless solutions in other mineral acids.

Di-*m*-nitrodiphenylmethane has m. p. 180°, and di-*m*-nitrobenzophenone, m. p. 160°; Gattermann and Rüdts (*loc. cit.*) give the m. p.'s 172° and 151°. 3 : 3'-Tetramethyldiaminobenzophenone,  $C_{17}H_{20}ON_2$ , prepared by the action of methyl sulphate on the diamino-compound, crystallises from dilute alcohol in yellow prisms, m. p. 59—60°, and forms colourless solutions in dilute or concentrated acids. 3 : 3'-Tetramethyldiaminobenzhydrol,  $C_{17}H_{22}ON_2$ , crystallises in prisms, m. p. 72—73°, and dissolves to colourless solutions in acids.

2 : 4'-Tetramethyldiaminotriphenylcarbinol,  $C_{23}H_{26}ON_2$ , prepared from *p*-dimethylaminobenzophenone and magnesium *o*-dimethylaminophenyl iodide (compare Abstr., 1905, i, 766), separates from alcohol in colourless crystals, m. p. 169.5—170°, and dissolves in glacial acetic acid forming a colourless solution which becomes dark green and, finally, yellow when heated.

2 : 4'-Tetramethyldiaminotriphenylcarbinyl chloride dihydrochloride,  $C_{23}H_{27}N_2Cl_3$ , crystallises in yellow needles, decomp. at 227°, and is unstable in moist air. The *stannichloride* is red.

3 : 4'-Tetramethyldiaminotriphenylcarbinol,  $C_{23}H_{26}ON_2$ , prepared from 3 : 4'-tetramethyldiaminobenzophenone and magnesium phenyl bromide, crystallises in colourless prisms, m. p. 140°.

3 : 4'-Tetramethyldiaminotriphenylmethane,  $C_{23}H_{26}N_2$ , prepared by reduction of the carbinol with zinc dust and hydrochloric acid in presence of hydrogen iodide, forms irregular crystals, m. p. 83—84°.

2 : 2'-*Tetramethyldiaminotriphenylcarbinol*,  $C_{23}H_{26}ON_2$ , prepared from methyl benzoate and *o*-iododimethylaniline, or from 2 : 2'-tetramethyldiaminobenzophenone and bromobenzene, by Grignard's reaction, crystallises in colourless prisms, m. p.  $105^\circ$ , forms colourless solutions in acids, and does not give a coloration with stannic chloride or when dissolved in glacial acetic acid containing hydrogen bromide, and poured into water, but gives a transient blue coloration on treatment with phosphorus pentachloride in chloroform solution.

2 : 3'-*Tetramethyldiaminotriphenylcarbinol*,  $C_{23}H_{26}ON_2$ , from *o*-iododimethylaniline and *m*-dimethylaminobenzophenone, crystallises in colourless plates, m. p.  $183$ — $184^\circ$ , and dissolves in glacial acetic acid, forming a colourless solution becoming yellowish-green when heated.

3 : 3'-*Tetramethyldiaminotriphenylcarbinol*, from 3 : 3'-tetramethyldiaminobenzophenone and magnesium phenyl bromide, separates from ether in crystalline crusts, m. p.  $128$ — $129^\circ$ , and gives a yellow coloration with glacial acetic acid, mineral acids, or stannic chloride.

3 : 4' : 4''-*Hexamethyltriaminotriphenylmethane*,  $C_{25}H_{31}N_3$ , prepared by condensation of dimethylaniline with 3 : 4'-tetramethyldiaminobenzhydrol in presence of zinc chloride, crystallises in colourless prisms, m. p.  $153$ — $154^\circ$ , is superficially oxidised by air, and on treatment with lead dioxide yields the *carbinol*, which dissolves in cold alcohol or cold dilute hydrochloric acid, forming colourless solutions becoming blue when heated ; it becomes blue also when exposed to air containing carbon dioxide.

2 : 2' : 4''-*Hexamethyltriaminotriphenylcarbinol*,  $C_{25}H_{31}ON_3$ , from *o*-iododimethylaniline and methyl *p*-dimethylaminobenzoate, forms rhombic crystals, m. p.  $172$ — $173^\circ$ .

2 : 3' : 4''-*Hexamethyltriaminotriphenylcarbinol*, prepared from *o*-iododimethylaniline and 3 : 3'-tetramethyldiaminobenzophenone, crystallises in rhombic plates, m. p.  $148$ — $150^\circ$ .

2 : 2' : 2''-*Hexamethyltriaminotriphenylcarbinol*, prepared from *o*-iododimethylaniline and 2 : 2'-tetramethyldiaminobenzophenone, or from *o*-iododimethylaniline and methyl dimethylantranilate, or *o*-iododimethylaniline and ethyl orthocarbonate, crystallises in prisms or plates, m. p.  $107$ — $108^\circ$ , forms colourless solutions in acids, and does not give Bassett's reaction.

2 : 2' : 3''-*Hexamethyltriaminotriphenylcarbinol*, from *o*-iododimethylaniline and methyl dimethyl-*m*-aminobenzoate, crystallises in colourless plates, m. p.  $151$ — $152^\circ$ .

2 : 3' : 3''-*Hexamethyltriaminotriphenylcarbinol*, from *o*-iododimethylaniline and 3 : 3'-tetramethylaminobenzophenone, crystallises in prisms, m. p.  $207$ — $208^\circ$ . G. Y.

**Synthetical Ephedrines.** ERNEST FOURNEAU (*J. Pharm. Chim.*, 1907, [vi], 25, 593—602. Compare Abstr., 1905, i, 57 ; Schmidt, *ibid.*, 370).—The *methochloride* of benzyldimethylaminomethylcarbinol, derived from allylbenzene (*loc. cit.*), is a syrup ; the *picrate* has m. p.  $143^\circ$  ; the aurichloride and platinichloride are identical with the salts of Schmidt and Emde's quaternary base derived from cinnamyltrimethylamine hydrochloride (Abstr., 1906, i, 946). The base must have the constitution  $OH \cdot CH(CH_2Ph) \cdot CH_2 \cdot NMe_3 \cdot OH$ , and not that ascribed to it by these authors.

When heated with trimethylamine in benzene solution at  $126^{\circ}$ , the *chlorohydrin*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , b. p.  $142^{\circ}/20$  mm., prepared by Grignard's reaction from  $\beta$ -chloropropaldehyde, yields the quaternary *chloride*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$ , m. p.  $210^{\circ}$  (decomp.); the *aurichloride*, m. p.  $155^{\circ}$ , decomp. about  $190^{\circ}$ ; the *platinichloride*, decomp. about  $230^{\circ}$ ; the *base* decomposes when heated, yielding trimethylamine and an *alcohol*, b. p.  $101-102^{\circ}/21$  mm., isomeric with cinnamyl alcohol.

$\gamma$ -Methylamino- $\alpha$ -phenylpropyl alcohol,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHMe}$ , the fifth isomeric of ephedrine, is prepared by the action of methylamine on the chlorohydrin; it forms prisms, m. p.  $70^{\circ}$ , b. p.  $170^{\circ}/31$  mm.; the *hydrochloride*, m. p.  $130^{\circ}$ : the *platinichloride*, m. p.  $108-110^{\circ}$ , decomposes when strongly heated.

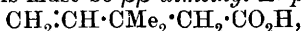
$\gamma$ -Dimethylamino- $\alpha$ -phenylpropyl alcohol,  
 $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ ,  
 crystallises in plates, m. p.  $55^{\circ}$ , b. p.  $182^{\circ}/64$  mm.; the *hydrochloride*, m. p.  $128^{\circ}$ ; the *aurichloride*, m. p.  $120^{\circ}$ , decomp. about  $160^{\circ}$ ; the *platinichloride*, m. p.  $130^{\circ}$  (decomp.); the *methiodide*,  $\text{C}_{13}\text{H}_{20}\text{ONI}$ , forms needles, m. p.  $118^{\circ}$ . The *hydrochloride* of the benzoyl derivative,  
 $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}\cdot\text{HCl}$ ,  
 crystallises in needles, m. p.  $167^{\circ}$ ; the *hydrochloride* of the cinuamoyl derivative, m. p.  $179^{\circ}$ .  
 G. Y.

**Action of Some  $\gamma$ - and  $\delta$ -Bromo-esters on Ethyl Cyanoacetate, Malonate, and Methylmalonate.** GUSTAVE BLANC (*Compt. rend.*, 1907, 145, 78-80).—By the successive action of phosphorus pentabromide and alcohol on the mixture of lactones, obtained (Abstr., 1905, i, 680, 681) by reduction of the acid anhydrides of the succinic or glutaric series,  $\gamma$ - or  $\delta$ -bromo esters are obtained according as a  $\gamma$ - or  $\delta$ -lactone is employed. These esters react readily with the sodium derivatives of ethyl cyanoacetate, malonate, or methylmalonate. Of the  $\gamma$ -bromo-esters, however, whilst those derived from lactones of the type  $\text{R}\cdot\text{CH}(\text{CO})\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  react normally according to the equation  $\text{CO}_2\text{Et}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br} + \text{CHNa}(\text{CO}_2\text{Et})_2 \rightarrow \text{CO}_2\text{Et}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , the ethers derived from lactones of the type  $\text{R}\cdot\text{CH}(\text{CO})\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  undergo a simple elimination of HBr with formation of a cyclopropanecarboxylic ester, thus:  $\text{CH}_2\text{Br}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{CHNa}(\text{CO}_2\text{Et})_2 = \text{NaBr} + \text{CH}_2(\text{CO}_2\text{Et})_2 + \text{CHR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ .

Thus condensation of ethyl  $\gamma$ -bromo- $\alpha\alpha$ -dimethylbutyrate with one of the above sodium derivatives gives a cyanodicarboxylic or a tricarboxylic ester, but by condensing ethyl  $\gamma$ -bromo- $\beta\beta$ -dimethylbutyrate, ethyl 2:2-dimethylcyclopropanecarboxylate is formed as a liquid, b. p.  $90^{\circ}/15$  mm. The corresponding acid is an oil of a strong butyric odour, b. p.  $100^{\circ}/10$  mm., and very stable towards potassium permanganate. It forms an amide crystallising in tablets, m. p.  $177^{\circ}$ . Ethyl 2-isopropylcyclopropanecarboxylate, similarly obtained from isopropylsuccinic acid, has b. p.  $95-100^{\circ}/10$  mm. The corresponding

*acid* is an oil with a butyric odour, b. p.  $115^{\circ}/15$  mm., also stable towards permanganate. It gives an *amide*, forming tablets, m. p.  $166-167^{\circ}$ , and an *anilide*, crystallising in needles, m. p.  $117^{\circ}$ , and is probably identical with Ipatieff's acid (Abstr., 1902, i, 588).

When ethyl  $\gamma$ -bromo- $\beta\beta$ -dimethylvalerate is condensed with the sodium derivative of ethyl malonate or methylmalonate, besides the expected tricarboxylic ester, a quantity of an *ester*, b. p.  $90^{\circ}/8$  mm., is formed, which gives an oily *acid*, b. p.  $112-115^{\circ}/12$  mm., and an *amide*, m. p.  $98^{\circ}$ . This must be  $\beta\beta$ -dimethyl- $\Delta\gamma$ -pentenoic acid,



since it is oxidised by permanganate solution at  $-5^{\circ}$  giving chiefly *aa*-dimethylsuccinic acid. E. H.

**Affinity Constants of Tyrosine and Phenylalanine.** ARISTIDES KANITZ (*Pflüger's Archiv*, 1907, 118, 539—546).—The basic and acidic dissociation constants for tyrosine and phenylalanine have been calculated from the degree of hydrolysis of their hydrochlorides and sodium salts by the method previously described (Abstr., 1906, ii, 603). As the compounds were only sparingly soluble, the degree of hydrolysis was determined by electrical conductivity methods.

The results obtained at  $25^{\circ}$  are for tyrosine:

First acid dissociation constant, $K_s$ ,	$4 \times 10^{-9}$
Second „ „ „ „ $K_{ss}$ ,	$4 \times 10^{-10}$
Basic „ „ „ „ $K_b$ ,	$2.6 \times 10^{-12}$

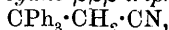
And for phenylalanine:

Acid dissociation constant, $K_s$ ,	$2.5 \times 10^{-9}$
Basic „ „ „ „ $K_b$ ,	$1.3 \times 10^{-12}$

The acid dissociation constant of phenylaniline, calculated from the conductivities of solutions of phenylalanine itself, was high, but this value was reduced considerably when the compound had been repeatedly recrystallised. The salts of the specially purified compound gave the same results as the original salts. J. J. S.

**Triphenylcarbinol: Action of Malonic and Cyanoacetic Acids.** ROBERT FOSSE (*Compt. rend.*, 1907, 145, 196—198).—The action of malonic acid transforms triphenylcarbinol quantitatively into  $\beta\beta$ -triphenylpropionic acid.

The action of cyanoacetic acid on triphenylcarbinol yields: (1) *a*-cyano- $\beta\beta\beta$ -triphenylpropionic acid A,  $\text{CPh}_3\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$ , m. p.  $155^{\circ}$ , which is more soluble in ordinary solvents and less stable than the isomeric B-acid; on heating the acid, or an alcoholic solution of its sodium salt, it yields (2) *a*-cyano- $\beta\beta\beta$ -triphenylethane A,



m. p.  $140^{\circ}$ , which is also formed during the reaction between cyanoacetic acid and triphenylcarbinol; (3) *a*-cyano- $\beta\beta\beta$ -triphenylpropionic acid B, m. p.  $175^{\circ}$  (decomp.), which on heating yields *a*-cyano- $\beta\beta\beta$ -triphenylethane B,  $\text{C}_{21}\text{H}_{17}\text{N}$ , m. p.  $211^{\circ}$ .

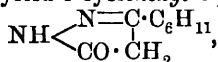
The nature of the isomerism of the two *a*-cyano- $\beta\beta\beta$ -triphenylpropionic acids and of their products of decarboxylation is unknown.

T. H. P.

**Trimethylcoumarone.** JOHANNES BOES (*Chem. Zentr.*, 1907, i, 1426; from *Apoth.-Zeit.*, 22, 177).—A mixture of trimethylcoumarones has been isolated from a fraction of tar oil of b. p. 235—245°. The mixture had the characteristic odour of coumarone, did not solidify when cooled in ice and salt, and had b. p. 240°,  $D_{20}^{17}$  1.0204, and  $n_D^{17}$  1.5471; it decolorised bromine water in the cold, and gave a dark red coloration with concentrated sulphuric acid. The picrate, m. p. 105°, crystallised from alcohol in yellow needles, and was unstable. E. W. W.

**Ethyl Hexahydrobenzoylacetate.** ANDRÉ WAHL and A. MEYER (*Compt. rend.*, 1907, 145, 192—194).—The authors give an account of their incomplete work, owing to the appearance of Zelinsky and Schwedoff's paper (this vol., i, 704).

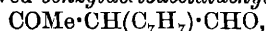
*Ethyl hexahydrobenzoylacetate*,  $C_6H_{11} \cdot CO \cdot CH_2 \cdot CO_2Et$ , prepared by condensing ethyl hexahydrobenzoate (1 mol.) and ethyl acetate (1 mol.) in presence of sodium (1 at.), has b. p. 140—143°/25 mm. The *methyl ester*,  $C_6H_{11} \cdot CO \cdot CH_2 \cdot CO_2Me$ , has b. p. 140—141°/23 mm. These esters possess very persistent odours, which, when diluted, recall that of leather. They yield well crystallised copper salts, and have the properties of  $\beta$ -ketonic esters. Thus, with hydrazine hydrate in aqueous alcohol, they yield 3-cyclohexyl-5-pyrazolone,



which crystallises in white scales, m. p. 244—245°.

T. H. P.

**Complete Reduction of Ethyl Benzylacetoacetate.** JULIUS TAFEL and HANS HAIL (*Ber.*, 1907, 40, 3312—3318).—The reduction was carried out electrolytically with a lead cathode, using 7.5 grams of ester, 22.5 grams of 30% sulphuric acid, and 70 c.c. of 96% alcohol; the current employed was 2.4 amperes with a cathode surface of 20 cm<sup>2</sup>. The nearly colourless reduction product, after washing with soda and drying, was treated with sodium hydrogen sulphite and ether, which removed *benzylacetoacetaldehyde*,

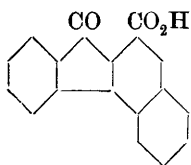


an intensely yellow oil, b. p. 76—81°, in the vacuum produced by liquid air; the *bisphenylhydrazone* is light yellow, m. p. 149°. The oil, freed from ether and water, was next fractionally distilled under 35 mm. pressure at 110°; the fraction consisted mainly of  $\beta$ -*benzylbutane*,  $CH_3Me \cdot CH(C_7H_7) \cdot CH_3$ , a colourless, mobile oil, b. p. 203—204°/750 mm. The residual oil was next distilled in the vacuum produced by liquid air and charcoal, and collected in three fractions: (1) up to 80°; (2) 80—125°; (3) 125—185°. Fraction (2) consisted largely of ethyl  $\beta$ -hydroxy- $\alpha$ -benzylbutyrate, and the second and third fractions both contained ethyl  $\alpha$ -benzylbutyrate. The portion of (2), not hydrolysed, contained an alcohol (?) and  $\beta$ -*benzylbutyl ethyl ether*,  $CH_3 \cdot CH_2 \cdot CH(C_7H_7) \cdot CH_2OEt$ , b. p. 156—162°. W. R.

**A Bordeaux-red Chrysoketonecarboxylic Acid and its Yellow Derivatives.** A Contribution to the Theory of Colour. HANS STOBBE [and, in part, WILLY KEDING and FERDINAND GOLLÜCKE] (*Ber.*, 1907, 40, 3383—3389).—Derivatives of chrysoketone or

naphthafluorenone and of isochrysoketone have been described previously by Bamberger and by Graebe and Gnehm (Abstr., 1905, i, 60).

An *allochrysoketonecarboxylic acid* is formed when 1-phenylnaphthalene-2:3-dicarboxylic acid (this vol., i, 769) is treated with concentrated sulphuric acid for two days at the ordinary temperature and the product poured on to ice. It crystallises from benzene or cumene in bordeaux-red needles, m. p. 285—286° (decomp.). It is sparingly soluble in all solvents, and is stable towards oxidising agents.

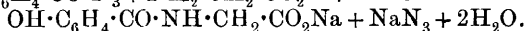


Chromic anhydride yields an acid which is neither benzoic nor *o*-benzoylbenzoic acid. It can be reduced with sodium amalgam at 100°.

The *sodium* salt,  $C_{18}H_9O_3Na$ , crystallises in orange-red needles, and the *potassium* salt in orange needles. The *ethyl* ester,  $C_{20}H_{14}O_3$ , obtained from the silver salt, crystallises from dilute alcohol in yellow needles, m. p. 187—188°. The *phenylhydrazone*,  $C_{24}H_{16}O_2N_2$ , also forms yellow needles, m. p. 241°. The absorption spectra of the acid and its derivatives have been examined in solution. All yield a continuous absorption band, but that of the acid extends further towards the red end of the spectrum.

The difference in colour between the acid and its salts does not appear to be due to any molecular rearrangement during the salt formation, as would be required by Hantzsch's theory. J. J. S.

**Synthesis of Salicyluric Acid.** SAMUEL BONDI (*Zeitsch. physiol. Chem.*, 1907, 52, 170—176).—Salicyluric acid has been synthesised by the action of glycine on an alkaline solution of the azoimide of salicylic acid,  $OH \cdot C_6H_4 \cdot CO \cdot N_3 + NH_2 \cdot CH_2 \cdot CO_2H + 2NaOH =$



A by-product formed in the reaction is sparingly soluble in alcohol and has m. p. 230—231°. The analyses of salicyluric acid invariably gave too high a percentage of carbon.

Salicylic acid hydrazide,  $OH \cdot C_6H_4 \cdot CO \cdot NH \cdot NH_2$ , obtained by heating ethyl salicylate and hydrazine hydrate for two and a half hours on the water-bath, has m. p. 147° (Struve and Radenhausen, Abstr., 1896, i, 35, give 145°). Sodium nitrite reacts with a nitric acid solution of the hydrazide, yielding the azoimide,  $OH \cdot C_6H_4 \cdot CO \cdot N_3$ , in the form of crystalline plates with a pungent odour. J. J. S.

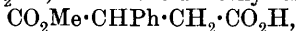
**Ester- and Amide-acids of Phenylsuccinic Acid.** RICHARD ANSCHÜTZ (*Annalen*, 1907, 354, 117—151).—In conjunction with the investigation of the partial esterification of itaconic and mesaconic acids and the partial hydrolysis of their methyl and ethyl esters (Abstr., 1898, i, 128; this vol., i, 468), the same reactions have been studied with *aa*-dimethylsuccinic (Güttes, *Diss.*, Bonn, 1901; compare Blaise, Abstr., 1898, i, 560) and phenylsuccinic (Hahn, *Diss.*, Bonn, 1902) acids in order to compare the behaviour of an asymmetrical saturated acid with that of asymmetrical unsaturated acids, and to determine the influence of the negative phenyl group on the activity of the carboxyl attached to the same carbon atom. At the same time, the



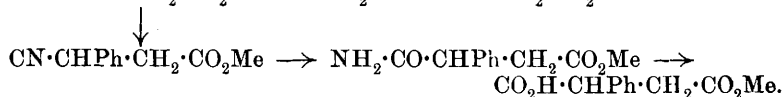
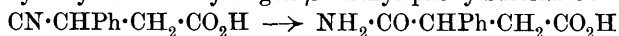
manner in which the anhydrides of these acids combine with alcohols, ammonia, and substituted ammonias has been studied.

In the present paper, the author describes the preparation of phenylsuccin- $\alpha$ -amic acid and hydrogen  $\beta$ -methyl phenylsuccinate from  $\beta$ -cyano- $\beta$ -phenylpropionic acid, the formation of the hydrogen methyl phenylsuccinates and of the corresponding acid-chlorides from phenylsuccinic acid, the isomerism of the phenylsuccin-amic, -anilic, -*p*-toluidic, and -piperidic acids, and the synthesis of  $\beta$ -benzoyl- $\alpha$ -phenyl- and  $\beta$ -benzoyl- $\beta$ -phenyl-propionic acids from phenylsuccinic acid.

The hydrogen methyl phenylsuccinates were prepared by Wegscheider and Hecht (Abstr., 1903, i, 760), who considered the ester, m. p. 102°, obtained by partial hydrolysis of methyl phenylsuccinate, to be the  $\alpha$ - and that, m. p. 92°, formed by partial esterification to be the  $\beta$ -methyl ester. These assumptions are shown now to have been correct, since on conversion into the corresponding ester-chloride and treatment with benzene and aluminium chloride, the  $\beta$ -methyl ester,  $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , yields methyl  $\beta$ -benzoyl- $\beta$ -phenylpropionate,  $\text{COPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , whilst the  $\alpha$ -methyl ester,



forms methyl  $\beta$ -benzoyl- $\alpha$ -phenylpropionate,  $\text{CO}_2\text{Me}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$ . Moreover,  $\beta$ -cyano- $\beta$ -phenylpropionic acid on partial hydrolysis yields phenylsuccin- $\alpha$ -amic acid, but on esterification and subsequent partial hydrolysis forms hydrogen  $\beta$ -methyl phenylsuccinate:



The action of methyl alcohol on phenylsuccinic anhydrides leads to the formation of a mixture containing about 25% of the more feebly acid hydrogen  $\alpha$ -methyl and about 75% of the more strongly acid hydrogen  $\beta$ -methyl phenylsuccinates. The mixture of methyl amates, formed from this by way of the acid-chlorides, is readily separated in consequence of the difference in solubility of the isomerides in ether. The - $\beta$ -amic, - $\beta$ -anilic, -*p*-toluidic, and - $\beta$ -piperidic acids are obtained directly and without admixture of the  $\alpha$ -isomerides by the action of ammonia or substituted ammonias on phenylsuccinic anhydride, the basic group combining with the carbonyl of the more feebly acid carboxyl.

*Conversion of  $\beta$ -Cyano- $\beta$ -phenylpropionic Acid and its Methyl Ester into Phenylsuccin- $\alpha$ -amic Acid and Hydrogen  $\beta$ -Methyl Phenylsuccinate.*—[With PAUL WALTER.]—*Phenylsuccin- $\alpha$ -amic acid*,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$ , prepared by the action of concentrated sulphuric acid on  $\alpha$ -cyano- $\alpha$ -phenylpropionic acid (Bredt and Kallen, Abstr., 1897, i, 154) at the ordinary temperature, crystallises from water in small plates, m. p. 158—159°; the *silver* salt,  $\text{C}_{10}\text{H}_{10}\text{O}_3\text{NAg}$ , is a white powder. The *methyl ester*,  $\text{CN}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , prepared in the same manner as the ethyl ester (Bredt and Kallen, *loc. cit.*), crystallises in needles or prisms, m. p. 55°, b. p. 155—159°/10 mm., and when treated with concentrated sulphuric acid at the ordinary temperature yields  $\beta$ -methyl phenylsuccin- $\alpha$ -amate,  $\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , m. p. 145°, which

is only sparingly soluble in ether, and is converted by sulphuric and nitrous acids into hydrogen  $\beta$ -methyl phenylsuccinate, m. p. 92°.

*Formation of the Hydrogen Methyl Phenylsuccinates and their Chlorides.*

—[With CARL HAHN and PAUL WALTER.]—Methyl phenylsuccinate (Wegscheider and Hecht, *loc. cit.*), m. p. 57—58°, b. p. 160—162°/12 mm. Phenylsuccinic anhydride, b. p. 191—192°/12 mm.

*Phenylsuccinyl dichloride*,  $\text{COCl}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COCl}$ , is obtained as a colourless liquid, b. p. 150—151°/12 mm., and has an irritating odour.

On hydrolysis with methyl alcoholic potash at the ordinary temperature, 12.7 grams of methyl phenylsuccinate gave 6.3 grams of the  $\alpha$ -monomethyl ester and 3.3 grams of the acid, 2.6 grams remaining unchanged; in another experiment, 8.8 grams of the dimethyl ester gave 6.0 grams of the  $\alpha$ -methyl ester and 0.2 gram of acid, 1.2 grams being unchanged.

The *methyl phenylsuccinyl chlorides*,  $\text{CO}_2\text{Me}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COCl}$  and  $\text{COCl}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , formed by heating the monomethyl esters, or a mixture of these, with phosphorus trichloride at 60—70°, are obtained as colourless oils which could not be purified, as they decompose on distillation in a vacuum.

*The Isomeric Phenylsuccinamic, -anilic, -p-toluidic, and -piperidic Acids.*—[With CARL HAHN and PAUL WALTER.]—*Phenylsuccin- $\beta$ -amic acid*,  $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 144—145°, prepared by the action of anhydrous ammonia on phenylsuccinic anhydride in ethereal solution, crystallises from water; the white *silver salt*,  $\text{C}_{10}\text{H}_{10}\text{O}_3\text{NAg}$ , darkens on exposure to light; the *methyl ester*,  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$ , m. p. 119°, formed by the action of methyl iodide on the silver salt or of ammonia on the ester-chloride, is readily soluble in ether, and yields hydrogen  $\alpha$ -methyl phenylsuccinate when treated with nitrous acid.

The methyl phenylsuccinanilates are prepared by the action of aniline on the ester-chlorides, and, when formed together from a mixture of these, can be partially separated by crystallisation from ether, the  $\beta$ -methyl anilate being the more readily soluble. On careful hydrolysis, the esters yield the anilic acids.

*Phenylsuccin- $\beta$ -anilic acid*, m. p. 169—170°, was prepared by Hann and Lapworth (Trans., 1904, 85, 1367) by the action of aniline on phenylsuccinic anhydride, and considered by these authors to be the  $\alpha$ -anilic acid; the *silver salt*,  $\text{C}_{16}\text{H}_{14}\text{O}_3\text{NAg}$ , was analysed; the *methyl ester*,  $\text{CO}_2\text{Me}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , crystallises in white needles, m. p. 149°. The  *$\alpha$ -anilic acid*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , has m. p. 175°; the *methyl ester*,  $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$ , m. p. 96°. A mixture of the two anilic acids has m. p. 159—160°. When heated with acetyl chloride, both anilic acids yield phenylsuccinanil (Hann and Lapworth, *loc. cit.*).

*Phenylsuccindianilide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 222°, is formed by shaking phenylsuccinyl dichloride with aniline in ethereal solution; if the reacting substances are present in molecular proportions, half of the dichloride remains unchanged.

The *p*-toluidic and piperidic acids are formed and behave in the same manner as the anilic acids.

*Phenylsuccin- $\beta$ -p-toluidic acid*,  $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , m. p. 168—169°; the *silver salt*,  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{NAg}$ , was analysed; the *methyl ester*,  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}$ , m. p. 118°. The  *$\alpha$ -p-toluidic acid*, m. p.

175°; the *methyl* ester, m. p. 118°. A mixture of the two methyl esters has m. p. about 105°. When heated with acetyl chloride, the *p*-toluidic acids form phenylsuccino-*p*-tolil (Hann and Lapworth, *loc. cit.*).

*Phenylsuccin-β-piperidic acid*,  $\text{CO}_2\text{H} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_5\text{NH}_{10}$ , crystallises in white needles, m. p. 95°; the *silver* salt was analysed; the ester,  $\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$ , forms monoclinic crystals, m. p. 109°. The *α-piperidic acid*,  $\text{C}_{15}\text{H}_{19}\text{O}_3\text{N}$ , m. p. 165°; the *methyl* ester, m. p. 97°. A mixture of the methyl esters has m. p. 79–80°.

*Synthesis of Desylacetic and Phenylphenacylacetic Acids from Phenylsuccinic Acid.*—[With PAUL WALTER.]—*Methyl β-benzoyl-β-phenylpropionate*,  $\text{C}_{17}\text{H}_{19}\text{O}_3$ , m. p. 49°, is prepared by the action of β-methyl phenylsuccinyl chloride on benzene in presence of aluminium chloride, and on hydrolysis with potassium hydroxide yields β-benzoyl-β-phenylpropionic (desylacetic) acid (Meyer and Oelkers, *Abstr.*, 1888, 704), which is formed also by the action of phenylsuccinic anhydride on benzene in presence of aluminium chloride.

The methyl ester, obtained by the action of α-methyl succinyl chloride on benzene in presence of aluminium chloride, is identical with methyl β-benzoyl-α-phenylpropionate prepared from benzylideneacetophenone (Anschütz and Montfort, *Abstr.*, 1895, i, 179).

G. Y.

**A Product of the Action of Light on Diphenylfulgide and the Polymerisation of Phenylpropionic Acid.** HANS STOBBE [and, in part, WILLY KEDING, PHOKION NAOUM, and VICTOR VON VIGIER] (*Ber.*, 1907, 40, 3372–3382).—The colourless anhydride (*Abstr.*, 1904, i, 589), obtained by exposing a benzene solution of diphenylfulgide (dibenzylidenesuccinic anhydride) to sunlight, is identical with the anhydride obtained by the action of acetic anhydride or phosphoryl chloride on phenylpropionic acid (Michael and Bucher, *Abstr.*, 1898, i, 256; Lanser, *ibid.*, 1899, i, 916; Manthey, *ibid.*, 1901, i, 31; Lanser and Halvorsen, *ibid.*, 1902, i, 458; compare also Ruhemann and Merriman, *Trans.*, 1905, 87, 1389). This anhydride is shown to have the constitution attributed to it by Michael and Bucher, namely, 1-phenylnaphthalene-2:3-dicarboxylic anhydride, and not that suggested by Lanser, namely, diphenylcyclobutadienedicarboxylic anhydride. When oxidised with chromic anhydride in acetic acid solution, it yields *o*-benzoylbenzoic acid, a reaction which is not compatible with Lanser's formula.

Oxidation with alkaline permanganate gives rise to resinous acids, oxalic and benzoic acids, and in one experiment to a soluble acid, m. p. 200°, and in another to benzaldehyde. Diphenyltetracarboxylic acid, phthalic acid, and *o*-benzoylbenzoic acid could not be detected (compare Michael and Bucher, *loc. cit.*). Reduction with sodium amalgam converts the 1-phenylnaphthalene-2:3-dicarboxylic acid into Michael and Bucher's 1:2:3:4-tetrahydro-derivative, which melts at 204° and decomposes at 207°. Chromic acid oxidises this reduction product also to *o*-benzoylbenzoic acid. The anhydride of the tetrahydro-acid has m. p. 155°.

β-Truxillic acid, which is isomeric with the phenylnaphthalene-

dicarboxylic acid, is less readily oxidised than the naphthalene acid and yields as final product benzil.

The lactone,  $C_{18}H_{12}O_2$ , described by Michael and Bucher, could not be obtained by the action of zinc dust and acetic anhydride on the anhydride; the only product isolated was the tetrahydro-anhydride.

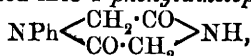
J. J. S.

**Isomeric Esters of Carbethoxyglycylglycine.** HERMANN LEUCHS and WILHELM MANASSE (*Ber.*, 1907, 40, 3235—3249).—Ethyl carbethoxyglycylglycine presents two points of interest; it exists in two apparently structurally identical forms, which, however, exhibit marked differences in chemical and physical properties, and, secondly, it yields by hydrolysis glycylglycine-*N*-carboxylic acid, which has an unusual degree of stability (Fischer, *Abstr.*, 1902, 350; 1903, 465). The authors claim that the acid obtained by hydrolysis cannot be glycylglycine-*N*-carboxylic acid, which has been synthesised by Siegfried (*Abstr.*, 1906, i, 144) and Leuchs (*ibid.*, i, 236); moreover, they assert that the isomerism of the ester is an example of lactam and lactim formation. The ester and its derivatives having the lactam formula  $CO_2Et \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$  are termed members of the  $\alpha$ -series, whilst members of the  $\beta$ -series have the lactim formula  $CO_2Et \cdot NH \cdot CH_2 \cdot C(OH) : N \cdot CH_2 \cdot CO_2Et$ . The ester of the  $\alpha$ -series undergoes transformation during hydrolysis, and yields the dicarboxylic acid of the  $\beta$ -series.

To obtain confirmation of this view, *ethyl carbethoxyglycyl-N-phenylglycine*,  $CO_2Et \cdot NH \cdot CH_2 \cdot CO \cdot NPh \cdot CH_2 \cdot CO_2Et$ , m. p. 58—59°, and *ethyl carbethoxy-N-phenylglycylglycine*,  $CO_2Et \cdot NPh \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$ , have been examined. The former, which is prepared from carbethoxyglycyl chloride and ethyl *N*-phenylglycine in dry ether at 0°, is incapable of undergoing transformation into the lactim, and consequently yields by hydrolysis the crystalline peptide, *glycyl-1-phenylglycine*,

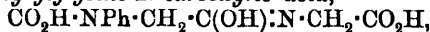


which when heated passed into 1-phenyldiketopiperazine,

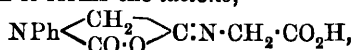


m. p. 251° (corr.); this is also obtained from chloroacetylphenylglycine and ammonium hydroxide at 100°.

*Ethyl carbethoxy-N-phenylglycylglycine* ( $\alpha$ -series), m. p. 62—63°, is prepared from carbethoxy-*N*-phenylglycyl chloride and ethyl glycine in anhydrous ether. By hydrolysis with normal sodium hydroxide, it yields *N-phenylglycylglycine-N-carboxylic acid*,

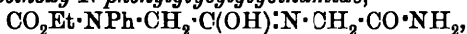


which does not lose carbon dioxide, and is the analogue of Fischer's so-called glycylglycine-*N*-carboxylic acid; it differs from the latter in the ease with which it forms the *lactone*,

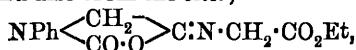


m. p. 255—256° (corr.), the change occurring slowly at the ordinary temperature, instantly on heating, or in the presence of hydrochloric acid. A similar anhydride formation is observed with the derivatives of *N*-phenylglycylglycine-*N*-carboxylic acid; thus, when ethyl carb-

ethoxy-*N*-phenylglycylglycine ( $\alpha$ -series) is treated with cold alcoholic ammonia, *carbethoxy-N-phenylglycylglycinamide*,



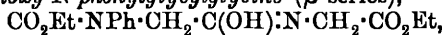
is formed, which has m. p.  $137^\circ$  (corr.), and at  $220^\circ$  evolves alcohol, forming the *lactone*,  $\text{NPh}\langle\text{CH}_2\text{CO}\cdot\text{O}\rangle\text{C}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $305^\circ$  (corr.), which is produced directly from the original ester and methyl alcoholic ammonia at  $100^\circ$ , and also from the *ester*,



m. p.  $155^\circ$  (corr.), which is prepared by esterifying the corresponding lactone-acid or its crude parent dicarboxylic acid.

The normal *silver* salt of the dicarboxylic acid,  $\text{C}_{11}\text{H}_{10}\text{O}_5\text{N}_2\text{Ag}_2$ , is obtained by heating the lactone acid,  $\text{NPh}\langle\text{CH}_2\text{CO}\cdot\text{O}\rangle\text{C}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , with sodium hydroxide on the water-bath, neutralising the solution with nitric acid, and adding silver nitrate, whereby the silver salt is precipitated. It is a voluminous, white powder, which quickly darkens in the light, and is decomposed by boiling water, silver oxide being precipitated with the formation of the *silver* salt of the lactone acid,  $\text{C}_{11}\text{H}_9\text{O}_4\text{N}_2\text{Ag}$ .

*Ethyl carbethoxy-N-phenylglycylglycine* ( $\beta$ -series),



m. p.  $107^\circ$  (corr.), prepared from the first-mentioned silver salt and ethyl iodide, differs from the isomeric ester of the  $\alpha$ -series in its tendency to form a lactone; by heating at  $220^\circ$  or with alcoholic hydrogen chloride, it loses alcohol and yields the lactone ester, m. p.  $153$ — $154^\circ$ , described previously.

The *carbethoxy-N-phenylglycyl chloride*,  $\text{CO}_2\text{Et}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{COCl}$ , used in the preparation of the ester of the  $\alpha$ -series, is obtained from carbethoxy-*N*-phenylglycine (Lumière and Barbier, Abstr., 1906, i, 245) and excess of thionyl chloride in a freezing mixture. If only the calculated quantity of thionyl chloride is employed, the main product of the reaction is *N-carboxy-N-phenylglycine anhydride*,  $\text{NPh}\langle\text{CH}_2\text{CO}\cdot\text{CO}\rangle\text{O}$ , which at

its m. p.  $142^\circ$  (corr.), loses carbon dioxide, forming an amorphous *substance*,  $(\text{NPh}\cdot\text{CH}_2\cdot\text{CO})_x$ , and is converted by alcoholic ammonia into *N*-phenylglycinamide. C. S.

**Synthesis of Alcaptonic Acids.** OTTO NEUBAUER and LEOPOLD FLATOW (*Zeitsch. physiol. Chem.*, 1907, 52, 375—398. Compare Kirk, Abstr., 1890, 188; Wolkow and Baumann, Abstr., 1891, 1128; Baumann and Fränkel, *Zeitsch. physiol. Chem.*, 1894, 20, 210; Huppert, Abstr., 1897, ii, 576; 1899, ii, 706).—Synthetical  $\alpha$ -2:5-dihydroxyphenylpropionic acid is not identical with Kirk's uroleucic acid. The synthesis consists in condensing gentisaldehyde (2:5-dihydroxybenzaldehyde) with hippuric acid, hydrolysing the condensation product with concentrated sodium hydroxide to  $\alpha$ -2:5-trihydroxycinnamic acid or the corresponding keto-form, 2:5-dihydroxyphenylpyruvic acid, and reducing this keto-acid with sodium amalgam and water.

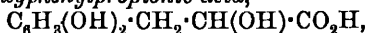
Only a small yield of gentisaldehyde is obtained by condensing quinol with chloroform in the presence of potassium hydroxide, but an excellent yield may be obtained by oxidising salicylaldehyde with potassium persulphate in the presence of sodium hydroxide, the aldehyde group remaining intact.

The condensation product obtained from hippuric acid and gentisaldehyde in the presence of acetic anhydride and sodium acetate is the *inner* anhydride of  $\alpha$ -benzoylamino-2:5-diacetoxycinnamic acid,

$\text{CO} \left\langle \begin{array}{c} \text{C}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{OAc})_2 \\ \text{N}\cdot\text{COPh} \end{array} \right\rangle$ , which forms a yellow, crystalline powder consisting of minute prisms, m. p. 190°. When hydrolysed with 40% sodium hydroxide solution in the absence of air, it yields ammonia, benzoic acid, and the *anhydride* of 2:5-dihydroxyphenylpyruvic acid,

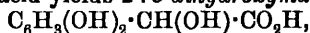
$\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ \text{CO} \text{---} \text{CO} \end{array} \right\rangle \text{CH}_2$ , which crystallises in plates containing water of crystallisation, or from boiling water in anhydrous needles, m. p. above 200°. It gives a characteristic green coloration with ferric chloride, especially in alcoholic solution; its alkaline solutions turn brown on exposure to the air, and reduce warm ammoniacal silver nitrate solution. The corresponding *acid*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , is obtained when a solution of the sodium salt is acidified, but tends to reform the anhydride, especially in faintly acid solution. With ferric chloride in 50% alcoholic solution, it yields a reddish-violet coloration, which changes to an evanescent green colour.

$\alpha$ :2:5-Trihydroxyphenylpropionic acid,



is somewhat difficult to obtain in a crystalline state, it forms well developed, colourless prisms containing  $1\frac{1}{2}\text{H}_2\text{O}$ , and has m. p. 87°.

2:5-Dihydroxycinnamic acid,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , obtained by oxidising a 5% solution of *o*-coumaric acid in excess of sodium hydroxide with a 10% solution of potassium persulphate and hydrolysing the alkyl sulphate thus formed with concentrated hydrochloric acid, has m. p. 207° (decomp.). The *anhydride* of 2:5-dihydroxyphenylpropionic acid,  $\text{C}_9\text{H}_5\text{O}_3$ , obtained in a similar manner from *o*-hydrocoumaric acid, has m. p. 163°. 2:5-Dihydroxyphenylglyoxylic acid,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , obtained from *o*-hydroxyphenylglyoxylic acid, crystallises from a mixture of ether, benzene, and light petroleum in yellow needles. When dried over sulphuric acid, or heated at 40°, or when exposed to sunlight, it is transformed into a red modification, m. p. 141°, which can be reconverted into the yellow compound by moistening with water. When reduced with sodium amalgam and water, the glyoxylic acid yields 2:5-dihydroxymandelic acid,



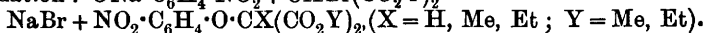
m. p. 143° (decomp.), insoluble in benzene or light petroleum; but when reduced with excess of hydriodic acid, it yields homogentisic acid (2:5-dihydroxyphenylacetic acid).

The following properties are characteristic of all these alcaptonic acids. 1. Their alkaline solutions darken on exposure to air. 2. They reduce Fehling's solution and also cold ammoniacal silver nitrate. 3. They produce a black coloration with osmic acid.

4. They do not yield precipitates with bromine water or with dilute lead acetate solution. J. J. S.

### Formation of Chains. LXX. Nitrophenoxymalonic Esters.

CARL A. BISCHOFF (*Ber.*, 1907, 40, 3134—3150. Compare Abstr., 1900, i, 442; this vol., i, 35).—Sodium *o*-, *m*-, and *p*-nitrophenoxides react with malonic esters in benzene or xylene solution, according to the equation:  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{CXBr}(\text{CO}_2\text{Y})_2 =$



A pure product has been obtained from sixteen of the eighteen possible reactions. The products of the action of sodium *o*-nitrophenoxide on methyl and ethyl bromoethylmalonate could not be isolated. In some cases, the potassium nitrophenoxides are employed in benzene or toluene solution. A table is given showing the extent, estimated by titration of the sodium bromide formed, to which the reactions take place in boiling benzene and boiling xylene, under varying conditions as to time and concentration of the ester. The reaction takes place most easily with the *m*-nitrophenoxide and  $\text{X} = \text{Me}$ , least so with the *o*-nitrophenoxide and  $\text{X} = \text{Et}$ . With  $\text{X} = \text{Et}$  and *o*- or *p*-nitrophenoxide, the difference of the reaction temperature in 0.07*N*-benzene or 0.35*N*-xylene solution has little influence on the yields, but with  $\text{X} = \text{Me}$  and *o*-nitrophenoxide, the reaction takes place to the extent of 17% in xylene, but not at all in benzene, whilst with other combinations the influence of the solvent is more marked, and with *m*-nitrophenoxide and  $\text{X} = \text{H}$ , the yields in both solvents approach the theoretical. In most cases, the group Y has little or no influence on the reaction, but with *p*-nitrophenoxide and  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{Me}$  gives an 83%, but  $\text{Y} = \text{Et}$  only a 54% yield, whilst with  $\text{X} = \text{Et}$ ,  $\text{Y} = \text{Me}$  gives a 71%, but  $\text{Y} = \text{Et}$  a 45% yield.

*Methyl bromomethylmalonate*,  $\text{C}_6\text{H}_9\text{O}_4\text{Br}$ , is a colourless oil, b. p.  $101^\circ/16$  mm.

*Methyl ethylmalonate*,  $\text{C}_7\text{H}_{12}\text{O}_4$ , is a colourless oil, b. p.  $178-179^\circ$ ,  $D_4^{20} 1.104$  (corr.). The bromo-derivative,  $\text{C}_7\text{H}_{11}\text{O}_4\text{Br}$ , is a colourless oil, b. p.  $111^\circ/16$  mm.

*Ethyl bromoethylmalonate*, b. p.  $115-119^\circ/16$  mm. ( $125^\circ/10$  mm. : Ruhemann, Abstr., 1894, i, 14).

The following nitrophenoxymalonic esters,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CX}(\text{CO}_2\text{Y})_2$ , are described.

*o*-Nitro-derivatives:  $\text{X} = \text{H}$ ,  $\text{Y} = \text{Me}$ , colourless needles, m. p.  $123^\circ$ ;  $\text{X} = \text{H}$ ,  $\text{Y} = \text{Et}$ , colourless needles, m. p.  $116-118^\circ$ ;  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{Me}$ , yellow plates, m. p.  $75-76^\circ$ ;  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{Et}$ , yellowish-brown plates, m. p.  $118-119^\circ$ .

*m*-Nitro-derivatives:  $\text{X} = \text{H}$ ,  $\text{Y} = \text{Me}$ , yellow leaflets, m. p.  $100^\circ$ ;  $\text{X} = \text{H}$ ,  $\text{Y} = \text{Et}$ , colourless leaflets, m. p.  $78^\circ$ ;  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{Me}$ , yellow prisms, m. p.  $94^\circ$ ;  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{Et}$ , a viscid oil, b. p.  $210-212^\circ/16$  mm.;  $\text{X} = \text{Et}$ ,  $\text{Y} = \text{Me}$ , yellow plates, m. p.  $95-96^\circ$ , b. p.  $234 = 236^\circ/49$  mm.;  $\text{X} = \text{Et}$ ,  $\text{Y} = \text{Et}$ , a viscid, yellow oil, b. p.  $218^\circ/25$  mm.

*p*-Nitro-derivatives:  $\text{X} = \text{H}$ ,  $\text{Y} = \text{Me}$ , yellow, monoclinic prisms, m. p.  $101^\circ$ , b. p.  $221-222^\circ/15$  mm. (slight decomp.), forms a brownish-yellow, amorphous sodium derivative,  $\text{C}_{11}\text{H}_{10}\text{O}_7\text{NNa}$ ;  $\text{X} = \text{Pr}$ ,  $\text{Y} = \text{Me}$ , white needles or plates, m. p.  $112^\circ$ ;  $\text{X} = \text{H}$ ,  $\text{Y} = \text{H}$ , white needles, decomp.  $168-170^\circ$ , forming *p*-nitrophenoxyacetic acid. On treatment

with red phosphorus, bromine, and methyl alcohol, this acid yields a substance, m. p. 89—90°, which does not form potassium bromide when boiled with alcoholic potassium hydroxide. Ethyl *p*-nitrophenoxyacetate, b. p. 203—206°/15 mm. (Kym, Abstr., 1897, i, 283), does not form a bromo-derivative at 150°. X = H, Y = Et, white needles, m. p. 86°, b. p. 241—242°/15 mm. (slight decomp.), forms a brownish-yellow sodium derivative,  $C_{13}H_{14}O_7NNa$ , and a bromo-derivative,  $C_{13}H_{14}O_7NBr$ ,

plates, m. p. 95°. X = Me, Y = Me, colourless needles, m. p. 174°; X = Me, Y = Et, needles, m. p. 141—142°; X = Et, Y = Me, white needles, m. p. 173—174°; X = Et, Y = Et, colourless needles, m. p. 142°. G. Y.

**Formation of Chains. LXXI. Bisnitrophenoxymalonic Esters, Bisnitrophenoxyethanetetracarboxylic Esters, and an Unexpected Case of Isomerism with the Former.** CARL A. BISCHOFF (*Ber.*, 1907, 40, 3150—3177. Compare Abstr., 1897, i, 267; Conrad and Brückner, Abstr., 1892, 39; Curtiss, Abstr., 1897, i, 556).—The sodium nitrophenoxides react with methyl and ethyl dibromomalonates in boiling xylene solution, forming bisnitrophenoxymalonic esters,  $C(O \cdot C_6H_4 \cdot NO_2)_2(CO_2R)_2$ . The manner in which the reaction is influenced by the position of the nitro-group, by the group R, and by the concentration of the ester is shown by the following quantitative results. The percentages are the amounts of sodium bromide formed; the concentrations are those of the esters in the xylene.

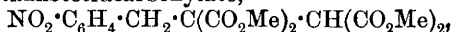
Sodium *o*-nitrophenoxide: R = Me, 0.35*N*, 25%; 0.62*N*, 32%; 2*N*, 92%; R = Et, 0.35*N*, 31%; 2*N*, 87%. *m*-Nitrophenoxide: R = Me, 0.35*N*, 91%; R = Et, 0.35*N*, 93%. *p*-Nitrophenoxide: R = Me, 0.35*N*, 88%; R = Et, 0.35*N*, 86%.

The six methyl and ethyl bisnitrophenoxymalonates have been isolated and are described. The esters of the para-series are obtained in two modifications; that melting at the higher temperature is distinguished as the A-, the other as the B-, modification. Bis-*p*-nitrophenoxymalonic acid is obtained in only one modification, which, on esterification with alcohol and hydrochloric acid, yields a mixture of the two isomeric esters. The constitutions of these are discussed and possible formulæ suggested.

Bisnitrophenoxyethanetetracarboxylic esters,

$NO_2 \cdot C_6H_4 \cdot O \cdot C(CO_2R)_2 \cdot C(CO_2R)_2 \cdot O \cdot C_6H_4 \cdot NO_2$ , are formed in small amounts by the action of bromonitrophenoxymalonic esters,  $NO_2 \cdot C_6H_4 \cdot O \cdot CBr(CO_2R)_2$ , on sodionitrophenoxymalonic esters,  $NO_2 \cdot C_6H_4 \cdot O \cdot CNa(CO_2R)_2$ , in boiling xylene, but not in alcoholic solution; the main product of the reaction in either solvent is the bisnitrophenoxymalonic ester, which is formed also by the action of iodine on the sodionitrophenoxymalonic ester. Small amounts of nitrophenoxymalonic and bisnitrophenoxymalonic esters are also formed.

Attempts to prepare methyl bis-*p*-nitrobenzylethanetetracarboxylate by the action of *p*-nitrobenzyl chloride on methyl disodioethanetetracarboxylate led to the formation of methyl *p*-nitrobenzylethanetetracarboxylate,





together with 4 : 4'-dinitrostilbene and an oil which may be *p*-nitro benzyl methyl ether.

*Methyl bis-o-nitrophenoxy-malonate*,  $C_{17}H_{14}O_{10}N_2$ , yellow needles, m. p.  $131^\circ$ . The *ethyl ester*,  $C_{19}H_{18}O_{10}N_2$ , yellow leaflets, m. p.  $119^\circ$ .

*Methyl bis-m-nitrophenoxy-malonate*, yellow prisms, m. p.  $100^\circ$ . The *ethyl ester*, yellowish-white prisms, m. p.  $72^\circ$ . These two esters decompose when distilled in a vacuum.

*Methyl chlorobromomalonate*,  $C_5H_6O_4ClBr$ , colourless leaflets, m. p.  $40-42^\circ$ .

*Methyl bis-p-nitrophenoxy-malonate* *A* crystallises in colourless needles, m. p.  $175^\circ$ . The *B-ester* crystallises in white needles, m. p.  $136^\circ$ , is more readily soluble than the *A-ester* in organic solvents, and decomposes at  $190/20$  mm. When hydrolysed with alcoholic sodium hydroxide in acetone solution at  $25^\circ$ , the two modifications have approximately the same velocity constant for the first half of the reaction. Both esters are unimolecular. On treatment with sodium methoxide in acetone solution, the *A-ester* is partially hydrolysed and partially transformed into the *B-ester*. The action of sodium on methyl bromo-*p*-nitrophenoxy-malonate in alcoholic solution leads to the formation of the *A-ester*, m. p.  $175^\circ$ , together with *methyl p-nitrophenoxy-methoxymalonate*,  $NO_2 \cdot C_6H_4 \cdot O \cdot C(CO_2Me)_2 \cdot OMe$ , which crystallises in white leaflets, m. p.  $65-67^\circ$ , b. p.  $188/12$  mm.

*Ethyl bis-p-nitrophenoxy-malonate A*,  $C_{19}H_{18}O_{10}N_2$ , hexagonal plates or needles, m. p.  $144^\circ$ . The *B-ester*, yellowish-white needles, m. p.  $119^\circ$ , more readily soluble than the *A-ester*. The *A-ester* is obtained by the action of sodium *p*-nitrophenoxide on ethyl dichloromalonate, chlorobromomalonate, dibromomalonate, or bromo-*p*-nitrophenoxy-malonate, or of ethyl sodio-*p*-nitrophenoxy-malonate on ethyl bromo-*p*-nitrophenoxy-malonate in xylene solution. A mixture of the *A*- and *B*-esters is obtained by the action of hydrogen chloride on bis-*p*-nitrophenoxy-malonic acid in alcoholic solution, or of ethyl sodio-*p*-nitrophenoxy-malonate on ethyl bromo-*p*-nitrophenoxy-malonate in alcoholic solution, or of ethereal iodine on ethyl sodio-*p*-nitrophenoxy-malonate in alcohol.

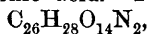
*Bis-p-nitrophenoxy-malonic acid*,  $C_{15}H_{10}O_{10}N_2$ , forms rhombohedral crystals and loses carbon dioxide at  $127-129^\circ$ , m. p.  $189^\circ$ ; the *sodium salt*,  $C_{15}H_8O_{10}N_2Na_2$ , is obtained as a white, voluminous precipitate, and has the conductivity  $\lambda_{1024} - \lambda_{32} = 32$ , whereas disodium salts of dibasic organic acids have usually the value 15 - 20. The *silver salt* forms the *A-methyl ester* when boiled with methyl iodide and benzene.

*Bis-p-nitrophenoxyacetic acid*,  $CH(O \cdot C_6H_4 \cdot NO_2)_2 \cdot CO_2H$ , formed from the malonic acid by heating at  $170^\circ$  or by prolonged boiling with water, crystallises in white needles, m. p.  $188-189^\circ$ , and when heated at  $195-200^\circ$  decomposes, forming chiefly *p*-nitrophenol. The *methyl ester*,  $C_{15}H_{12}O_8N_2$ , formed by the action of hydrogen chloride and methyl alcohol on the acid, or of iodine or methyl bromo-*p*-nitrophenoxy-malonate on methyl sodio-*p*-nitrophenoxy-malonate, or of methyl iodide on potassium *p*-nitrophenoxy-malonate in alcoholic solution, or in small amount by the action of methyl iodide on the sodiomalonate

in xylene, crystallises in prismatic needles, m. p. 146°. The *ethyl* ester,  $C_{16}H_{14}O_3N_2$ , prepared by the action of hydrogen chloride on the acid in alcoholic solution, crystallises in white needles, m. p. 137°.

Ethanetetracarboxylic esters are readily identified by conversion into the *tetra-anilide*,  $C_2(CO \cdot NPh)_4$ , which crystallises in microscopic prisms or needles, m. p. 270° (decomp.).

*Methyl bis-p-nitrophenoxyethanetetracarboxylate*,  $C_{22}H_{20}O_{14}N_2$ , crystallises in colourless leaflets or prisms, m. p. 203°, and on hydrolysis yields *p*-nitrophenol and a small amount of colourless needles, m. p. 180—181°, resembling succinic acid. The *ethyl* ester,



crystallises in yellowish-white needles, m. p. 107—109°.

*Methyl p-nitrobenzylethanetetracarboxylate*,  $C_{17}H_{19}O_{10}N$ , crystallises in slightly yellow needles, m. p. 119—120°. G. Y.

**2:6- and 2:7-Naphthalenedicarboxylic Acids.** FELIX KAUFER and OSKAR THIEN (*Ber.*, 1907, 40, 3257—3262).—The hydrolysis of the nitriles of 2:6- and of 2:7-naphthalenedicarboxylic acids by potassium hydroxide in amyl-alcoholic solution at 120° and 126° (Kaufer, *Abstr.*, 1906, ii, 424) proceeds with the greater velocity in the case of the latter. Of the nitriles of the three phthalic acids, the hydrolysis of the meta-isomeride is most rapid, and that of the para-compound least.

*Methyl 2:6-naphthalenedicarboxylate*, m. p. 191°, and *methyl 2:7-naphthalenedicarboxylate*, m. p. 135—136°, prepared from the corresponding acid chlorides and methyl alcohol, were hydrolysed at 37° by an equivalent quantity of methyl-alcoholic potassium hydroxide; the rates of hydrolysis are practically equal, the same result being observed in the hydrolysis of methyl terephthalate and methyl isophthalate under the same conditions.

The m. p.'s. of the *nitrile-carboxylic acids*, *-amides*, and *-anilides* are above 300°, with the exception of 2:7-naphthalenedicarboxydianilide, which has m. p. 297—298°. C. S.

**A Benzoylpolypeptide from Asparagine.** TAKAOKI SASAKI (*Beitr. chem. Physiol. Path.*, 1907, 10, 120—122).—Both alanine and asparagine, when heated with benzoic anhydride, yield products which give the biuret reaction, owing to the formation of polypeptides under the condensing influence of the anhydride.

Asparagine, kieselguhr, and benzoic anhydride, when heated at 110°, yield a product from which, after extraction in a Soxhlet apparatus, solution in water, and salting out, a *substance*,  $C_{19}H_{24}O_8N_6$ , has been isolated. It forms a hard mass which can be readily pulverised, decomposes at 210°, is soluble in warm water, dilute alcohol or aqueous acetone and acids or alkalis, but insoluble in dry organic solvents. It can be separated from its solutions by the addition of ammonium sulphate or zinc sulphate, and is precipitated by mercuric nitrate, ferric ammonium alum, basic lead acetate, and tannic acid, and by phosphotungstic and phosphomolybdic acids in acidified solutions. The compound probably contains one benzoyl and three asparagine residues. J. J. S.

**Lichens and their Characteristic Constituents. XI.** OSWALD HESSE (*J. pr. Chem.*, 1907, [ii], **76**, 1—57. Compare Abstr., 1906, i, 280).—The lichens treated of in the latter parts of this investigation have been extracted successively with ether and almost boiling acetone, or, in some cases, chloroform, without preliminary pulverisation.

*Usnea articulata* var. *intestiformis*, from East Indian cinchona bark, contains *d*-usnic acid, about 1% of barbatic acid, and *articulatic acid*,  $C_{18}H_{16}O_{10}$ (?), which crystallises in colourless leaflets, sinters at  $260^{\circ}$ , becoming black, has a bitter flavour, gives a brownish-red coloration with alcoholic ferric chloride, and dissolves in alkalis, alkali carbonates, or concentrated sulphuric acid, forming yellow solutions gradually becoming reddish- or dark brown; it differs from protocetraric and ramalic acids in not giving a coloration when heated with alcohol and small amounts of sulphuric acid.

*Ramalina armorica* contains atranorin, 0.9% of armoricaic acid, and 1.4% of armoric acid.

*Armoricaic acid* crystallises from alcohol or glacial acetic acid in microscopic needles, decomp.  $240$ — $260^{\circ}$ , has an intensely bitter flavour, reddens blue litmus, gives a brownish-red coloration with alcoholic ferric chloride, dissolves in alkalis, forming yellow solutions which gradually become red, and gives with hot concentrated sulphuric acid a reddish-brown coloration, becoming purple and finally dark red.

*Armoric acid*,  $C_{18}H_{18}O_7 \cdot H_2O$ , crystallises in long leaflets, loses  $H_2O$  at  $100^{\circ}$ , m. p.  $226$ — $228^{\circ}$  (decomp.), gives with alcoholic ferric chloride a bluish-violet, or with hot concentrated sulphuric acid an intense green, coloration, and when boiled with aqueous baryta yields betorcinol and evernic acid.

Evernic acid, m. p.  $200^{\circ}$  ( $191$ — $192^{\circ}$ : Abstr., 1903, i, 702), which, contrary to Zopf's statement, is not identical with physodic acid, has been obtained in varying amounts from eight specimens of *Evernia furfuracea* var. *ceratea*; the amorphous *triacetate*,  $C_{24}H_{23}O_9Ac_3$ , has m. p.  $66$ — $68^{\circ}$ . This lichen contains also physodylic acid and a substance, probably Zopf's supposed furfuracic acid, which is decolorised by animal charcoal in ethereal solution, and yields a white, crystalline acid, m. p.  $118^{\circ}$ , resembling furevernic acid and hence termed *furevernic acid*.

*Physodylic acid*,  $C_{23}H_{26}O_8$ , crystallises in white needles, m. p.  $192^{\circ}$ , is tasteless, has an acid reaction in alcoholic solution, gives a bluish-green coloration with ferric chloride, forms colourless alkaline solutions, which rapidly become yellow and finally reddish-brown, is decomposed when heated with hydrogen iodide, D 1.7, and yields a red, amorphous potassium salt. A brown, amorphous modification of the acid is obtained by evaporation of the aqueous solution of the potassium salt at  $30^{\circ}$ . When boiled with aqueous baryta, the acid forms barium carbonate and amorphous *physodol*,  $C_{22}H_{26}O_6$ , m. p. above  $120^{\circ}$ , which in alcoholic solution gives with ferric chloride a violet, or with calcium hypochlorite a dark red, coloration. Acetylation of the acid leads to the formation of *diacetylphysodic acid*,  $C_{23}H_{22}O_7Ac_2$ , white needles, m. p.  $158^{\circ}$ , and *triacetylphysodic acid*,  $C_{23}H_{21}O_7Ac_3$ , m. p.  $74^{\circ}$ . Physodic acid,  $C_{23}H_{24}O_7$ , is considered to be physodylic anhydride.

*Parmelia physodes* var. *vulgaris* has been reinvestigated and found

to contain evernuric, physodylic, and capraric acids and traces of atranorin, but not physodic acid or physol (compare Abstr., 1898, i, 680; Zopf, Abstr., 1897, i, 436).

*Menegazzia pertusa* (*Parmelia pertusa*) contains atranorin and small amounts of a white crystalline substance, which is insoluble in potassium carbonate, and of amorphous farinacic acid; capraric and physodic acids (Zopf, Abstr., 1898, i, 489) were not obtained. The crystalline acid, m. p. 198°, obtained from this lichen by Zopf (*loc. cit.*), could not be physodic acid, as it gave a violet coloration with ferric chloride, but was probably farinacic acid.

Zopf's destrictic acid (Abstr., 1903, i, 763) is found to be an alkaline derivative of the pigment of *Cladonia destricta*; a small amount of blue crystals, obtained from the chloroform solution, consisted of an unstable compound of the pigment with a substance which might be squamatic acid.

*Cladonia rangiferina* var. *silvatica* (*Cladonia A silvatica*), gathered at a height of about 2400 m. on the Vorarlberg, contains *d*-usnic and *silvatic* acids, but not *l*-usnic, protocetraric, or fumarprotocetraric acids (compare Abstr., 1898, i, 533; 1899, i, 381; Widman, Abstr., 1900, i, 235; Zopf, Abstr., 1906, i, 672).

*Silvatic acid*,  $\text{CO}_2\text{Me} \cdot \text{C}_{18}\text{H}_{34}\text{O}_8 \cdot \text{CO}_2\text{H}$ , crystallises in needles, m. p. 100—102°, and forms a crystalline potassium salt. *Norsilvatic acid*,  $\text{C}_{20}\text{H}_{36}\text{O}_7$ , formed together with methyl iodide when silvatic acid is heated with hydrogen iodide, D 1.7, is obtained as a white, crystalline powder, m. p. 109°, forms amorphous salts, and on prolonged heating at 60—80° is converted partially into an acid crystallising in needles, m. p. 128°.

*Cetraria islandica* contains, in addition to protolichesteric,  $[\alpha]_D^{20} + 22.7^\circ$ , and proto-*a*-lichesteric acids, an acid containing smaller percentages of carbon and hydrogen. The same lichen, from above the tree limit in Osterdalen in Norway, contains proto-*a*-lichesteric, but not protolichesteric, acid. When boiled with aqueous baryta, protolichesteric acid yields barium carbonate and a substance, m. p. 280—285° (decomp.), which on solution in glacial acetic acid is converted into an acid, crystallising in needles, m. p. 100—101°.

Physcion is contained in *Tornabenia chrysophthalma*, from the neighbourhood of Heidelberg, and *T. flavicans* var. *crocea*, from Lindi, German East Africa.

*T. flavicans* var. *acromela* (*Physcia acromela*), from Amani, German East Africa, contains *acromelin* and *acromelidin*. *T. flavicans* var. *cinerascens*, from Amani, and *T. flavicans*, from East Usambara, which is identical with *Teloschistes flavicans* from Brittany, contain physcion and acromelin.

*Acromelin*,  $\text{C}_{17}\text{H}_{16}\text{O}_9$ , is a lactone; it crystallises in colourless needles, m. p. 242°, is converted slowly by potassium hydroxide into a gelatinous potassium salt of the corresponding acid, forms barium carbonate on prolonged boiling with aqueous baryta, is reduced by hydrogen iodide, D 1.7, to a brown flocculent substance, and on treatment with hot concentrated sulphuric acid forms a blackish-brown, amorphous substance, which dissolves to a greenish-blue solution. *isoAcromelin*,

$C_{17}H_{16}O_9$ , formed on heating acromelin with acetic anhydride, crystallises in colourless leaflets, m. p.  $188^\circ$ , and, when boiled with aqueous baryta, yields *acromelol*,  $C_{16}H_{18}O_8$ , crystallising in colourless prisms, m. p.  $134^\circ$ .

*Acromelidin*,  $C_{19}H_{20}O_9$ , forms slightly yellow, granular crystals, m. p.  $162^\circ$ , and gives with alkalis a rose-red, or with hot concentrated sulphuric acid a greenish-blue, coloration.

*Physcia leucomelas*, from Amani, contains atranorin and an acid, which crystallises in leaflets, m. p.  $175^\circ$ , and gives a brownish-red coloration with alcoholic ferric chloride.

The occurrence of lecanoric acid in *Urceolaria scruposa* var. *vulgaris* is confirmed. Zopf's diploschistessic acid (Abstr., 1906, i, 672) is considered to be a mixture of 80% of lecanoric acid and 20% of an acid, which gives a blue coloration with calcium hydroxide and for which it is suggested Weigelt's term patellaric acid may be retained.

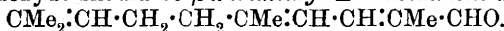
*Hämatomma coccineum* var. *abortivum* does not contain zeorin. Small amounts of lecanoric acid, obtained from *Hämatomma coccineum* var. (?) (Abstr., 1906, i, 281), may have been derived from an admixture of the sterile lichen which could not be avoided entirely.

*Biatora lucida* contains atranorin in addition to the rhizocarpic acid found by Zopf.

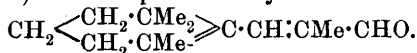
*Rhizocarpon geographicum* (L.) DC. f. *geronticum*, from Rossegal in the Engadine, contains parellic and rhizocarpic acids, but not rhizocarpic acid (Abstr., 1899, i, 384). Ethyl norrhizocarpate,  $C_{24}H_{16}O_3(CO_2Et)_2$ , m. p.  $171^\circ$  ( $159^\circ$ : loc. cit.). The rhizocarpic acid, m. p.  $170^\circ$ , referred to by Zopf (Abstr., 1906, i, 672), had been shown to be non-existent before the description under the same name of the acid, m. p.  $156^\circ$  (Abstr., 1899, i, 384). G. Y.

### Synthesis of an Aldehyde with the Odour of Violets.

*$\beta$ -cycloCitralidenepropenal*. PHILIPPE BARBIER (*Compt. rend.*, 1907, 144, 1442—1443).—By treating an aqueous alcoholic solution of citral and propaldehyde in molecular proportions with dilute soda, an odourless, oily liquid is obtained, which can be separated into two fractions: (1) b. p.  $147\text{--}148^\circ/13$  mm., and (2) b. p.  $158\text{--}160^\circ/13$  mm., having the same composition,  $C_{13}H_{20}O$ . From the method of formation, the resulting aldehyde should be  *$\beta$ -tri-methyl- $\Delta^{8,9}$ -decatriene  $\alpha$ -al*,



By dissolving the latter in 60% sulphuric acid, heating at  $50\text{--}60^\circ$  for a few minutes, and pouring on to ice, an oily liquid is formed, which also can be separated into two fractions, both of the same composition. The constitution of the cyclic aldehydes ( *$\beta$ -cyclo-citralidenepropenal*) can be represented by the formula

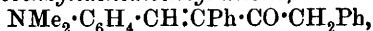


They have an intense odour of freshly-gathered violets. The two fractions give two *semicarbazones*, one forming crystals, m. p.  $174\text{--}175^\circ$ , the other viscous. The aldehydes have no commercial value, owing to the rapidity with which they oxidise.

E. H.

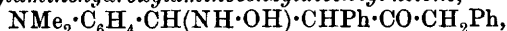
**Condensation of *p*-Dimethylaminobenzaldehyde with Dibenzyl Ketone and Phenylacetone.** ERNST MAYERHOFER (*Monatsh.*, 1907, 28, 589—604. Compare Schimetschek, *Abstr.*, 1906, i, 368).—Both dibenzyl ketone and phenylacetone condense with *p*-dimethylaminobenzaldehyde under the influence of hydrogen chloride in benzene solution with the formation, in each case, of two unsaturated ketones.

*p*-Dimethylaminobenzylidenedibenzyl ketone,



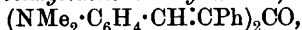
crystallises in brilliant, canary-yellow, prismatic needles, m. p. 118—119°; the *hydrochloride* forms colourless crystals; the *dibromide* could not be obtained in a crystalline form. The *oxime*,  $\text{C}_{24}\text{H}_{24}\text{ON}_2$ , prepared by the action of hydroxylamine hydrochloride on the ketone, crystallises in almost pure, white needles, m. p. 184—185°; it does not reduce Fehling's solution.

*p*-Dimethylaminohydroxylaminobenzylidibenzyl ketone,



is obtained by treating the ketone with hydroxylamine hydrochloride in the presence of sodium acetate; it crystallises in almost white needles, m. p. 156° (decomp.), and reduces Fehling's solution.

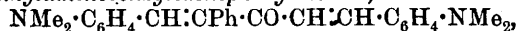
*Di-p*-dimethylaminobenzylidenedibenzyl ketone,



forms greenish-yellow crystals, m. p. 211°; the *hydrochloride* forms colourless crystals. This ketone does not give an oxime.

*p*-Dimethylaminobenzylidenephénylacetone forms yellow crystals, m. p. 70—71°; it could not be determined whether it has the formula  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{COMe}$  or  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ ; the *hydrochloride* is colourless. The ketone is decomposed on treatment with bromine in chloroform solution, probably into acetyl bromide and *p*-dimethylaminobromostilbene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPhBr}$ , obtained as light yellow crystals, m. p. 98—92°. The *oxime*,  $\text{C}_{18}\text{H}_{20}\text{ON}_2$ , crystallises in brilliant, white needles, m. p. 181—182°; it does not reduce Fehling's solution.

*Di-p*-dimethylaminobenzylidenephénylacetone,



forms yellow crystals, m. p. 225·5°; the *hydrochloride* is colourless. An oxime could not be prepared.

W. H. G.

**cycloNonanone and cycloNonane.** NICOLAI D. ZELINSKY (*Ber.*, 1907, 40, 3277—3279).—Dry distillation of sebacic acid yields in small quantities *cyclononanone*,  $\text{C}_9\text{H}_{16}\text{O}$ , an oil, b. p. 95—97°/17—18 mm.,  $D_4^{25}$  0·8665,  $n_D^{25}$  1·4412, and volatile in steam; the *semi-carbazone*,  $\text{C}_{10}\text{H}_{19}\text{ON}_3$ , has m. p. 105°. On reduction of the ketone by sodium, conversion into iodide, and reduction of the iodide by zinc, *cyclononane*,  $\text{C}_9\text{H}_{18}$ , is obtained as an oil, b. p. 170—172°,  $D_4^{18}$  0·7733,  $n_D^{18}$  1·4328. The molecular refraction of these two compounds is higher than the calculated value, owing to the ring formation.

W. R.

**Terpene and Benzoic Acid.** PIETRO CESARIS (*Boll. chim. farm.*, 1907, 46, 495—496).—On dissolving terpene and benzoic acid in molecular proportions in an excess of boiling water, the solution

deposits a readily volatile *substance* in broad, rectangular, shining plates, m. p.  $97^{\circ}$ ; it has an aromatic odour and a sweetish taste, and dissolves in alcohol (6 : 100), glycerol or chloroform (0.05 : 5), and, to a slight extent, in ether (0.01 : 15). It gives no characteristic reaction with sulphuric, hydrochloric, or nitric acid or ferric chloride.

T. H. P.

**Constituents of Ethereal Oils. The Sesquiterpenes Present in East Indian Sandal-Wood Oil.** FRIEDRICH W. SEMMLER (*Ber.*, 1907, 40, 3321—3224. Compare this vol., i, 714; also von Soden and Müller, *Abstr.*, 1899, i, 924; Guerbet, *Abstr.*, 1900, i, 242, 401).— $\alpha$ -Santalene has b. p.  $118\text{--}120^{\circ}/9$  mm.,  $D^{20}$  0.8984,  $n_D$  1.491,  $a_D$   $-15^{\circ}$  (100 mm.).  $\beta$ -Santalene has b. p.  $125\text{--}127^{\circ}/9$  mm.,  $D^{20}$  0.892,  $n_D$  1.4932, and  $a_D$   $-35^{\circ}$ . These properties correspond closely with those of the  $\alpha$ - and  $\beta$ -santalols.

When oxidised with ozone in benzene solution,  $\alpha$ -santalene yields *tricycloeksantaldehyde* (this vol., i, 431), and the nitrile of *tricycloeksantalic acid* (*loc. cit.*), when reduced with sodium and alcohol, yields *tricycloeksantalamine*,  $C_{11}H_{17}\cdot NH_2$ . This has b. p.  $113\text{--}116^{\circ}/9$  mm.,  $D^{20}$  0.94,  $n_D$  1.4895, and  $a_D$   $+4^{\circ}30'$  (100 mm.). The *picrate*,  $C_{11}H_{17}NH_2\cdot C_6H_3O_7N_3$ , has m. p.  $183\text{--}184^{\circ}$ .

$\beta$ -Santalene, when oxidised in a similar manner, yields an aldehyde from which *dicycloeksantalic acid*, m. p.  $64^{\circ}$  (this vol., i, 432), has been obtained.

J. J. S.

**Ethereal Oils.** HEINRICH HAENSEL (*Chem. Zentr.*, 1907, i, 1332; from *Geschäftsber.*, March, 1907. Compare *Abstr.*, 1906, i, 524).—Traces of an aldehyde have been found in a rhododendron oil, which has  $D^{18}$  0.8620,  $a_D^{18}$   $-4.33^{\circ}$ ; the saponification number of the oil from which the aldehyde has been removed is 20.5, and that of the acetyl derivative, 36.2. The fraction of b. p.  $150\text{--}160^{\circ}/742$  mm. yields a small quantity of a nitrosochloride of m. p.  $102\text{--}103^{\circ}$ , which does not react with piperidine or benzylamine. Cineol could not be detected in the oil.

A sample of camomile oil, which has  $D^{15}$  0.9368, acid number, 24.2, and saponification number, 55.7 (acetyl derivative, 117.7), contains nonolic acid, but neither aldehydes nor phenols. The oil boils at  $100\text{--}250^{\circ}/10\text{--}12$  mm. and forms a considerable quantity of resin. None of the fractions appear to contain alcoholic substances.

*Grindelia* oil, prepared from *Grindelia robusta*, is brown and has a strong odour; it has  $D^{15}$  0.9582,  $a_D$   $-8.08^{\circ}$  in alcoholic solution, saponification number, 75.1 (acetyl derivative, 162.1), and contains borneol and about 8% of a brown oil which has the character of a phenol.

German curled mint oil contains *l*-carvone, dipentene, and cineol.

Opoponax oil is greenish-yellow and has a strong, persistent odour; it has  $D^{15}$  0.9154,  $a_D$   $-13.94^{\circ}$ , acid number, 2.7, saponification number, 17.3 (acetyl derivative 75.6), and b. p.  $80\text{--}195^{\circ}/16$  mm. Attempts to isolate alcoholic substances failed.

Heptoic acid has been detected in parsnip oil and butyric acid is probably present.

E. W. W.

**Ethereal Oils.** SCHIMMEL & Co. (*Chem. Zentr.*, 1907, i, 1413—1414; from *Geschäftsber.*, April, 1907. Compare Abstr., 1906, i, 524).—Ayapana oil or essence d'Ayapana, prepared from *Eupatorium triplinerve*, is pale green and has a peculiar odour;  $D^{15}$  0.9808,  $n_D + 3^\circ 10'$ , ester number, 8.0 (acetyl derivative, 23.4), and consists mainly of a homogeneous substance, which has b. p.  $237^\circ$ — $238^\circ/750$  mm. and  $D^{15}$  0.9891. The latter compound is attacked by potassium permanganate with difficulty, yielding an acid of m. p.  $93^\circ$ .

Oil of cassia flowers, prepared from a French extract, has  $D^{15}$  1.0575,  $n_D - 0^\circ 30'$ ,  $n_D^{20}$  1.51500, acid number, 25.4, and ester number, 22.9.

The constants quoted for the sesquiterpene alcohol from copaiva oil (Abstr., 1906, i, 524) correspond with those of the hydrocarbon obtained from the alcohol by the action of formic acid.

A fraction of elemi oil, which had  $D^{15}$  1.025,  $n_D + 2^\circ 15'$ , and saponification number, 2.8 (acetyl derivative, 81.4), yielded a fraction which probably consisted of alcohols; the acetyl derivative had the odour of curled mint oil, but did not appear to contain the acetate of dihydrocumin alcohol. By the action of concentrated formic acid on the higher fractions of b. p.  $277^\circ$ — $278^\circ$ , a hydrocarbon is obtained, which on oxidation with potassium permanganate yields an acid,  $C_{12}H_{16}O_6$ , of m. p.  $167.5^\circ$ — $169^\circ$ . The acid crystallised from dilute alcohol in needles and from benzene in prisms; silver salt, m. p.  $192^\circ$ — $193^\circ$ . Rectified fir-cone oil, prepared from cones of *Picea excelsa*, is greenish-yellow and has a stale and somewhat musty odour; it has  $D^{15}$  0.8743,  $n_D - 1^\circ 15'$ , acid number, 1.8, ester number, 3.9, corresponding with 1.4% bornyl acetate.

The components of iris oil, which are more volatile than irone, form a golden-yellow oil which has an unpleasant basic odour somewhat resembling that of scatole. The oil contains furfuraldehyde, decaldehyde, nonaldehyde, naphthalene, a terpene of  $D^{15}$  0.8611,  $n_D + 10^\circ 40'$ , a ketone,  $C_{10}H_{18}O$ , which has an odour resembling that of mint (*semicarbazone*, m. p.  $217^\circ$ — $218^\circ$ ), and traces of a base, a phenol, and of an alcohol which reacts with phthalic acid. The oleic acid aldehyde which Tiemann and Krüger found in iris oil, prepared by extraction, is not contained in the distilled oil. The aldehyde, prepared by distilling calcium oleate and formate, has a rather faint odour and, on cooling, forms a wax-like mass; it has b. p.  $168^\circ$ — $169^\circ/3$ — $4$  mm.,  $D^{15}$  0.8513,  $n_D^{20}$  1.45571, and yields a semicarbazone of m. p.  $87^\circ$ — $89^\circ$ .

The composition of kuromoji oil is somewhat variable, probably because different samples are prepared from different portions of the plant; it has  $D^{15}$  0.8942,  $n_D - 7^\circ 35'$ , and ester number, 27.3, and is a slightly yellow oil with an odour similar to that of coriander; it contains terpenes, cineol, linalool, and geraniol, the last being present mainly in the form of the acetate.

Experiments on the distillation of lavender oil have shown that when the best yield is obtained by using fresh flowers and distilling as rapidly as possible in steam, the oil is richest in esters, and also differs from the ordinary oil in other properties.

The oil from *Mentha rotundifolia* is dark orange yellow, and has a faint musty odour somewhat like that of curled mint; it has



D<sup>15</sup> 0.9777,  $\alpha_D$  -37°30', acid number, 1.5, and ester number, 71.2 (acetyl derivative, 209).

Myrtle oil, on distillation, yields pinene and a hydrocarbon which behaves like camphene.

Two samples of origanum oil, from Cyprus, had D<sup>15</sup> 0.9624, 0.9655,  $\alpha_D$  +0°20', 0°, and contained 77% and 70% of phenol respectively; a Syrian oil had D<sup>15</sup> 0.936—0.960,  $\alpha_D$  0 to +1°35', and contained 65—72% of phenol, and corresponded with the ordinary Spanish hop oil.

Thyme lemon oil is orange-yellow and has the odour of lemon oil with a slight admixture of thyme oil; it has D<sup>15</sup> 0.9085,  $\alpha_D$  +9°45'.

Vetiver oil, from E. African roots, is identical with that obtained from other sources, and forms a brown oil which has a strong odour; it has D<sup>15</sup> 1.0166,  $\alpha_D$  +36°35', acid number, 40, and ester number, 22.8.

The rotatory power of juniper oil, distilled from berries and needles, differs from that of the ordinary oil; it has D<sup>15</sup> 0.8675,  $\alpha_D$  +8°46', and ester number, 11.4.

The following new oils are described. A yellowish-green ethereal oil from *Xanthoxylum aubertia* (*Evodia aubertia* of Cordemoy; *Rutaceæ*), from Réunion, has a distinct odour of parsley, but does not contain phellandrene; it has D<sup>15</sup> 0.9052,  $\alpha_D$  -62°10', acid number, 1.3, and ester number, 7.3 (acetyl derivative, 51). The properties of a second sample, which had a similar odour, very closely resembled those of the oil from *Evodia simplex* (*loc. cit.*); it had D<sup>15</sup> 0.9708,  $\alpha_D$  -19°20', acid number, 1.1, and ester number, 8.7 (acetyl derivative, 33).

A sample of pilea oil had a green tinge and was considerably more dextrorotatory than that previously described (*loc. cit.*), but resembled it in other properties; it had D<sup>15</sup> 0.8520,  $\alpha_D$  +58°20',  $n_D^{20}$  1.46902, acid number, 0, and ester number, 7.7 (acetyl derivative, 34.4). A pale yellow ethereal oil has been obtained by distilling the buds of black currants (*Ribes nigrum*); it had D<sup>15</sup> 0.8741,  $\alpha_D$  +2°30',  $n_D^{20}$  1.48585, acid number, 0, and ester number, 5.6. The odour of the oil suggested the presence of cymene. E. W. W.

**Lupeol.** ÉMILE JUNGFLAISCH and HENRI LEROUX (*Compt. rend.*, 1907, 144, 1435—1437. Compare Abstr., 1906, i, 525).—From the gutta-percha of *Palaquium Treubi*, the authors have isolated a substance crystallising in monoclinic needles (Wyruboff), having  $\alpha_D$  +50.0° in a 1% solution in chloroform, apparently identical with the lupeol cinnamate found by van Romburgh in other guttas (Abstr., 1904, i, 905). The lupeol obtained from it, when heated gradually on the Maquenne block, melts at 212°, but when thrown suddenly on the heated block it melts at 190—192°, quickly resolidifies, and on continued heating re-melts at 212°. This behaviour, which explains the difference in melting points observed by different authors, is due to the lupeol losing water and forming a hydrocarbon. The lupeol has m. p. 190—192°, whilst the hydrocarbon, *lupeylene*, which crystallises in fine needles, has m. p. 212°, and  $\alpha_D$  24.57°. The dehydration of lupeol occurs slowly at 130°, but very rapidly at 150—160°, and this is probably the explanation of the fact that Likiernik (Abstr., 1891, 551, 1446) and later Cohen (this vol., i, 211) obtained an acetate,

m. p. 223°, and a monobromo-derivative, m. p. 185°, whilst Sack and Tollens (Abstr., 1904, i, 1011), who were probably dealing with lupeylene, failed to obtain an acetate and obtained a dibromo-derivative, m. p. 154°. By the action of bromine on lupeol, the authors obtained Likiernik's monobromo-derivative, with evolution of hydrogen bromide, whilst from lupeylene they obtained Sack and Tollens' dibromo-derivative, m. p. 160°, without evolution of hydrogen bromide. Instead of the formula  $C_{26}H_{42}O$ , suggested by Likiernik, or  $C_{31}H_{50}O$ , proposed by Cohen, for lupeol, the authors suggest the formula  $C_{30}H_{50}O$ , identical with that of the amyrins and paltreubin. This is supported by the molecular weight of lupeol, 406—412, and of its cinnamate, 540—543.

The lupeol isolated from bresk or djetulung is also decomposed by heat into water and hydrocarbon. E. H.

**Isomerism of the Hydrogen Cyanide Glucosides, Sambunigrin and Prulaurasin.** ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm. Chim.*, 1907, [vi], 26, 5—12).—The authors discuss the isomerism of (1) amygdalin and *iso*amygdalin and (2) Fischer's mandelonitrile glucoside, prulaurasin, and sambunigrin.

When treated with concentrated hydrochloric acid, amygdalin yields ammonia, dextrose, and *l*-mandelic acid, whilst with *iso*amygdalin, *r*-mandelic acid is obtained.

Dunstan and Henry (*Brit. Ass. Rep.*, 1906) stated that the differences between the three mandelonitrile glucosides, assuming that they are different, lie probably in the nature of the residual sugars. It had, however, previously been shown that the three glucosides are chemically distinct individuals and that the sugar yielded by sambunigrin (Bourquetot and Danjou, Abstr., 1903, i, 912) and by prulaurasin (Hérissey, Abstr., 1906, i, 31) is identical with dextrose. The authors show that, when hydrolysed by hydrochloric acid, Fischer's mandelonitrile glucoside yields *l*-mandelic acid, whilst sambunigrin gives *d*-mandelic acid. They find also that, when sambunigrin is racemised by the action of a small quantity of barium hydroxide solution, it is converted into prulaurasin, which, when hydrolysed with hydrochloric acid, yields *r*-mandelic acid.

T. H. P.

**Chlorophyll. III. Action of Acids and Alkalis on Chlorophyll.** RICHARD WILLSTATTER and FERDINAND HOCHEDER (*Annalen*, 1907, 354, 205—258. Compare this vol., i, 69, 71).—Chlorophyll is a complex magnesium compound. The authors have been able, by treatment of alcoholic solutions of chlorophyll with the calculated amount of oxalic acid, to remove the magnesium quantitatively and to obtain for the first time an ashless compound closely related to chlorophyll. This derivative is an *ester*, termed *phaeophytin*, and is hydrolysed readily by alkalis, yielding an unsaturated alcohol, *phytol*,  $C_{20}H_{40}O$ , which is formed also by the action of alkalis on chlorophyll. For the hypothetical saturated hydrocarbon, corresponding with this alcohol, the authors propose the name *phytane*, and for the coloured,

nitrogenous nucleus of chlorophyll, the name *phytochromin*; the phytochlorins and phytorhodins are phytochromin derivatives.

*Phaeophytin* is obtained in nearly quantitative yields as an almost black, wax-like substance, or occasionally in needles, m. p. 133—138° (decomp.), evolves a vapour with an odour of tobacco when strongly heated, can be purified by solution in boiling alcohol, from which it separates on cooling, is dark olive-brown with a slight red fluorescence in solution, and resembles chlorophyll in forming green to blue complex salts when treated with zinc, copper, or ferric acetate in glacial acetic acid solution; the zinc and ferric salts are fluorescent. *Phaeophytin* is an indifferent substance, and does not react with alkalis or dilute mineral acids in ethereal solution, but is decomposed in ethereal solution by 30% sulphuric acid, or when solid by concentrated acids, gives a blue coloration with concentrated nitric acid in ethereal or glacial acetic acid solution, forms an intense green solution with bromine in chloroform, and has a characteristic absorption spectrum. The composition of *phaeophytin* varies slightly with the source of the chlorophyll and the time of year at which the leaves are gathered; it yields about 30% of its weight of phytol, and has an equivalent weight of 219—230, calculated from its percentage of nitrogen. From these results, the molecular formula is calculated to be approximately  $C_{50}H_{70}O_5N_4$ ,  $C_{54}H_{72}O_5N_4$ , or  $C_{56}H_{76}O_6N_4$ .

The identity of the chlorophylls from different plants is questioned, and it is concluded that there is not one chlorophyll, but a group of similar substances differing in the phytochromin nucleus.

The hydrolysis of *phaeophytin* leads to the formation of phytol together with phytochlorins and phytorhodins, which have been isolated in the manner described previously. *Phaeophytin*, obtained from the stinging nettle, yields on hydrolysis with hot concentrated hydrochloric acid a phytorhodin (7), or with cold concentrated hydrochloric acid chiefly a phytochlorin (11) together with a phytochlorin (17), or with hot alcoholic potassium hydroxide, phytochlorins (1, 3, and 11) together with small amounts of a phytorhodin (7) and more feebly basic substances (13 and 20). The numbers given in brackets are the percentage strengths of the hydrochloric acid by which the bases are extracted from their solutions in ether.

*Phaeophytin*, obtained from grass, yields on hydrolysis chiefly *phytochlorin e* and *phytorhodin g*, whilst that from green algae yields *phytochlorin f* and *phytorhodin h*.

*Phytochlorin e*,  $C_{30}H_{32}O_4N_4$ , is extracted from its ethereal solution by 3% hydrochloric acid when freshly prepared, but by 12% acid after being dried; it forms black, microcrystalline aggregates, does not melt at 300°, is soluble in acids or alkalis, forming coloured solutions, and yields an intense green *copper* compound with copper acetate in glacial acetic acid solution.

*Phytochlorin f*,  $C_{31}H_{32}O_4N_4$ , is extracted from ether by 12% hydrochloric acid; it crystallises in black plates, is green by transmitted light, sinters and decomposes at 265—270°, and when dried is dissolved only by 17—20% acid, but regains its colour and basicity on solution.

*Phytorhodin g*,  $C_{30}H_{33}O_6N_4$ , crystallises in stout, dark red prisms, commences to sinter at 250°, does not melt, is soluble in ammonia or

dilute acids, forming coloured solutions, and is extracted from its ethereal solution by 9%, but is dissolved when dry only by 17—20%, hydrochloric acid.

*Phytorhodin h* is extracted from its ethereal solution by 4.5% hydrochloric acid, and crystallises in bluish-black, microscopic rosettes.

*Phytol*,  $C_{20}H_{40}O$  ( $C_{19}H_{38}O?$ ), is a colourless oil, b. p.  $145^{\circ}/0.03$  mm., commences to decompose at  $150$ — $160^{\circ}$ ,  $D_4^0$  0.864,  $D_4^{20}$  0.852, and has a slight characteristic odour; the crude substance has  $[\alpha]_D^{20} + 0.79^{\circ}$ , but after distillation is optically inactive. It is not reduced by sodium and alcohol, reduces potassium permanganate, forms an oily *additive* compound, together with traces of a crystalline *additive* compound, with 1 mol. of bromine in chloroform solution at  $0^{\circ}$ , yields small amounts of hydrogen bromide with an excess of bromine, and, when heated with phthalic anhydride at  $170$ — $180^{\circ}$ , forms phthalic acid, and an *oil*, which is only sparingly soluble in methyl alcohol, is formed also by heating phytol with glacial acetic acid at  $200^{\circ}$ , and contains various high molecular, oxygenated compounds.

Phytol esterifies, by Menshutkin's method (Abstr., 1879, 36, 215), 65.6% of acetic acid in 144 hours at  $98^{\circ}$ , but only 36.2% in one hour at  $155^{\circ}$ , the yield diminishing on longer heating at the higher temperature. Under the same conditions, cetyl alcohol esterifies 47.8% of acetic acid in one and a quarter hours, and 75.7% in 145 hours at  $155^{\circ}$ . These results are compared with those obtained by Menshutkin for octyl and allyl alcohols, and are considered to show that phytol is a primary alcohol of the ethylene series.

The *sodium* derivative of phytol,  $C_{20}H_{39}ONa$ , differs from those of cetyl alcohol and cholesterol in that it is soluble in ether; it reacts with *p*-nitrobenzoyl chloride in ethereal solution forming *p*-nitrobenzoic anhydride. The *phenylurethane*,  $C_{20}H_{39}O \cdot CO \cdot NHPh$ , crystallises in colourless prisms, m. p.  $25.8$ — $28.8^{\circ}$ . The  *$\alpha$ -naphthylurethane*,  $C_{20}H_{39}O \cdot CO \cdot NH \cdot C_{10}H_7$ , formed together with small amounts of di- *$\alpha$ -naphthylcarbamide* by the action of phytol on  *$\alpha$ -naphthylcarbimide*, crystallises in colourless needles, m. p.  $23.5$ — $29.5^{\circ}$ . On oxidation with chromic acid, phytol yields an indifferent, viscid *oil*,  $C_{20}H_{38}O_2$ , and an oily *lactone-acid*,  $C_{20}H_{34}O_3$ , which forms a sparingly soluble, crystalline *barium* salt.

*Phytene*,  $C_{20}H_{40}$ , formed by reduction of phytol with hydrogen iodide in glacial acetic acid solution at the ordinary temperature, is obtained as a colourless, odourless, mobile *oil*, b. p.  $106.5$ — $108^{\circ}/0.04$ — $0.05$  mm. or  $167$ — $168^{\circ}/7.5$  mm.,  $D_4^0$  0.817, reduces potassium permanganate slowly in glacial acetic acid solution, and forms an *additive* compound with 1 mol. of bromine.

The residues obtained on distillation of crude phytol, obtained from grass, closely resemble phytol, but that derived from phytol, prepared from nettles, yields a viscid *oil*,  $C_{40}H_{78}O$  or  $C_{40}H_{74}O$ , which is sparingly soluble in methyl alcohol and is probably an ether of phytol or of a more unsaturated alcohol. Distillation of phytol under 1 mm. pressure leads to the formation of the *aldehyde*,  $C_{20}H_{38}O$ , which is obtained as an *oil*, and forms an oily *oxime*, whilst on distillation under higher pressures, the alcohol forms *phytadiene*,  $C_{20}H_{38}$ , b. p.  $185$ — $188^{\circ}/22$  mm.

G. Y.

**The Chemistry of Chlorophyll, Phylloxanthin, Phyllocyanin, and the Chlorophylls.** M. TSVETT (*Biochem. Zeitsch.*, 1907, 5, 6—32. Compare Abstr., 1900, i, 50, 67; 1901, i, 94, 222; 1906, i, 973; Marchlewski, this vol., i, 435).—By means of the adsorption analytical method already described (this vol., ii, 144), it can be shown that chlorophyll (that is, the total leaf pigment) consists of at least seven distinct colouring matters. Five of these, including carotin, are yellow, are not fluorescent, and do not show absorption bands in the red half of the spectrum. The two remaining pigments are the  $\alpha$ - and  $\beta$ -chlorophyllins. The  $\alpha$ -compound is present in larger quantity, and in concentrated ethereal solution has a pure indigo-blue colour, whereas  $\beta$ -chlorophyllin has a chlorophyll-green colour. Both compounds have six characteristic absorption bands between lines B and G. Each of the chlorophyllins is transformed into a characteristic derivative,  $\alpha$ - and  $\beta$ -chlorophyllan, under the influence of dilute mineral acids. Hoppe-Seyler's chlorophyllan is a mixture of the two. Each has a characteristic absorption spectrum; they are not acidic, but their ethereal solutions when treated with potassium hydroxide solution undergo characteristic changes in colour. The chlorophyllins and chlorophyllans dissolve in concentrated mineral acids, but are, at the same time, decomposed. Schunck's phyllocyanin is the product formed by the action of hydrochloric acid on  $\alpha$ -chlorophyllan, whereas phylloxanthin is derived from, if not identical with,  $\beta$ -chlorophyllan.

It has not been found possible to transform phylloxanthin into phyllocyanin. J. J. S.

**Aniline-black.** W. NOVER (*Ber.*, 1907, 40, 3389).—A claim for priority as regards the investigation of emeraldine (compare this vol., i, 262, and Willstätter and Moore, *ibid.*, i, 641). J. J. S.

**Action of a Solution of Iodine in Potassium Iodide on Some Basic Dyes.** LOUIS PELET and E. GILLIÉRON (*Chem. Zentr.*, 1907, i, 1259; from *Schweiz. Woch. Chem. Pharm.*, 1907, 45, 88—90).—When a solution of iodine in potassium iodide is added to solutions of the hydrochlorides of safranin, magenta, chrysoidine, methylene-blue, phosphine, or muscarine, heavy, dark coloured precipitates of a di-iodohydriodide,  $M, HI, I_2$ , are formed; crystal-violet and auramine yield tri-iodohydriodides,  $M, HI, I_3$ . The dyes may be estimated volumetrically by means of this reaction. The precipitates may be dried at 50° without decomposition, and form black substances, some of which have a metallic lustre. All the iodohydriodides are very sparingly soluble in cold water, sparingly so in hot water or carbon disulphide, somewhat more readily soluble in acetone, alcohol, chloroform, nitrobenzene, or aniline, practically insoluble in benzene, toluene, or xylene, and rather readily soluble in cold mineral acids or alkalis; the solutions have the colours of the original dyes, but do not contain free iodine.

When tolusafranin and chrysoidine are treated with an excess of a solution of iodine in potassium iodide, tri-iodohydriodides are formed, and, under similar conditions, methylene-blue yields a tetraiodohydriodide.

By the action of a concentrated solution of sodium hydrogen

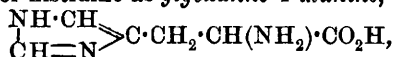
carbonate on the di-iodohydriodide of tolusafranine for five days, 1 atom of iodine is removed and the tetraiodohydriodide of methylene-blue also loses 1 atom of iodine when extracted sixty times with chloroform; the latter compound is not attacked, however, by sodium hydrogen carbonate. E. W. W.

**Thiophen.** VINCENZO PAOLINI (*Gazzetta*, 1907, **37**, i, 58—62).—The compound formed by the action of saturated aqueous mercuric acetate solution on thiophen is found to have the formula  $C_4H_4S(Hg \cdot OAc)_4$  (compare Dimroth, *Abstr.*, 1899, i, 428), the reaction being probably represented by the equation:  $C_4H_4S + 4Hg(OAc)_2 + 2H_2O = S \begin{matrix} \text{CH}(Hg \cdot OAc) \cdot \text{CH} \cdot Hg \cdot OAc \\ \text{CH}(Hg \cdot OAc) \cdot \text{CH} \cdot Hg \cdot OAc \end{matrix} + 4C_2H_4O_2 + O_2$ ; the oxygen formed is not liberated, but is used up in oxidising about one-half of the thiophen.

When treated with sodium chloride, the compound  $C_4H_4S(Hg \cdot OAc)_4$  yields the corresponding *mercuric chloride* derivative,  $C_4H_4S(HgCl)_4$ , which is a white, microcrystalline powder insoluble in all the neutral solvents and in acetic acid, and gives the indophenine reaction with isatin and sulphuric acid; it is gradually decomposed by light, is reduced to thiophen by zinc and sodium hydroxide, and does not melt at  $270^\circ$ . The corresponding *bromo*-compound,  $C_4H_4S(HgBr)_4$ , is a white, microcrystalline powder, and the *iodo*-compound,  $C_4H_4S(HgI)_4$ , a yellow powder. When boiled with aqueous alkali hydroxide solution, the mercuric chloride derivative is converted into the corresponding *hydroxy*-compound,  $C_4H_4S(Hg \cdot OH)_4$ , which is a brown, basic substance, exploding with formation of a mercury mirror when warmed, and yielding the mercuric acetate derivative when treated with acetic acid. T. H. P.

**Picrolonates of Certain Nuclein Bases.** PHOEBUS A. LEVENE (*Biochem. Zeitsch.*, 1907, **4**, 320—321. Compare Steudel, *Abstr.*, 1903, i, 431; Otori, *ibid.*, 1905, i, 126).—*Adenine picrolonate*,  $C_5H_5N_5 \cdot C_{10}H_8O_5N_4$ , crystallises from water and melts at  $265^\circ$ . *Guanine picrolonate*,  $C_5H_5ON_5 \cdot 2C_{10}H_8O_5N_4$ , and *cytosine picrolonate*,  $C_4H_6N_3 \cdot C_{10}H_8O_5N_4$ , have also been prepared and analysed. J. J. S.

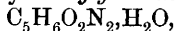
**Degradation and Constitution of Histidine.** FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1907, **10**, 111—119. Compare Knoop and Windaus, *Abstr.*, 1905, i, 834; Fränkel, *ibid.*, 1906, i, 547).—The constitution of histidine as *glyoxaline-4-alanine*,



has been established by the oxidation of oxydeaminohistidine to free glyoxaline. The first product obtained by boiling the oxydeaminohistidine with nitric acid (4 : 1) for six hours is *glyoxaline-4-glyoxylic acid*,  $C_5H_4O_5N_2$ . It has no definite m. p., but begins to turn brown at  $220^\circ$ , and is completely charred at  $290^\circ$ . The *oxime*,  $C_5H_5O_3N_3$ , crystallises in colourless needles, m. p.  $229^\circ$ . Histidine itself yields the same product when oxidised, but is not so readily attacked.

*Glyoxaline-4-carboxylic acid*,  $C_4H_4O_2N_2$ , is obtained when a dilute acetic acid solution of the glyoxylic acid is oxidised with hydrogen peroxide at the ordinary temperature. It crystallises in needles and decomposes at  $286^\circ$ , yielding glyoxaline. The same acid has been synthesised from tartaric acid.

The oxidation of oxydeaminohistidine in sulphuric acid solution with barium permanganate yields *glyoxaline-4-acetic acid*,



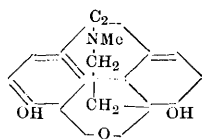
which crystallises from water in flat needles, m. p.  $220^\circ$  (decomp.).

J. J. S.

**Morphine. XII. The Point of Attachment of the Side-Ring Containing Nitrogen in Codeine and the Constitution of Morphine Alkaloids.** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, 40, 3341—3355. Compare Pschorr and Einbeck, this vol., i, 547).—Schryver and Lees' *isocodeine* (*Trans.*, 1901, 79, 576; this vol., i, 547) is a mixture of two bases, the one with m. p.  $145^\circ$  and the other  $170^\circ$  (compare Lees and Tutin, *Proc.*, 1906, 253; Lees, *Trans.*, 1907, 91, 1408). The base of high melting point is shown to be identical with  $\psi$ -codeine (Merck, *Abstr.*, 1891, 1121). The ketone obtained by oxidising  $\psi$ -codeine and Schryver and Lees' *isocodeine* is termed  $\psi$ -codeinone, as it undoubtedly corresponds with  $\psi$ -codeine.

$\psi$ -Codeinone methiodide, when heated with alcohol, undergoes decomposition in a manner similar to codeinone methiodide (Knorr, *Abstr.*, 1904, i, 916), yielding a dihydroxymethoxyphenanthrene, which on methylation gives 1:5:6-trimethoxyphenanthrene (Pschorr, *Abstr.*, 1900, i, 234).  $\psi$ -Codeinone thus contains the carbonyl oxygen in position 1, and by the conversion of codeine into  $\psi$ -codeine a wandering of the alcoholic hydroxyl group from 3 to 1 occurs. The point of union of the side-ring remains unaffected during this change, since both codeine and  $\psi$ -codeine yield the same deoxycodine. It follows that in  $\psi$ -codeine, morphine, codeine, and thebaine, the carbon chain of the side-ring cannot be attached to position 1. This position in the morphine alkaloids is not substituted, and in the formation of *apomorphine* from morphine the carbon chain of the side-ring is freed from its original attachment, and only as a secondary process becomes united to carbon atom 1.

The formation of *apomorphine* is thus a more complex reaction than as stated by Pschorr. Similarly, the side-ring cannot be attached to position 3, and, since it can be shown by Claisen's methods that both codeinone and  $\psi$ -codeinone contain the group  $\cdot CO \cdot CH_2 \cdot$ , position 7 must be a methylene group. The conclusion is drawn that the bridge  $\cdot CH_2 \cdot CH_2 \cdot NMe \cdot$  is attached, on the one side, to position 4 in the reduced benzene ring and, on the other, to position 9 or 10, probably 10, and the annexed formula is suggested for morphine.



The constitution of morphine, codeine, and thebaine is thus quite distinct from that of the other opium bases, papaverine, narcotine, and laudanoline.

$\psi$ -Codeinone condenses with benzaldehyde in dry ethereal solution in the presence of sodium ethoxide, yielding *benzylidene- $\psi$ -codeinone* in the form

of an oil. Its *methiodide*,  $C_{25}H_{23}O_3N, MeI$ , crystallises from methyl alcohol in rectangular needles and plates, and decomposes at about  $250^\circ$ .  $\psi$ -Codeinone also yields an *isonitroso*-derivative,  $C_{18}H_{13}O_4N_2$ , in the form of a yellow powder which begins to blacken at  $200^\circ$ .

$\psi$ -Codeinone, in contradistinction from codeine and  $\psi$ -codeine, reacts with solutions of diazonium salts, yielding dyes which are to be regarded as hydrazones of  $\psi$ -codeine-1:2-dione. With diazobenzene chloride, a red product is obtained. Codeinone also condenses with diazo-salts; with diazobenzene chloride in acetic acid solution, the red crystalline compound,  $C_{24}H_{23}O_3N_3, CH_3 \cdot CO_2H$ , is obtained, m. p.  $210$ — $220^\circ$  (decomp.). J. J. S.

**Morphine. XIII. Action of Oxalic Acid on Codeine.** LUDWIG KNORR and PAUL ROTH (*Ber.*, 1907, 40, 3355—3358. Compare Beckett and Wright, this Journ., 1875, 28, 696).—When perfectly dry codeine is heated with anhydrous oxalic acid at  $150^\circ$ ; it yields a mixture of  $\psi$ -codeine (Merck, Abstr., 1891, 1121; Knorr and Hörlein, this vol., i, 151) and a new compound,  $\psi$ -apocodeine,  $C_{18}H_{19}O_2N$ . The two compounds may be separated by means of alcohol, in which the *apo*-base is less readily soluble, or of sodium hydroxide solution, in which  $\psi$ -codeine is insoluble.

$\psi$ -apocodeine is not a direct product from codeine, but is formed from the  $\psi$ -codeine, and a better yield is obtained by heating  $\psi$ -codeine with oxalic acid. It crystallises from alcohol in brilliant plates containing 1EtOH and melting and decomposing at  $100$ — $110^\circ$ . The *hydriodide*,  $C_{18}H_{19}O_2N, HI$ , is sparingly soluble, and crystallises from water in slender needles, m. p.  $288^\circ$  (decomp.). The *diacetyl* derivative crystallises from alcohol in glistening plates, m. p.  $135^\circ$ . J. J. S.

**Transformation of Narcotine into Nornarceine. The Cinchona-toxines.** PAUL RABE (*Ber.*, 1907, 40, 3280—3287. Compare this vol., i, 78).—The correctness of the formula for cinchonine has been further tested by comparing narcotine and cinchonine. Narcotine methiodide is converted into narceine by heating with alkalis (Roser, Abstr., 1888, 1316; Freund and Frankforter, Abstr., 1894, i, 58), a change analogous with that of cinchonine into methylcinchotoxine; in both cases, the ring opens, an alcoholic hydroxyl disappears, and a ketonic group is formed. Dilute acetic acid converts cinchonine into cinchotoxine, a keto-base (v. Miller and Rhode, Abstr., 1894, i, 432), and the present communication deals with the action of this acid on narcotine. When heated together for seventy-two hours at  $105$ — $110^\circ$  and the product neutralised with sodium hydroxide, a mixture of four compounds is precipitated. Nornarceine and meconine are extracted from this mixture by normal sodium hydroxide at the ordinary temperature; carbon dioxide precipitates the nornarceine, and the meconine is obtained from the filtrate by addition of mineral acid. The residue insoluble in alkali consists of unaltered narcotine and gnoscopine (Smith, Abstr., 1878, 987), which are separated by using alcohol, gnoscopine being sparingly soluble. Addition of sodium hydroxide to the neutral solution precipitates cotarnine. Forty-three grams of nar-



cotine gave 9 grams of narcotine, 4 gnoscopine (m. p. 228—233°), 6 nornarceine, 9 cotarnine, and 7 meconine.

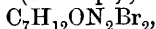
*Nornarceine*, obtained from its aqueous solution, crystallises in felted needles with  $3\text{H}_2\text{O}$  and has no definite m. p. (between 205—222° decomp.). When heated at 105° the water is driven off, and the extremely hygroscopic substance then decomposes at 147°. If, however, the substance is recrystallised from alcohol, another modification is obtained, m. p. 229° (decomp.), forming prismatic crystals. This may be reconverted into the other isomeride by recrystallisation from water. The *hydrochloride*,  $\text{C}_{22}\text{H}_{25}\text{O}_8\text{N}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , has m. p. 144°. Hydroxylamine hydrochloride yields an *oximinoanhydride hydrochloride*,  $\text{C}_{22}\text{H}_{25}\text{O}_7\text{N}_2\text{Cl}$ , which crystallises with 1 mol. of ethyl alcohol, m. p. 138°; the *oxime*,  $\text{C}_{22}\text{H}_{26}\text{O}_7\text{N}_2$ , obtained by treating the above hydrochloride with the calculated amount of silver carbonate, crystallises in rhombic leaflets, m. p. 171°, and is not converted into anhydride at 108° in contradistinction from narceineoxime (Freund and Frankforter, *loc. cit.*). A methyl-alcoholic solution of nornarceine (1 mol.), 2 mols. of methyl sulphate, and excess of methyl iodide yields Freund's narceinium methiodide methyl ester (this vol., i, 235).

Nornarceine undergoes no change on heating with dilute acetic acid, whereas gnoscopine is converted into cotarnine, meconine, and nornarceine; the conclusion is therefore drawn that gnoscopine is an intermediate product in the reaction. As gnoscopine is inactive, racemisation must have occurred.

W. R.

**Tetrahydropyridine Bases.** WILHELM KOENIGS, CARL BERNHART, and JOS. IBELE (*Ber.*, 1907, 40, 3199—3210. Compare Abstr., 1905, i, 824; 1906, i, 36).—Pyridine bases, having an ethyl group in position 3, yield a not inconsiderable amount of the tetrahydro-base by reduction with sodium and alcohol.

The basic reduction products of 3-ethylpyridine are converted into the hydrobromides and the salts treated with bromine in cold chloroform solution, whereby the tetrahydro-base is isolated to the extent of 10—11% in the form of *dibromo-3-ethylhexahydropyridine hydrobromide*,  $\text{C}_7\text{H}_{13}\text{NBr}_2\cdot\text{HBr}$ , m. p. 173° (decomp.); the *nitroso-derivative*,



has m. p. 90—91°, and responds only faintly to Liebermann's test. An isomeric 3-ethyltetrahydropyridine is formed in very small amount in the preceding reduction, and is isolated as the *dibromohydrobromide*,  $\text{C}_7\text{H}_{13}\text{NBr}_2\cdot\text{HBr}$ , m. p. 195° (decomp.), which yields an oily *nitroso-compound*. 3-Ethyltetrahydropyridine, b. p. 157—159°/724.5 mm., obtained by treating the first-mentioned dibromo-3-ethylhexahydropyridine with zinc dust and dilute sulphuric acid, is a colourless oil with the odour of piperidine and decolorises acidified permanganate; the *hydrogen tartrate* has m. p. 134°; the

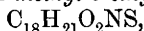
*platinichloride*, m. p. 164—165° (decomp.); the *aurichloride*, m. p. 89°, and the *picrate*, m. p. 123—125°.

*s*-Trimethylpyridine yields by reduction with sodium and alcohol about 2% of the tetrahydro-base, which is isolated in the form of the *dibromonitrosoamine*, m. p. 146° (decomp.), the main product being *s*-trimethylpiperidine, which forms two isomeric hydrobromides having m. p. 204—209° and >270° respectively.

Tetrahydroaldehydecollidine (2-methyl-5-ethyltetrahydropyridine) is not attacked by sodium and alcohol, but is reduced to copellidine by hydriodic acid (D 1.96) and red phosphorus at 220°.

2-Methyl-5-ethylpyridine is regenerated from 2-methyl-5-ethyltetrahydropyridine dibromide hydrobromide by heating it to its melting point, by warming on the water-bath with 50% acetic acid and silver acetate, or by boiling its solution in glacial acetic acid with anhydrous sodium acetate with or without bromine. The hydrobromide is also decomposed by the prolonged boiling of its aqueous solution, yielding a *dihydroxy-2-methyl-5-ethyltetrahydropyridine*,  $C_8H_{17}O_2N$ , m. p. 155°, the *hydrochloride* of which has m. p. 200—201°, and the *hydrobromide*, 180—181°; the *picrate*, *platinichloride*, and *aurichloride* are very soluble in water.

1- $\beta$ -Naphthalenesulphonyl-2-methyl-5-ethyltetrahydropyridine,



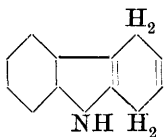
has m. p. 71—72°.

C. S.

**Some New Bromo-derivatives of Pyridine.** LÉONCE BARTHE (*Compt. rend.*, 1907, 145, 75—77).—When a mixture of pyridine and sodium hypobromite is gradually treated with hydrochloric acid in amount sufficient to liberate all the bromine and the product heated in a reflux apparatus, a golden-yellow solution is obtained. From the latter, *pyridine hydrobromide*,  $C_5NH_5HBr$ , is isolated in white, deliquescent crystals, m. p. 25°, which can be kept in a desiccator containing calcium chloride, but dissociate in one containing sulphuric acid. The aqueous solution has an acid reaction. By treating a mixture of pyridine and excess of hypobromite, heated on a water-bath, with hydrochloric acid, or by adding bromine to the yellow solution obtained above, a *tribromopyridine*,  $C_5NH_3Br_3$ , is formed in red needles, m. p. 89—90°, b. p. 230°, which thus differs from Willstätter's *tribromopyridine*, m. p. 167—168°. When pyridine is treated with bromine and the excess evaporated on a water-bath, a gummy residue is obtained from which, after some months, colourless, slightly deliquescent crystals of *bromopyridine*,  $C_5NH_5Br$ , m. p. 212° (decomp.), are isolated. The latter is not identical with either of the bromopyridines described by Hofmann, Ciamician, and Dennstedt (*Abstr.*, 1882, 1214), or Ciamician and Silber (*Ber.*, 1886, 18, 721). E. H.

**Dihydrocarbazole.** JULIUS SCHMIDT and RICHARD SCHALL (*Ber.*, 1907, 40, 3225—3230).—*Dihydrocarbazole*,  $C_{12}H_{11}N$ , obtained among the products of the reduction of carbazole by sodium and boiling amyl alcohol, separates from toluene in colourless leaflets which still contain traces of carbazole. It has m. p. 228—229° and b. p. 337—338°.

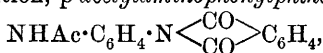
possesses feebly basic properties, and is easily reconverted into carbazole. In the light of Thiele's theory, the two additional hydrogen atoms are assumed to occupy positions 1 and 4.



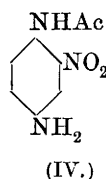
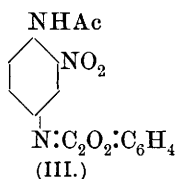
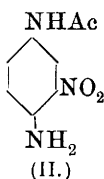
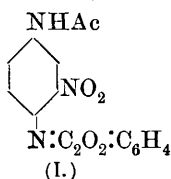
The *nitroso*-derivative, m. p. 72–73° (decomp.), forms golden-yellow needles and is very unstable. The *picrate* has m. p. 179–180°.

Dihydrocarbazole is easily reduced to tetrahydrocarbazole by sodium and amyl alcohol, and to the hexahydro-base by hydriodic acid and phosphorus at 150–160°. C. S.

**Monosubstitution Products of Diacylated *p*-Phenylenediamines with Different Acid Radicles.** ARNOLD CHAZEL (*Ber.*, 1907, 40, 3177–3185).—The influence of two fatty acylamino-groups on the position assumed by a negative-substituting group on introduction into the benzene nucleus was studied by Koller (*Abstr.*, 1903, i, 281). The present paper is a similar study of the influence of two acylamino-groups, one of which contains a fatty, the other an aromatic, acid radicle. It is found that, on nitration in concentrated sulphuric acid solution, *p*-acetylaminophenylphthalimide,



yields *o*-nitro-*p*-acetylaminophenylphthalimide, I, which on partial hydrolysis with ammonia forms *m*-nitro-*p*-aminoacetanilide, II, but on nitration with fuming nitric acid yields *m*-nitro-*p*-acetylaminophenylphthalimide, III, which on hydrolysis forms *o*-nitro-*p*-aminoacetanilide, IV.



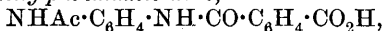
*p*-Acetylaminophenylphthalimide,  $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ , formed together with the corresponding *phthalamic acid* by the condensation of *p*-aminoacetanilide with phthalic anhydride in boiling aqueous solution, crystallises in white needles, m. p. above 270°, and is readily soluble in alcohol, but insoluble in alkalis.

*o*-Nitro-*p*-acetylaminophenylphthalimide,  $\text{C}_{16}\text{H}_{11}\text{O}_5\text{N}_3$ , crystallises in yellow needles, m. p. 246°.

*m*-Nitro-*p*-acetylaminophenylphthalimide,  $\text{C}_{16}\text{H}_{11}\text{O}_5\text{N}_3$ , crystallises in yellow needles, m. p. 248·5–249°.

*o*-Nitro-*p*-aminoacetanilide,  $\text{C}_8\text{H}_9\text{O}_3\text{N}_3$ , crystallises in dark red needles, m. p. 162·5°.

*p*-Acetylaminophenylphthalamic acid,



is a white, crystalline substance, m. p. above 270°, and is insoluble in alcohol, but dissolves in alkali carbonates; the *barium* salt,  $\text{C}_{32}\text{H}_{16}\text{O}_8\text{N}_4\text{Ba}$ , forms reddish-white needles. On nitration in concentrated sulphuric acid solution, the acid yields *o*-nitro-*p*-acetyl-

*aminophenylphthalamic acid*,  $C_{16}H_{13}O_6N_3$ , which crystallises in orange-yellow needles, m. p.  $177^\circ$ , and on hydrolysis forms *m*-nitro-*p*-aminoacetanilide. *Dinitro-p-acetylaminophenylphthalamic acid*,  $C_{16}H_{12}O_8N_4$ , prepared by nitration of the acid with fuming nitric acid, crystallises in yellow needles commencing to decompose at  $180^\circ$  G. Y.

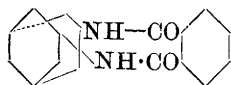
**Stereochemical Conceptions of Polycyclic Compounds. II.** FELIX KAUFLE (Ber., 1907, 40, 3250—3252. Compare this vol., i, 307, 776, and following abstracts).—The following evidence is brought forward in favour of the space formulæ of diphenyl and naphthalene (*loc. cit.*). Phthalaldianisidine is unimolecular and is represented by the formula  $C_6H_4 \begin{matrix} \text{CO} \cdot \text{NH} \cdot C_6H_3 \cdot \text{OMe} \\ \text{CO} \cdot \text{NH} \cdot C_6H_3 \cdot \text{OMe} \end{matrix}$ . The proximity of the para-positions is also proved by the existence of 3 : 3'-dimethoxy-4 : 4'-diphenylthiocarbamide,  $\begin{matrix} \text{OMe} \cdot C_6H_3 \cdot \text{NH} \\ \text{OMe} \cdot C_6H_3 \cdot \text{NH} \end{matrix} > \text{CS}$ , which is shown to be unimolecular by the ebullioscopic method in nitrobenzene.

4 : 4'-Diaminodiphenylmethane condenses with carbon disulphide to form diphenylmethanethiocarbamide,  $\text{CH}_2 \begin{matrix} \text{C}_6\text{H}_4 \cdot \text{NH} \\ \text{C}_6\text{H}_4 \cdot \text{NH} \end{matrix} > \text{CS}$ ; 4 : 4'-diaminodiphenylethane reacts similarly.

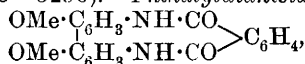
The influence of steric hindrance in 2 : 7-naphthylenediamine is seen in the fact that only one amino-group can be diazotised.

By a comparison of the physical properties and of the velocity of hydrolysis of the nitriles and of the methyl esters of 2 : 6- and 2 : 7-naphthalenedicarboxylic acids with those of the corresponding compounds of terephthalic and of *isophthalic* acids, it is shown that the 2 : 6- and the 2 : 7-positions in naphthalene are analogous with the para- and meta-positions respectively in the benzene nucleus. This analogy is manifested, not only in the case of Willstätter and Parnas' 2 : 6-naphthaquinone, but also in the behaviour of dihydroxynaphthalenes to diazo-compounds; 2 : 7-dihydroxynaphthalene yields a disazo-compound, whilst the 2 : 6-compound forms substances of high molecular weight, probably dinaphthyl derivatives. This behaviour recalls that of resorcinol and of quinol under similar treatment.

The condensation of 2 : 7-naphthylenediamine and phthalic acid to form phthalynaphthylenediamine is inexplicable by plane formulæ, and the author suggests that it is best represented by the annexed spacial formula. C. S.

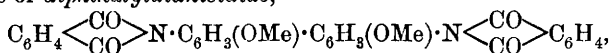


**Ring Formation in Derivatives of Diphenyl, Diphenylmethane, and Diphenylethane.** FELIX KAUFLE and H. BOREL (Ber., 1907, 40, 3253—3256).—*Phthalaldianisidine*,



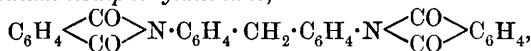
m. p.  $216$ — $217^\circ$ , is prepared by heating dianisidine and phthalic anhydride with water for fourteen to sixteen hours. If the two

substances are heated at 200—250° in the absence of water, yellow crystals of *diphthalylaldianisidide*,



are obtained, m. p. above 330°.

*Diphthalyldiaminodiphenylmethane*,

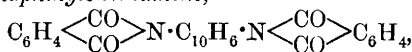


m. p. 324°, prepared by boiling phthalic anhydride and 4:4'-diaminodiphenylmethane with water for ten to twelve hours, forms yellow leaflets. When 4:4'-diaminodiphenylmethane is heated with alcohol and carbon disulphide for eighteen to twenty hours, *diphenylmethane-thiocarbamide*,  $\text{CH}_2 \begin{array}{c} \diagup \text{C}_6\text{H}_4 \cdot \text{NH} \\ \diagdown \text{C}_6\text{H}_4 \cdot \text{NH} \end{array} \text{CS}$ , m. p. 205° (decomp.), is obtained, which separates from dimethylaniline in yellowish-grey crusts, and is insoluble in acids.

4:4'-Diaminodiphenylethane yields similar compounds. *Diphthalyl-diaminodiphenylethane*,  $\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_2$ , has m. p. above 330°, and *diphenyl-ethanethiocarbamide*,  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{S}$ , m. p. 272—273°. C. S.

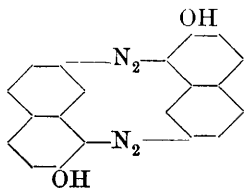
**2:7-Derivatives of Naphthalene.** FELIX KAUFLE and U. KARRER (*Ber.*, 1907, 40, 3262—3269).—2:7-Naphthylenediamine is best diazotised in alcoholic solution by hydrobromic acid and amyl nitrite, whereby the *hydrobromide* of an *aminodiazonaphthalene bromide*,  $\text{C}_{10}\text{H}_9\text{N}_3\text{Br}_2$ , is precipitated in glistening, yellow needles, which explode by heating or in contact with concentrated nitric acid; it couples with  $\beta$ -naphthol in alkaline alcoholic solution to form 7-*aminonaphthalene-2-azo- $\beta$ -naphthol*,  $\text{C}_{20}\text{H}_{15}\text{ON}_3$ , m. p. above 300°, which forms a yellowish-brown, microcrystalline powder. The hydrochloride of the corresponding diazo-chloride reacts with dimethylaniline to form 7-*aminonaphthalene-2-azodimethylaniline*,  $\text{C}_{18}\text{H}_{18}\text{N}_7$ , m. p. 259—260°, which separates from pyridine in glistening, reddish-brown leaflets.

*Phthalyl-2:7-naphthylenediamine*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \diagup \text{NH} \cdot \text{CO} \\ \diagdown \text{NH} \cdot \text{CO} \end{array} \text{C}_6\text{H}_4$ , m. p. 215°, is obtained by heating 2:7-naphthylenediamine and phthalic anhydride with water for two days; it separates from dimethylaniline in yellowish crusts, and is shown to be unimolecular by the ebullioscopic method with the same solvent, the molecular elevation of which is 50.8 experimentally, 49.4 by Nernst's formula, and 48.5 by Trouton's formula. *Diphthalyl-2:7-naphthylenediamine*,



m. p. 306°, obtained by heating phthalic anhydride and 2:7-naphthylenediamine at 250°, forms glistening, greenish-yellow leaflets.

7-Amino-2-naphthol is best diazotised by hydrochloric acid and amyl nitrite in alcoholic solution; the precipitated diazo-chloride and dimethylaniline yield 7-*hydroxynaphthalene-2-azodimethylaniline*,  $\text{C}_{18}\text{H}_{17}\text{ON}_3$ , which forms yellow solutions with alkalis and red solutions with acids. If the diazo-chloride is dissolved in a solution of sodium carbonate, a red substance



is obtained, m. p. above 330°, which is shown by the ebullioscopic method in pyridine to have a molecular weight corresponding with the formula  $C_{20}H_{12}O_2N_4$ ; it probably has the annexed constitution.

C. S.

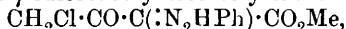
### Action of Diazo-Chlorides on $\gamma$ -Chloroacetylacetic Esters.

G. FAYREL (*Compt. rend.*, 1907, 145, 194—196. Compare Abstr., 1902, i, 644).—The action of diazobenzene on ethyl  $\gamma$ -chloroacetylacetate yields the  $\gamma$ -phenylhydrazone of ethyl- $\alpha$ -chlorobutane- $\beta\gamma$ -dione- $\delta$ -carboxylate,  $CH_2Cl \cdot CO \cdot C(N_2HPh) \cdot CO_2Et$ , which crystallises from alcohol in yellow needles, m. p. 92—93°. The prolonged action of diazobenzene chloride on this compound yields ethyl diphenylformazylformate,  $CO_2Et \cdot C(N:NPh) : N_2HPh$ .

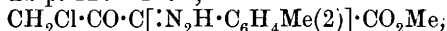
The  $\gamma$ -*o*-tolylhydrazone of ethyl  $\alpha$ -chlorobutane- $\beta\gamma$ -dione- $\delta$ -carboxylate, obtained by the action of diazo-*o*-toluene chloride on ethyl  $\gamma$ -chloroacetylacetate, forms slender, yellow needles, m. p. 121—122°, and is sparingly soluble in alcohol.

The  $\gamma$ -*p*-tolylhydrazone of ethyl  $\alpha$ -chlorobutane- $\beta\gamma$ -dione- $\delta$ -carboxylate is obtained as an orange-yellow, crystalline powder, m. p. 96—97°, soluble in alcohol.

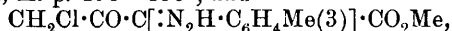
Similarly, methyl  $\gamma$ -chloroacetylacetate yields:



yellow needles, m. p. 126—127°;



slender needles, m. p. 158—159°, and

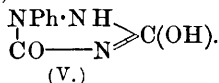
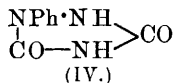
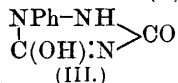
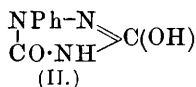
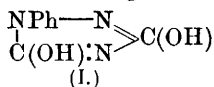


m. p. 139—140°.

T. H. P.

### Constitution of Phenylurazole. III. Study of Tautomerism.

SALOMON F. ACREE (*Amer. Chem. J.*, 1907, 38, 1—91. Compare Abstr., 1902, i, 242; 1903, i, 867; 1904, i, 270, 351, 453; this vol., i, 258).—In continuation of the work on the constitution of phenylurazole, the following five formulæ have been considered:



In order to study the equilibrium phenomena of the tautomeric amide groups,  $\cdot NH \cdot CO \cdot$  and  $\cdot N : C(OH) \cdot$ , the action of diazomethane has been investigated. When a solution of phenylurazole in ether is treated with excess of diazomethane, 3-methoxy-1-phenyl-4-methylurazole (3-methoxy-5-keto-1-phenyl-4-methyl-4 : 5-dihydrotriazole),  $NPh-N > C \cdot OMe$  (Abstr., 1903, i, 867), is formed together with traces of other dimethyl derivatives not yet identified. If, however, the phenylurazole is in excess, the chief product is 3-methoxy-1-phenylurazole (3-methoxy-5-keto-1-phenyl-4 : 5-dihydrotriazole), a small quantity (about 5%) of 1-phenyl-2-methylurazole being also formed.

These results indicate that there is equilibrium between the enolic and ketonic forms of the 2:3-amide group, the enolic form largely preponderating. When 3-methoxy-1-phenylurazole, 3-ethoxy-1-phenylurazole, 2-acetyl-1-phenylurazole, or 3-thio-1-phenylmethylurazole is treated with diazomethane, the corresponding 4-methyl derivatives are produced almost to the exclusion of the 5-methoxy-derivatives, whence it seems probable that the 4:5-amide group also exists in two tautomeric forms in equilibrium, but with the ketonic form in excess.

Both phenylurazole and 3-thio-1-phenylurazole are moderately strong acids and redden litmus. A study of the strength of the acid groups in phenylurazole has shown that the 2:3-amide group has an affinity constant  $K = 0.00001$  and the 4:5-amide group,  $K = 0.00000005$ , which confirms the conclusion that the 2:3-amide group is enolic, whilst the 4:5-group is ketonic.

Although both phenylurazole and 3-thio-1-phenylurazole have two hydrogen atoms replaceable by metals, yet when treated with alkali in presence of phenolphthalein they behave as monobasic acids. If, however, the first hydrogen atom is replaced by an alkyl group, the resulting compound (for example, 3-methoxy-1-phenylurazole) also behaves as a monobasic acid, whence it is evident that, like many other dibasic acids, these urazoles ionise in steps. It is calculated that the ionisation of the 4:5-amide group is depressed by the 2:3-amide group, or its sodium salt, to 1/15 of its normal amount.

It is pointed out that the evidence afforded as to the constitution of the urazoles by their reactions with diazomethane is only qualitative, and it is shown by a consideration of the mass law that the relative amounts of two stable derivatives formed by the reaction of a tautomeric compound, existing in two forms in equilibrium, with another reagent depends on (1) the relative reactivity of the two tautomeric forms towards the reagent; (2) the ratio between the amounts of the two tautomeric forms when they are in constant equilibrium with each other, and (3) the rapidity of the change of the tautomeric forms into one another as the equilibrium between is disturbed. In some cases, the reaction may be complicated by the rearrangement of one or each of the tautomeric forms into the other or into some other product.

Various phases of the equilibrium conditions existing in a solution of a tautomeric acid or base, or their salts, have been studied, but for an account of these the original must be consulted.

A discussion is given of the conditions under which normal and abnormal hydrolysis of salts of tautomeric compounds can be determined, and it is shown that it is necessary to know (1) that equilibrium has been established in the solution of the tautomeric salt, or salts, when the hydrolysis is measured; (2) that equilibrium has been established in the solution of the tautomeric acid when its affinity constant is determined, and (3) that all the conditions of temperature, solvent, &c., are the same in (1) and (3).

The two modifications of  $\alpha$ -ethyl phenylsemicarbazidecarboxylate (Wheeler and Beardsley, *Abstr.*, 1902, i, 503), m. p.  $172^\circ$  and  $154^\circ$ , have the same molecular weight in aqueous solution. When the modification

melting at 154° is heated above its m. p., it changes rapidly into the less fusible form. The change of one modification into the other by crystallisation from solvents depends on conditions of temperature, time, and the solvent employed. The solubility of the two forms in water is practically identical. It seems probable therefore that they are not chemical isomerides, but physical modifications.

When the potassium salt of phenylurazole is warmed with a solution of iodine, a soluble compound is formed, which is under investigation. By the action of alkyl haloids on potassium phenylurazole, 1-phenyl-2-alkylurazoles are formed together with very small quantities of 3-alkyloxy-1-phenylurazoles, whilst by their action on the silver salt, the latter compounds are obtained in comparatively large quantities.

*Dibenzoylphenylurazole* has m. p. 178—180°. *2-Benzoyl-1-phenyl-4-methylurazole*, m. p. 185°, is readily hydrolysed by concentrated hydrochloric acid. The *potassium* and *silver* salts of 3-ethoxy-1-phenylurazole are described.

1-Phenyl-2-methyl-4-ethylurazole,  $\begin{matrix} \text{NPh} \cdot \text{NMe} \\ | \\ \text{CO} - \text{NEt} \end{matrix} > \text{CO}$ , m. p. 113°, is obtained by the action of ethyl iodide on the potassium salt of 1-phenyl-2-methylurazole.

[With FREDERICK LAIST.]—An account of the acetyl derivatives of phenylurazole (compare Abstr., 1905, i, 160). The *silver* derivative of 2-acetyl-1-phenylurazole is described. E. G.

**Azo-derivatives of Certain Cresotic [Hydroxytoluic] Acids.** ERNESTO PUXEDDU and ENRICO MACCIONI (*Gazzetta*, 1907, 37, i, 68—82).—The authors have prepared a number of azo-derivatives of *o*-, *m*-, and *p*-cresotic or homosalicyclic acids [ $\text{Me} : \text{CO}_2\text{H} : \text{OH} = 1 : 3 : 2$ ,  $1 : 4 : 3$ , and  $1 : 3 : 4$  respectively]. All the compounds obtained are partially soluble in cold, and completely in hot, dilute alkali hydroxides, but are insoluble in water or dilute mineral acids. With nitric acid, they react violently, and with sulphuric acid they yield deep brown solutions. With phenylhydrazine, they give the corresponding amino-hydroxy-acids.

5-Benzeneazo-2-hydroxy-3-toluic acid,  $\text{CMe} < \begin{matrix} \text{C(OH)} \cdot \text{C(CO}_2\text{H)} \\ \text{CH} = \text{C(N}_2\text{Ph)} \end{matrix} > \text{CH}$ , crystallises from alcohol in shining, yellowish-red scales, m. p. 199°, and in absolute ethereal solution gives with ferric chloride a wine-red coloration which turns brown when fresh ferric salt is added. The *sodium* salt forms prismatic, acicular crystals, and does not melt at 300°. Reduction of the acid with phenylhydrazine yields 5-amino-2-hydroxy-3-toluic acid, m. p. 267° (decomp.) (Nietzki and Ruppert, Abstr., 1891, 308, gave m. p. above 300°).

5-*Tolueneazo*-2-hydroxy-3-toluic acid,  $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2$ , separates from alcohol in microscopic, greenish-yellow crystals, m. p. 210° (decomp. at 212°).

5-*p-Tolueneazo*-2-hydroxy-3-toluic acid,  $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2$ , forms reddish-yellow crystals, m. p. 195°.

5- $\beta$ -*Naphthaleneazo*-2-hydroxy-3-toluic acid,  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2$ , forms dark brown, microscopic, mammillary masses, m. p. 229°.



6-*Benzeneazo-3-hydroxy-4-toluic acid*,  $C_{14}H_{12}O_3N_2$ , crystallises from alcohol in dark yellow, silky, prismatic needles, m. p.  $216^\circ$ . The *sodium salt*,  $C_{14}H_{11}O_3N_2Na$ , forms prismatic needles, not melting at  $300^\circ$ .

6-*o-Tolueneazo-3-hydroxy-4-toluic acid*,  $C_{15}H_{14}O_3N_2$ , is obtained as a grey, faintly yellow powder, m. p.  $212^\circ$ .

6-*p-Tolueneazo-3-hydroxy-4-toluic acid*,  $C_{15}H_{14}O_3N_2$ , crystallises from alcohol in twinned or curved, brick-red needles, m. p.  $225^\circ$ .

6- $\beta$ -*Naphthaleneazo-3-hydroxy-4-toluic acid* is deposited from alcohol as a greenish-yellow, amorphous powder, m. p.  $237^\circ$ .

When 4-hydroxy-3-toluic acid is treated with diazo-salts, the corresponding azo-compound is not obtained, but carbon dioxide is eliminated and mono- and bisazo-*p*-cresols are formed.

*Bisbenzeneazo-p-cresol*,  $C_{19}H_{16}ON_4$  [ $Me : OH : (N_2Ph)_2 = 1 : 4 : 3 : 5$ ], crystallises from sulphol in minute, dark red, acicular prisms, m. p.  $180^\circ$ , and dissolves in dilute alkali hydroxide solution forming a reddish-violet liquid.

T. H. P.

**Peri-derivatives of Naphthalene.** FELIX KAUFLEDER and E. BRÄUER (*Ber.*, 1907, 40, 3269—3276).—5-*Nitro-1-naphthol*, m. p.  $165^\circ$ , is obtained in 30% yield by adding a solution of 5-nitro-1-diazonaphthalene sulphate to boiling 25% sulphuric acid; the *acetate* has m. p.  $114^\circ$ , and the *benzoate*,  $109^\circ$ . When the solution of the diazo-sulphate is kept at the ordinary temperature for three weeks, 5-nitro-4-nitroso-1-naphthol is formed, the *acetate* of which has m. p.  $136^\circ$ .

The reaction between *p*-nitrodiazobenzene chloride and 5-nitro-1-naphthol, dissolved in the calculated quantity of 10% sodium hydroxide, results in the formation of *p*-nitrobenzene-4-azo-5-nitro-1-naphthol, decomposing at  $252$ — $260^\circ$ , *p*-nitrobenzene-2-azo-5-nitro-1-naphthol, m. p.  $210^\circ$ , and the *bisazo*-compound, m. p.  $265^\circ$ , which are separated by means of their different solubilities in toluene or in dilute sodium hydroxide; the *bisazo*-compound is also formed by treating a cold alcoholic solution of the *p*-hydroxyazo-compound with excess of sodium acetate and *p*-nitrodiazobenzene chloride.

2 : 7-Dihydroxynaphthalene reacts with *p*-nitrodiazobenzene chloride in alkaline solution to form a mixture of the *monoazo*- and the *bisazo*-compound, which is separated by means of the greater solubility of the former in toluene. It decomposes at  $280$ — $285^\circ$ , separates from toluene in glistening, reddish-brown leaflets, and develops a violet coloration with sulphuric acid. The *bisazo*-compound decomposes above  $300^\circ$ , and gives a brownish-red coloration with sulphuric acid.

2 : 7-Dihydroxynaphthalene, dissolved in glacial acetic acid and treated with sodium nitrite, yields a *mononitroso*-compound,  $C_{10}H_7O_3N$ , decomposing at  $230$ — $240^\circ$ ; by nitration with nitric acid, D 1.4, in the same solvent, 2 : 7-dihydroxynaphthalene yields 1 : 8-dinitro-2 : 7-dihydroxynaphthalene, which forms yellow crystals, decomposing at  $250^\circ$ .

By the reaction between 2 : 6-dihydroxynaphthalene and diazobenzene chloride in alkaline solution, the *bisazo*-compound,  $C_{22}H_{16}O_2N_4$ , is precipitated; it crystallises in red needles, m. p. above  $290^\circ$ .

C. S.

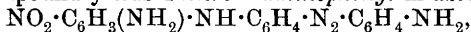
**Trisbenzeneazophenol.** GUSTAV HELLER and OTTO NÖTZEL (*J. pr. Chem.*, 1907, [ii], 76, 58—61. Compare Vignon, *Abstr.*, 1904, i, 699; Grandmougin and Freimann, this vol., i, 664).—Having obtained trisbenzeneazophenol in the course of an investigation to be described later, the authors have confirmed its constitution by reduction with stannous chloride and hydrochloric acid and benzylation of the stannichloride so obtained by the action of benzoyl chloride in pyridine solution. The product is identical with the tetrabenzoyl-2:4:6-triaminophenol formed from picric acid by reduction and benzylation in the same manner. Trisbenzeneazophenol is formed also by the action of diazobenzene chloride on bisbenzeneazophenol in alkaline solution. The *benzoate*,  $C_{31}H_{22}O_2N_6$ , crystallises in needles, m. p. 142°. The *sulphonic acid*, prepared by heating trisbenzeneazophenol with sulphuric acid containing 20% of anhydride, is readily soluble in water and dyes wool a weak red in an acid bath.

In view of the work of Goldschmidt and Löw-Beer (*Abstr.*, 1905, i, 389), Willstätter and Veraguth (this vol., i, 453), and Auwers (*ibid.*, i, 554), trisbenzeneazophenol and its acyl derivatives are considered to be hydroxyazobenzene and not quinonehydrazone compounds. G. Y.

**2:4:6-Trisbenzeneazoresorcinol.** WILLIAM R. ORNDORFF and B. J. RAY (*Ber.*, 1907, 40, 3211—3214).—2:4:6-Trisbenzeneazoresorcinol,  $C_6H(OH)_2(N_2Ph)_3$ , m. p. 254°, prepared from diazobenzene chloride (3 mols.) and resorcinol in alkaline solution, forms micro-crystalline, brown needles. The *diacetate*,  $C_6H(OAc)_2(N_2Ph)_3$ , separates from ethyl acetate and alcohol in orange-yellow needles, m. p. 201°, and from ether in red, prismatic crystals, m. p. 203°, which by recrystallisation from alcohol change into the orange-yellow needles. The constitution of the azo-compound is determined by its preparation from 4:6-bisbenzeneazoresorcinol and 2:4-bisbenzeneazoresorcinol.

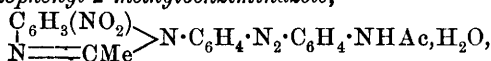
C. S.

**Derivatives of *m*-Aminobenzene-*m*-azodiphenylamine.** KURT BRAND (*Ber.*, 1907, 40, 3335—3340).—Chloro-2:4-dinitrobenzene readily reacts with a boiling alcoholic solution of *m*-azoaniline in the presence of sodium acetate, yielding 2:4-dinitrophenyl-*m*-azoaniline,  $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH_2$ , together with *s*-2:4:2':4'-tetranitrodiphenyl-*m*-azoaniline,  $N_2[C_6H_4 \cdot NH \cdot C_6H_3(NO_2)_2]_2$ . 2:4-Dinitrophenyl-*m*-azoaniline crystallises from ethyl acetate in glistening, red needles, m. p. 187—188°, and dissolves in alcoholic sodium or potassium hydroxide, yielding intense, deep red solutions. The *acetyl* derivative,  $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NHAc$ , separates from glacial acetic acid in orange-yellow crystals, m. p. 233°. When reduced with an aqueous alcoholic solution of sodium hydrogen sulphide at 60—70°, the dinitro-compound yields 4-nitro-2-aminophenyl-*m*-azoaniline,



which crystallises from dilute alcohol in slender, pale red needles, m. p. 176—177°. It yields yellow salts, the solutions of which turn red when kept or when heated. When boiled with acetic acid and

acetic anhydride, the nitroamino-compound yields 5-nitro-1-m-acet-anilino-m-azophenyl-2-methylbenziminazole,

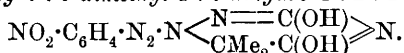


which crystallises from 96% alcohol in brilliant, glistening, yellowish-red prisms, melting at  $148^\circ$  with loss of water. When hydrolysed with sulphuric acid, it yields 5-nitro-1-m-anilino-m-azophenyl-2-methylbenziminazole,  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_6$ , which crystallises in glistening, orange-yellow prisms, m. p.  $175-176^\circ$ .

Tetranitrodiphenyl-m-azoaniline may also be obtained by the condensation of 2:4-dinitrophenylazoaniline with chloro-2:4-dinitrobenzene. It crystallises from pyridine in glistening, golden-yellow needles, m. p.  $285^\circ$ . J. J. S.

### I. Diazoamino-compounds from Semicarbazino-fatty Acids.

II. Chemical Behaviour of the Derivatives of Carbamidoazo-isobutyric Acid. JAMES R. BAILEY and LOUIS KNOX (*J. Amer. Chem. Soc.*, 1907, 29, 881-892).—It has been shown previously that semicarbazino-fatty acids react with acid chlorides (*Abstr.*, 1900, i, 528) and with thiocarbimides (*Abstr.*, 1904, i, 826) in the same manner as do secondary amines. The present paper is an account of an investigation into the action of diazo-salts on semicarbazino-fatty acids. Whilst aromatic diazoamino-compounds, which do not contain the semicarbazide grouping, are formed by the action of diazo-salts on semicarbazide, or in some cases on semicarbazino-acids, it is possible in most cases with the semicarbazino-acids to obtain diazoamino-compounds in which the diazo-group is coupled directly with the  $\alpha$ -nitrogen atom of the semicarbazide. Thus diazobenzene chloride and ethyl semicarbazinopropionate form *ethyl carbamidophenyldiazoaminopropionate*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{N}_2\text{Ph}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ . Such substances do not give the general reactions characteristic of the diazoamino-compounds. They differ from each other in their behaviour towards alcoholic potassium hydroxide; whilst *ethyl carbamido-m-nitrophenyldiazoaminopropionate* yields 3:5-dihydroxy-6-methyl-1:2:4-triazine,  $\text{N} \begin{smallmatrix} \text{N}=\text{C}(\text{OH}) \\ \text{CMe}-\text{C}(\text{OH}) \end{smallmatrix} \text{N}$ , nitrobenzene, nitrogen, and alcohol, *ethyl carbamido-m-nitrophenyldiazoaminoisobutyrate* forms 1-m-nitrophenyl-azo-3:5-dihydroxy-6:6-dimethyl-1:6-dihydro-1:2:4-triazine,



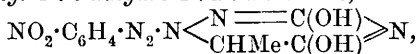
Attempts to prepare 3-hydroxy-5-keto-6:6-dimethyl-5:6-dihydro-1:2:4-triazine by this reaction and by other methods were unsuccessful.

Carbamidoazoisobutyric acid and the corresponding ketotriazine decompose at the moment of formation with loss of 1 mol. of nitrogen, whilst the *ethyl* ester decomposes a few degrees above its melting point, confirming Thiele and Heuser's observation (*Abstr.*, 1896, i, 340) that azo-compounds of the aliphatic series are, as a rule, not very stable, and in many cases are incapable of existence.

*Ethyl carbamidophenyldiazoaminopropionate*,  $\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}_5$ , crystallises in white, microscopic needles, m. p.  $125^\circ$  (exploding).

*Ethyl carbamido-m-nitrophenyldiazoaminopropionate*,  $C_{12}H_{16}O_5N_6$ , m. p.  $146^\circ$  (exploding), dissolves readily in cold bromine water, from which ammonia precipitates a brick-red substance, and on treatment with bromine in absolute alcoholic solution forms *m*-nitrodiazobenzeneimide. The acid,  $C_{10}H_{12}O_5N_6$ , has m. p.  $128^\circ$  (exploding); the potassium salt explodes at  $184^\circ$ ; the propyl ester,  $C_{13}H_{18}O_5N_6$ , m. p.  $149^\circ$  (exploding); the nitrile,  $C_{10}H_{13}O_3N_7$ , forms a slightly yellow precipitate, m. p.  $133^\circ$  (exploding), and is converted by hydrogen chloride in absolute alcoholic solution into a white, crystalline substance, or by hydroxylamine into the *amidoxime*.

3 : 5-Dihydroxy-6-methyl-1 : 6-dihydro-1 : 2 : 4-triazine, m. p.  $217^\circ$  ( $209^\circ$ : Thiele and Bailey, Abstr., 1899, i, 169), forms a potassium derivative,  $C_4H_4O_2N_3K$ , crystallising in white flakes, and couples with *m*-nitrodiazobenzene chloride, forming 1-*m*-nitrophenylazo-3 : 5-dihydroxy-6-methyl-1 : 6-dihydro-1 : 2 : 4-triazine,

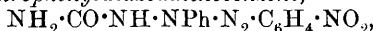


m. p.  $121^\circ$  (exploding).

*Ethyl carbamido-m-nitrophenyldiazoaminoisobutyrate*,  $C_{13}H_{18}O_5N_6$ , crystallises from benzene and explodes at  $133^\circ$ .

1-*m*-Nitrophenylazo-3 : 5-dihydroxy-6 : 6-dimethyl-1 : 6-dihydro-1 : 2 : 4-triazine,  $C_{11}H_{12}O_4N_6$ , formed from the preceding ester, or by coupling the triazine with *m*-nitrodiazobenzene chloride, crystallises in light lemon flakes, m. p.  $130^\circ$  (exploding); the potassium salt crystallises in vermilion prisms and explodes at  $166^\circ$ .

*Carbamido-m-nitrophenyldiazoaminobenzene*,



formed by coupling phenylsemicarbazide with *m*-nitrodiazobenzene chloride, is obtained as a dark lemon-yellow substance, m. p.  $104^\circ$  (exploding).

*m*-Nitrodiazobenzene chloride is reduced by semicarbazide forming nitroaniline, which couples with unchanged diazo-compound, yielding *mm'*-dinitrodiazoaminobenzene. Semicarbazino-acids, which have no hydrogen atom attached to the  $\alpha$ -nitrogen, as ethyl acetyl- and benzenesulphonyl-semicarbazinopropionates, do not couple with diazo-salts.

*Ethyl carbamidoazoisobutyrate*,  $NH_2 \cdot CO \cdot N : N \cdot CMe_2 \cdot CO_2Et$ , formed by oxidation of the semicarbazino-ester with bromine in aqueous solution, separates from benzene in yellow crystals, m. p.  $83^\circ$ , decomposes at  $120^\circ$ , and reacts violently with sodium ethoxide in alcoholic solution, evolving gas. The methyl ester is obtained as an oil, which when heated at  $135$ — $160^\circ$  evolves gas and yields an oil, b. p.  $232^\circ/750$  mm.

G. Y.

**Physical Changes in the Conditions of Colloids. VI. The Coagulation of Acid Albumin by Heat.** WOLFGANG PAULI (*Beitr. chem. Physiol. Path.*, 1907, 10, 53—79. Compare Abstr., 1906, ii, 180).—The coagulation of albumin by heat is not reversible (compare Corin and Ansiaux, Abstr., 1891, 1521). Experiments have been made to determine the limiting concentrations of various potassium salts required to nullify the inhibiting action of a 0.005*N*

solution of hydrogen chloride on the coagulation of a dialysed serum solution. The concentration required just to produce an opalescence in the boiled solution varied from 0.02*N* for potassium chloride to 0.002 for potassium citrate and acetate. The salts of the weakest acids appear to have the greatest coagulating effect. The action, however, is not due to a diminution of the concentration of the hydrogen ions, but is a direct action of the salt. Similar results were obtained when the same salts were used in the presence of acetic acid. An increase in the amount of acid required a considerable increase in the amount of neutral salt necessary to produce coagulation. A comparison of the action of different metallic chlorides in the presence of hydrochloric acid shows that the activity of the various salts increases in the order: calcium, magnesium, ammonium, potassium, sodium, lithium. The activity of nitrates in the presence of hydrochloric acid follows the order: barium, strontium, calcium, magnesium, potassium, but in both series the differences are not marked.

At the ordinary temperature, the thiocyanate ion has the most pronounced coagulating effect on acid albumin after forty-eight hours at the ordinary temperature; the effect of the thiocyanate ion is practically the same as that produced immediately after boiling. The various anions have not the same effect at the ordinary temperature as at the boiling point. At low temperatures, the increasing order of activity is acetate, sulphate, chloride, bromide, nitrate, thiocyanate, whereas at higher temperatures the order is nitrate, chloride, bromide, thiocyanate, sulphate, oxalate, acetate, citrate when the concentration of the acid is relatively low. If, however, the concentration of the acid is increased, the order at the higher temperature is the same as that at lower temperatures. For coagulation at both high and low temperatures, an increase in the amount of acid above a certain limit has practically no effect if the concentration of the salt remains constant. Similarly, for coagulation at high temperatures when the concentration of the acid is kept constant (0.005*N* hydrochloric acid) an increase in the concentration above a certain limit (about 0.2*N*) has practically no effect.

Coagulation produced in the cold is not increased by raising the temperature, but often disappears, leaving a clear liquid. J. J. S.

**The Tryptic Digestion of Egg-albumin.** PHÆBUS A. LEVENE and WALLACE A. BEATTY (*Bio-chem. Zeitsch.*, 1907, 4, 299—304. Compare Abstr., 1906, i, 469, 718).—Egg-albumin is extremely resistant to tryptic digestion, but, after four months in a 0.5% sodium carbonate solution of trypsin, a certain amount of hydrolytic decomposition had occurred. The products isolated were leucine, isoleucine, and tryptophan, together with a peptide which did not give the biuret reaction and, when hydrolysed, yielded lysine and glycine. A compound which belongs probably to the proteinochromogens was also obtained. J. J. S.

**The Analysis of the Cleavage Products of Egg-albumin.** PHÆBUS A. LEVENE and WALLACE A. BEATTY (*Bio-chem. Zeitsch.*, 1907, 4, 305—311. Compare Abderhalden and Pregl, Abstr., 1906, i, 53.)—Details are given for the isolation of the various products

obtained by the hydrolysis of egg-albumin with concentrated hydrochloric acid. Fischer's esterification method was not used, and difficulties were met with in obtaining the leucine and tyrosine in a pure state. From 100 grams of material, the following products were obtained: alanine and glycine, 2.0; aminovaleric acid and leucine, 17.0; glutamic acid, 8.75; inactive  $\alpha$ -proline, 0.5, and tyrosine, 1.25 grams. J. J. S.

**Lysylglycine.** PHÆBUS A. LEVENE and WALLACE A. BEATTY (*Proc. Amer. Sci. Biol. Chemists*, 1907, xxxix, *J. Biol. Chem.*, 3).—In the tryptic digestion of egg-albumin, a peptide was obtained, which on further cleavage yielded only lysine and glycine. It could not be crystallised. Fischer and Suzuki's peptides of the hexone bases also failed to crystallise. W. D. H.

**Equilibrium between Proteids and Electrolytes. V. Completion of the Equilibrium Surfaces in the System, Globulin, Magnesium Sulphate, and Water.** V. SCAFFIDI (*Zeitsch. physiol. Chem.*, 1907, 52, 42—53. Compare Abstr., 1904, i, 355; 1905, ii, 512; 1906, i, 912).—The four following curves have been determined for the system, globulin, magnesium sulphate, and water. 1. Isotherm at 55°. 2. Isotherm at 70°. 3. Coagulation curve of globulin. 4. Freezing point curve of the liquid phase.

At 55°, even after filtration, the solutions are opalescent. For all concentrations of magnesium sulphate, the solubility of globulin is less at 55° than at 40°, and for concentrations exceeding 17.9% the solubility diminishes rapidly until when the solution is saturated with the sulphate all the globulin is precipitated.

At 70°, the solutions become much more cloudy and cannot be filtered, so that another method of analysis must be used. At this temperature, a much less concentrated solution of magnesium sulphate is capable of completely precipitating the globulin.

The coagulation curve shows that the coagulating temperature has its minimum value when the concentration of the magnesium sulphate is small. It then rises rapidly with the concentration, afterwards more slowly, then falls again, and ultimately attains a practically constant value of 72° when the concentration of the sulphate is high.

These four curves, together with three of Galeotti's isotherms, are used for constructing equilibrium surfaces for the complete system.

J. J. S.

**Deaminoglobulin.** H. LAMPEL (*Monatsh.*, 1907, 28, 625—632).—It has been shown that neither deaminoglutin (Skraup, Abstr., 1906, i, 913) nor deaminocasein (Skraup and Hoernes, Abstr., 1906, i, 913) yield lysine on hydrolysis, although this compound is present in the hydrolysis products of gluten and casein. It is therefore probable that at least one of the amino-groups of the lysine residue is free in casein and gluten, and is hence attacked by the nitrous acid during the formation of the deamino-compound. The present investigation was carried out to see if the lysine residue in globulin is similarly destroyed during the treatment with nitrous acid, and such is found to be the case.

A quantitative estimation of the hexone bases, obtained by the hydrolysis of globulin from horses' blood, gave the following values: arginine, 2·8%, histidine, 3·4%, and lysine, 4·2%.

*Deaminoglobulin* is prepared by treating globulin in acetic acid solution with sodium nitrite; it is a light brown powder, insoluble in dilute acids and alkalis, but is turned intense red by the latter, which colour disappears on neutralisation; it does not give a decided Millon's or biuret reaction. On analysis, it is found to contain, roughly, the same quantities of hydrogen and sulphur, and slightly more carbon and nitrogen than globulin. When hydrolysed with sulphuric acid, it yields: arginine, 2·8%, histidine, 2·4%, lysine being absent from the product.

W. H. G.

**Iodothyryne.** A. NÜRNBERG (*Beitr. chem. Physiol. Path.*, 1907, 10, 125—130. Compare Rohde, *Abstr.*, 1905, i, 618).—Two specimens of iodothyryne, prepared from thyreoglobulin by Oswald's method, have been heated with water under varying conditions under pressure. The original preparations did not give the Adamkiewicz, Millon, or Ehrlich reaction; the one gave the biuret test, but not the other. After heating for several hours under a pressure of six atmospheres, the specimens gave the Millon reaction and to a certain extent the Ehrlich reaction.

The results are in harmony with the view that the iodothyryne contains iodotyrosine and iodotryptophan residues.

Iodothyryne also gives the Millon and Ehrlich reactions after treatment with sodium and alcohol.

J. J. S.

**Hydrolysis of Ichthylepidin and Fibrin.** EMIL ABDERHALDEN and ARTHUR VOITINOVICI (*Zeitsch. physiol. Chem.*, 1907, 52, 368—374).—The results of hydrolysis of ichthylepidin (from the scales of the carp, *Cyprinus Carpio*) and of blood-fibrin were as follows:

	Ichthylepidin.	Fibrin.
Glycine	5·7%	2·0—3·0%
Alanine	3·1	3·6
Valine	—	1·0
Leucine	15·1	15·0
Proline	6·7	3·6
Phenylalanine	—	2·5
Aspartic acid	1·2	2·0
Glutamic acid	9·2	10·4—12·5
Serine	—	0·8
Tyrosine	1·0	3·5

The variations noted in fibrin indicate that it is not a single protein.

W. D. H.

**The Hydrolysis of Proteins by Means of Dilute Sulphuric Acid.** PHCEBUS A. LEVENE and CARL L. ALSBERG (*Bio-chem. Zeitsch.*, 1907, 4, 312—315).—Gelatin, casein, and edestin have been heated with dilute sulphuric acid of different concentrations under pressure

at temperatures between 140° and 170°. In each experiment, after hydrolysis, the total nitrogen, the nitrogen contained in the filtrate after half saturating with zinc sulphate, and also after complete saturation were estimated, and also the nitrogen contained in the filtrate after precipitation with 10% phosphotungstic acid. Gelatin behaves somewhat differently from the other proteins, the gelatoses being readily decomposed. With gelatin, also, the maximum yield of amino-acids corresponds with the disappearance of the biuret reaction. With the other acids, the substances which give the biuret reaction are completely decomposed before the maximum yield of amino-acids is attained.

J. J. S.

**Action of Sodium Hypobromite on Casein.** ZDENKO H. SKRAUP and REINHOLD WITT (*Monatsh.*, 1907, 28, 605—624).—It is found that when casein, gelatin, egg-albumin, and globulin are treated with alkaline sodium hypobromite at the ordinary temperature, they give off roughly 20% of their total nitrogen as nitrogen, and, except in the case of globulin, the same quantity of nitrogen is evolved even after previous hydrolysis of the protein. Among the products formed by the action of sodium hypobromite on casein, were found histidine and lysine to about the same extent as obtained by the hydrolysis of casein, but no arginine, as was to be expected (compare Stuchetz, *Abstr.*, 1906, i, 812). Several other amino-acids are also destroyed by the sodium hypobromite, since, although small quantities of leucine and active proline were isolated, the presence of glutamic acid,  $\gamma$ -proline, aspartic acid, phenylalanine, glycine, and alanine could not be detected. An oil was also isolated, which, although an aldehyde and similar to benzaldehyde in properties, could not be definitely identified as this compound. Acetic, propionic, valeric, oxalic, and succinic acids were also identified. The formation of valeric acid by the oxidation of casein by sodium hypobromite is of great interest, for, since it cannot be derived from ordinary leucine, it shows that there is probably present in casein an isomeric, normal leucine. The investigation is being continued in this direction.

W. H. G.

**Hydrolysis of Legumin from the Pea.** THOMAS B. OSBORNE and SAMUEL H. CLAPP (*J. Biol. Chem.*, 1907, 3, 219—225).—The results of acid hydrolysis in parts per cent. are as follow: glycine, 0.38; alanine, 2.08; valine, not isolated; leucine, 8; proline, 3.22; phenylalanine, 3.75; aspartic acid, 5.3; glutamic acid, 13.8; serine, 0.53; cystine, not determined; tyrosine, 1.55; arginine, 10.12; lysine, 4.29; histidine, 2.42; ammonia, 1.99. This accounts for 57.43% of the protein. Tryptophan was present.

W. D. H.

**Azolitmin Compounds of Proteins.** JACOB ROSENBLUM and WILLIAM J. GIES (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxxix.—xl., *J. Biol. Chem.*, 3).—It is well known that mucoids are acid to litmus; pure moist mucoid mixed with blue litmus or azolitmin yields a product of raspberry-red colour. The colour is not removed by any washing process. It is turned blue by alkali; this blue is soluble in



water. The view is put forward that the phenomena are not due to adsorption, but that a definite compound is formed. Nucleo-proteins are stated to behave in a similar way. W. D. H.

**Oxidation of Oxyhæmoglobin.** I. SZRETER (*Compt. rend.*, 1907, 145, 203—205).—By gradually adding hydrogen peroxide solution to a solution of crystallised oxyhæmoglobin, prepared from horses' blood, the author obtains an almost white, extremely hygroscopic, amorphous powder, which gives a red biuret reaction. In aqueous solution, it is not precipitated by concentrated mineral acids, and is not coagulated by heating. It is precipitated in colourless flocks by strong alcohols, neutral salts, potassium ferrocyanide, metaphosphoric acid, or the alkaloid reagents. Analysis gives the following percentage composition. Mineral matter, 3·36; iron, 0·47—0·49; carbon, 41·18—41·46; hydrogen, 6·2—6·39, and nitrogen, 13·89—14·16. T. H. P.

**Hydrolysis of Spleen Nucleo-protein.** JOHN A. MANDEL and PHÆBUS A. LEVENE (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxiii—xxiv., *J. Biol. Chem.*, 3; *Bio-chem. Zeitsch.*, 1907, 5, 33—44).—Hydrolysis of the nucleo-protein of the spleen yielded in parts per cent. the following substances: glutamic acid, 25; leucine and valine, 6; glycine and alanine, 2; aspartic acid, 0·5; tyrosine, 1; lysine picrate, 7·5; arginine picrolonate, 2; histidine picrolonate, 0·5; adenine, 0·4; guanine, 0·6; cytosine, 0·7; thymine, 0·5; phenylalanine was present, and proline was not found. W. D. H.

**Hydrolysis of Keratin from Horn and Wool.** EMIL ABDEH-DALDEN and ARTHUR VOITINOVICI (*Zeitsch. physiol. Chem.*, 1907, 52, 348—367).—Keratins from the horns and wool of sheep were hydrolysed and the amounts of the various amino-acids are given in tables and compared with the results previously obtained from the keratin of hair and feathers, and from the horns of cattle. The results are in all cases different, and indicate that keratin is a mixture of proteins. W. D. H.

**The Degradation of Keratin by Oxidation with Hydrogen Peroxide.** FERDINAND BREINL and OSKAR BAUDISCH (*Zeitsch. physiol. Chem.*, 1907, 52, 159—169).—The products obtained by heating human hair, previously extracted with ether, with 30% hydrogen peroxide are sulphur, nitric and sulphuric acids; carbon dioxide, acetic, oxalic, and succinic acids; acetaldehyde, ammonia, and small amounts of amino-acids.

Glycine, alanine, leucine, aspartic acid, and cystine are oxidised when heated with 30% hydrogen peroxide, yielding ammonia, carbon dioxide, aldehydes, and organic acids. Tyrosine is not oxidised (compare Dakin, *Abstr.*, 1906, ii, 105). J. J. S.

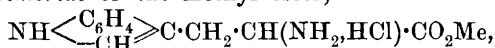
**Whey Albumose.** ERNST FULD (*Bio-chem. Zeitsch.*, 1907, 4, 488—499).—Numerous investigators have applied themselves to the problem of the origin and meaning of Hammarsten's whey-protein. The present experiments were carried out with solutions of pure caseinogen in lime water, which were neutralised with dilute phosphoric acid.

The solution was subjected to the action of rennet, and casein was precipitated by acetic acid; the filtrate gave no further precipitate on the addition of acetic acid, but gave the nitric reaction for albumoses. The name whey-albumose is therefore suggested. W. D. H.

**Tryptophan and its Derivatives.** EMIL ABDERHALDEN and MARTIN KEMPE (*Zeitsch. physiol. Chem.*, 1907, 52, 207—218. Compare Hopkins and Cole, *Abstr.*, 1902, i, 193; Neuberg and Popowsky, this vol., i, 253; Mayeda, *ibid.*, ii, 591).—Tryptophan prepared from casein by Hopkins and Cole's method has  $[\alpha]_D^{20} + 6^\circ$  in  $N/2$  sodium hydroxide solution and  $+1.31^\circ$  in  $N$ -hydrochloric acid solution. If the decomposition of the casein is allowed to proceed too long, the yield of tryptophan is small, and a by-product,  $C_{11}H_{12}O_3N_2$ , less soluble in water than tryptophan, is obtained. It crystallises in needles, turns yellow at  $276^\circ$ , and melts at  $293^\circ$  (corr.). When heated, it produces an odour of indole or scatole, but after boiling with concentrated hydrochloric acid, it yields an odour of quinoline when heated.

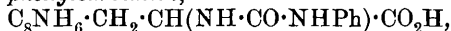
The copper salt of tryptophan,  $(C_{11}H_{11}O_2N_2)_2Cu$ , forms a pale blue precipitate, and when dry a greyish-blue powder; it is sparingly soluble in the usual solvents and in cold dilute mineral acids.

The hydrochloride of the methyl ester,



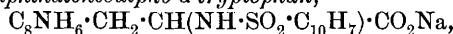
crystallises from a mixture of methyl alcohol and ethyl acetate, has m. p.  $214^\circ$  (corr. decomp.), and dissolves readily in water or alcohol. The methyl ester,  $C_{12}H_{14}O_2N_2$ , crystallises from ether in large plates, m. p.  $89.5^\circ$  (corr.).

d-Tryptophanphenylcarbimide,



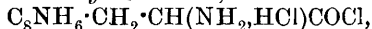
crystallises from dilute methyl alcohol in slender needles, m. p.  $166^\circ$  (corr.), and is remarkably sensitive to light, melting at  $132^\circ$  after exposure.

Sodium  $\beta$ -naphthalenesulpho-d-tryptophan,



crystallises from hot water in microscopic needles, m. p.  $304^\circ$  (corr.).

d-Tryptophan chloride hydrochloride,



melts and decomposes at  $228^\circ$  (corr.), and resembles the chlorides of amino-acids prepared by Fischer. J. J. S.

**Equilibrium and Final Condition of Enzyme Reactions.**

HANS EULER (*Zeitsch. physiol. Chem.*, 1907, 52, 146—158).—The question of equilibrium and final condition of typical enzyme reactions is discussed from the point of view that the enzyme forms compounds with the substrate and also with the products formed. It is pointed out that the numerical value for the end condition can only coincide with the "natural equilibrium" when the compounds enzyme-substrate and enzyme-reaction products are equally stable (compare Bodenstein and Dietz, *Zeitsch. Elektrochem.*, 1906, 12, 605). It follows that the concentrations of a system in stable equilibrium will be altered by the addition of an enzyme. The question of ferments and anti-ferments is

discussed. It is suggested that the injection of an enzyme destroys the normal relationship between the substrate and its decomposition products, and that the products produced by the injected ferment cause the secretion of an anti-ferment until the excess decomposition products are combined. The normal equilibrium between substrate and products is gradually re-established, but with a velocity which is small compared with that of the secretion of the anti-ferment, and thus an excess of free anti-ferment is found in the serum. If this is correct, it should follow that the injection into the organism of the decomposition products formed by the enzyme should produce the same effects as the injection of the enzyme. It should also follow that the anti-ferment action of a serum, obtained some time after the injection of the ferment, should continue to increase *in vitro*. J. J. S.

**Enzyme Action. IX. The Enzymes of Yeast: Amygdalase.** ROBERT J. CALDWELL and STEPHEN L. COURTAULD (*Proc. Roy. Soc.*, 1907, B, 79, 350—359).—The hydrolysis of amygdalin by yeast is due neither to maltase nor to invertase, but to a specific enzyme, *amygdalase*, not hitherto recognised.

Comparative experiments were made at 25° with solutions containing equivalent quantities of amygdalin, maltose, and methyl glucoside, and extracts of various yeasts which had been heated previously to different temperatures. The action on amygdalin and also on methyl- $\alpha$ -glucoside persisted after heating the extract to a temperature (50°) above that at which maltase is an active agent. At 60°, the hydrolysis of amygdalin and methyl- $\alpha$ -glucoside ceased, although the enzyme bringing about the inversion of sucrose was still active. The discovery of an  $\alpha$ -glucase different from maltase is of interest. Whether there are two enzymes, one of which attacks amygdalin and the other methyl- $\alpha$ -glucoside, was not determined conclusively. There is some evidence to indicate that maltase can attack methyl- $\alpha$ -glucoside, and that amygdalase attacks both methyl- $\alpha$ -glucoside and amygdalin.

Amygdalase is equally well extracted from dried yeast at all temperatures from 15° to 45°. Whereas a low temperature extract affords a very small proportion of amygdalase, the quantity is increased by heating the extract for a short time at 45°; that is to say, the amygdalase is originally dissolved as part of a more complex protein or zymogen molecule, which is hydrolysed at the higher temperature.

Dextrose has an inhibitory effect on the hydrolysis of amygdalin by amygdalase, and, in this respect, maltose, lactose, and galactose are inert. G. S. W.

**Enzyme Action. X. The Nature of Enzymes.** HENRY E. ARMSTRONG and EDWARD F. ARMSTRONG (*Proc. Roy. Soc.*, 1907, B, 79, 360—365).—As the investigation is extended, the evidence becomes more and more convincing that the action which an enzyme exercises is specific, being limited to compounds of a particular type. Maltase, in the authors' opinion, is capable of hydrolysing  $\alpha$ -glucosides alone, whilst emulsin hydrolyses  $\beta$ -glucosides. A table is given summarising

the experiments in relation to sucroclasts and their inhibitors, showing that the enzyme and hydrolyte must be in complete correlation. The extraordinary activity of invertase makes it necessary to work with highly dilute solutions of the enzyme; the influence of small quantities of impurities is counteracted by means of amino-acids.

*Nature of Enzymes.*—The collected evidence demonstrates that during hydrolysis invertase extends its influence over the whole of the sucrose molecule. The question arises whether this is true of other biases. There are many indications which make it probable, at all events in the case of lactose, that what is true of sucrose and its correlative enzyme applies generally.

In the case of enzymes other than those which affect carbohydrates, the range of activity would appear, however, often to be greater than is ever manifested in the case of enzymes of the sucroclastic class.

G. S. W.

#### Different Hydrolytic Actions Produced by a Single Enzyme.

LUIGI MARINO and G. SERICANO (*Gazzetta*, 1907, 37, i, 45—51).—The authors have prepared, from beer yeast, a sample of invertase which is capable of hydrolysing sucrose, but incapable of acting on  $\alpha$ -methylglucoside, maltose, lactose, or salicin, and hence is quite free from maltase. This purified invertase resolves amygdalin into dextrose (1 mol.) and amygdonitrile glucoside, which, according to Fischer, is formed from amygdalin by the action of the maltase contained in beer yeast. The disaccharide of amygdalin must therefore be distinct from ordinary maltose. The fact that one and the same enzyme can effect the hydrolysis of disaccharides of different constitution is regarded by the authors as evidence supporting the view that special enzymes, such as trehalase, melibiase, melizitase, and gentiobiase, are non-existent. It is also pointed out that in no instance has a reversible action been observed with a single, well-defined enzyme.

T. H. P.

**Behaviour of Peroxydase towards Hydroxylamine, Hydrazine, and Hydrogen Cyanide.** ALEXIS BACH (*Ber.*, 1907, 40, 3185—3191. Compare this vol., i, 268).—The amounts of hydroxylamine hydrochloride, hydrazine sulphate, and potassium cyanide required for the complete destruction of peroxydase are of such magnitude that these substances cannot function as poisons, but must enter into stoichiometric reaction with the peroxydase. The amount of peroxydase destroyed by 2 mols. of hydroxylamine hydrochloride or potassium cyanide, or  $\frac{1}{4}$  mol. of hydrazine sulphate, renders active 1 mol. of hydrogen peroxide.

G. Y.

**Rennet Action.** M. VAN HERWERDEN (*Zeitsch. physiol. Chem.*, 1907, 52, 184—206).—Whether the curdling action of rennet on caseinogen (casein) which results in the formation of casein (para-casein) is hydrolytic or not is still uncertain; the relation of whey-protein to the process is also a matter of speculation. It is, however, known that in curdling two processes occur, first, the action of the rennet, and then the precipitation of one or more of the products formed by calcium

salts. The view now put forward is that the enzyme forms, from the labile caseinogen molecule, one with another constitution, and this main end-product is termed para-casein *A*. This is regarded as a complex containing para-casein *B* (which differs from *A* in being more readily precipitable by ammonium sulphate, and less so by alcohol) and a substance, *C*, which is not precipitated by acetic acid, and requires still more ammonium sulphate to precipitate it; it is soluble in water, gives a weak Adamkiewicz and a strong biuret reaction. By long continued action, a primary proteose appears, which is the beginning of a new phase characterised by further decomposition of the casein molecule.

Free hydrogen ions are not necessary for the coagulation of milk or of solutions of caseinogen which contain calcium. W. D. H.

**Ferments and Anti-ferments. IV. MARTIN JACOBY** (*Bio-chem. Zeitsch.*, 1907, 4, 21—24).—In their adsorption phenomena (fibrin), the peptic and rennetic enzymes of Witte's rennet behave similarly. Horse serum manifests both an anti-peptic and an anti-rennetic action.

G. S. W.

**Ferments and Anti-ferments. V. MARTIN JACOBY** (*Bio-chem. Zeitsch.*, 1907, 4, 471—483. Compare Abstr., this vol., ii, 108).—The presence of anti-ferments in blood-serum is confirmed; the absolute quantity of these is a more important factor than their concentration. Ferments are placed in the same group as toxins and the anti-ferments in the same category as anti-toxins; but, in addition to anti-ferments, the serum contains other substances which are dialysable and resist heat and hinder ferment activity. Rennin and pepsin can be separated from fibrin flocculi by alkalis, whilst the rennin—anti-rennin union is broken by acids. The view that the union of a ferment with the substrate is not identical with the union with the anti-ferment is thus confirmed.

Rennin and pepsin are soluble in alkalis, and trypsin is soluble in acids, whereas pepsin acts in an acid, and trypsin in an alkaline medium. It is possible in view of the analogies of inorganic chemistry and of what is known as to the physico-chemical behaviour of ferments, that the insoluble condition of the ferment is a critical moment in its activity.

W. D. H.

**Existence of a Tyrosinase in Wheat Bran. GABRIEL BERTRAND and MUTERMILCH** (*Compt. rend.*, 1907, 144, 1285—1288).—According to Mège-Mouriès (*ibid.*, 1856, 42, 1122; 1857, 44, 40, 449; 1859, 48, 126) the colour of brown bread is caused by the action, during panification, of cerealin, a substance of a ferment nature contained in the bran. Boutroux (*ibid.*, 1895, 120, 934) states that the bran contains laccase, and a substance of an undetermined nature on which the ferment acts. By macerating bran in water, precipitating the extract with alcohol, redissolving the precipitate in water, separating the insoluble portion by a centrifuge, reprecipitating with alcohol, and drying in a vacuum, the authors have obtained a substance soluble in water which does not contain laccase,

since, when added to an aqueous solution of guaiacol, no tetraguaiacquinone is produced (Abstr., 1903, i, 157). It contains an enzyme of the nature of a tyrosinase, as its aqueous solution, sterilised by filtration through a Chamberland filter, is not coloured by contact with atmospheric oxygen, but acquires first a rose, then a cherry-red and, finally, a dark brown colour when treated under aseptic conditions with a solution of tyrosine. The coloration is prevented by removal of all the oxygen by means of a mercury pump, or by heating the enzyme solution previously for five minutes on a water-bath at  $100^{\circ}$  (compare Abstr., 1896, ii, 571; 1897, ii, 117). The substance contains other enzymes, among which is Raciborsky's peroxydase (*Ber. Deut. bot. Ges.*, 1898, 16, 119). Owing to the presence of the latter, the aqueous solution in the absence of oxygen, but in the presence of a little hydrogen peroxide, oxidises guaiacol to tetraguaiacquinone and quinol to quinhedrone, and gives an intense blue coloration with the dye from guaiacum resin.

E. H.

***p*-Aminophenylarsonic Acid.** I. PAUL EHRLICH and ALFRED BERTHEIM (*Ber.*, 1907, 40, 3292—3297).—Atoxyl is the sodium salt of the product obtained by Béchamp (*Compt. rend.*, 1863, 56, 1172) by heating aniline arsenate at  $190$ — $200^{\circ}$ , and described by him as the anilide. That it is not an anilide, but *p*-aminophenylarsonic acid, is shown. 1. It cannot be hydrolysed to aniline; 2. it contains a primary amino-group; 3. it possesses all the characteristic reactions described by Michaelis of arsonic acids,  $R \cdot AsO(OH)_2$ ; 4. the arsenic acid radicle can be replaced by iodine, yielding *p*-iodoaniline. The action of heat is therefore comparable with the conversion of aniline sulphate into sulphanilic acid, and the name arsanilic acid is suggested for the substance.

Arsanilic acid,  $NH_2 \cdot C_6H_4 \cdot AsO(OH)_2$ , possessed weak basic properties; the *hydrochloride*,  $C_6H_8O_3NAs, HCl$ , is immediately hydrolysed by water; the *sodium* salt is neutral to test paper and crystallises with varying quantities of water. The *acetate*,  $C_8H_{10}O_4NAs$ , forms glistening, white leaflets, easily hydrolysed by hot alkalis or acids, does not react with naphthaquinonesulphonic acid, and forms a *sodium* salt. Arsanilic acid may be diazotised, and then forms with naphthylamine a red azo-dye, dissolving in cold sodium carbonate solution with a red colour. Sodium arsanilate, when heated with dilute sulphuric acid and potassium iodide, is converted into *p*-iodoaniline.

W. R.

## Organic Chemistry.

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**Hanoverian Petroleum.** FELIX B. AHRENS and JOHANNES RIEMER (*Zeitsch. angew. Chem.*, 1907, **20**, 1557—1559).—The specimen of Wietze oil,  $D^{15}_4$  0·941, examined, is viscous, blackish-brown, opaque even in thin layers, has only a slight odour of petroleum, gives a transient blue fluorescence with concentrated sulphuric acid, and has the specific viscosity 12·16 at 60°, the flash point 105°, and the ignition temperature 143°; its vapour tension is small, only 3·06% evaporating at the laboratory temperature in eight weeks. It contains 0·06—0·07% of mechanical impurities, and 0·86% of water, which, on evaporation, yields 25·27% of a residue consisting chiefly of sodium chloride together with small amounts of potassium and magnesium chlorides, and traces of calcium sulphate. The oil yields 15·8% of a distillate, b. p. 200—300°,  $D^{15}_4$  0·86,  $n - 1/d$  0·5384, which has the specific viscosity 1·44 at 20°, the flash point 47°, and the ignition temperature 69°. The distillation residue forms a black, viscous mass,  $D$  0·9742, which, when “cracked,” yields 75% of distillate and 18% of coke. The brown distillate,  $D$  0·869, specific viscosity 1·51, flash point 45°, ignition temperature 64°, has a green fluorescence, and a strong, unpleasant odour; on fractionation, it yields 5%  $D$  0·813, b. p. below 150°, 45% b. p. 150—300°, and 50% b. p. above 300°. The intermediate fraction,  $D$  0·8292, has a specific viscosity 1·03, the flash point 34°, and the ignition temperature 49°. The fraction, b. p. above 300°,  $D$  0·9092, has a specific viscosity 3·16, a flash point 161°, and the ignition temperature 187°.

When distilled/50 mm., the crude oil yields 85% of distillate and 10% of coke. The coke has an odour of hydrogen sulphide. The distillate,  $D$  0·8753, specific viscosity 1·93, flash point 67°, ignition temperature 101°, yields on distillation 36·6% of illuminating oil,  $D$  0·8315, specific viscosity 1·4, flash point 44°, ignition temperature 61°, and 63·4% of lubricating oil,  $D$  0·9107, specific viscosity 4·14, flash point 153°, and ignition temperature 178°.

The examination of the various fractions shows that the oil consists chiefly of unsaturated and aromatic hydrocarbons, methane hydrocarbons, decane to pentadecane, and naphthenes, decanaphthene to tridecanaphthene, being present only in comparatively small amounts, and in the fractions boiling at the lower temperatures. The oil contains only 0·2879% of solid paraffins, and 1·03% of asphalt insoluble in light petroleum or 20 7% insoluble in ether-alcohol. G. Y.

**Hexyl and Octyl Fluorides.** EMANUELE PATERNÒ and ROSARIO SPALLINO (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 160—166).—sec.-Hexyl fluoride ( $\beta$ -fluorohexane),  $\text{CH}_2\text{Pr}\cdot\text{CHMeF}$ , prepared by the action of  $\beta$ -iodohexane on silver silicofluoride, has b. p. 82—86°,  $D^{20}_4$  0·819, and  $n^{20}_D$  1·3683.

**n-Octyl fluoride**,  $C_8H_{15}F$ , prepared from octyl iodide and silver silicofluoride, is a colourless liquid, b. p.  $131-134^\circ$ ,  $D_4^{20} 0.798$ .

T. H. P.

**Equilibria Involving the Addition of Ethylene.** JULIUS SAND (*Zeitsch. physikal. Chem.*, 1907, 60, 237—251. Compare Sand and Breest, this vol., ii, 537).—A theoretical paper. The author shows how it should be possible, from electrochemical measurements in aqueous solutions of mercuric and mercurous compounds, and from the study of certain equilibria in solution, to calculate the changes of free energy involved in the reactions:  $C_2H_4 + H_2O \rightleftharpoons C_2H_5 \cdot OH$ ;  $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ;  $C_2H_4 \rightleftharpoons C_2H_2 + H_2$ .

J. C. P.

**Comparative Oxidation of Diisobutylene by means of Potassium and Magnesium Permanganate.** NICOLAUS A. PRILERZAEFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 769—771).—Magnesium permanganate oxidises diisobutylene less rapidly and thoroughly than potassium permanganate, and yields a less homogeneous product.

Z. K.

**Bromomethylnitrolic Acid.** GIACOMO PONZIO and G. CHARRIER (*Gazzetta*, 1907, 37, ii, 99—104).—The authors have prepared bromoisnitrosoacetone by the action of hydrobromic acid on acetylmethylnitrolic acid (compare Behrend and Schmitz, Abstr., 1894, i, 108; Behrend and Tryller, Abstr., 1895, i, 201) and have then treated it with nitric acid in order to obtain bromomethylnitrolic acid (compare Ponzio, this vol., i, 744). The latter is only formed together with oxalic acid and carbon tetrabromide in small proportion, the main product being dibromodinitromethane, which is probably derived from bromodinitromethane (compare Wolff, Abstr., 1893, i, 689). This reaction may, indeed, be used advantageously for the preparation either of dibromodinitromethane or of the potassium derivative of bromodinitromethane.

**Bromoisnitrosoacetone**,  $CBrAc \cdot NOH$ , crystallises from benzene in white prisms, m. p.  $123-124^\circ$ , and dissolves readily in alcohol, ether, or chloroform, and to a less extent in water.

**Bromomethylnitrolic acid**,  $NO_2 \cdot CBr \cdot NOH$ , crystallises from chloroform in faintly yellow needles, m. p.  $93^\circ$  (decomp.), is readily soluble in ether or alcohol and moderately so in benzene, is less stable than chloromethylnitrolic acid, and is soluble in cold water, which decomposes it according to the equation:  $NO_2 \cdot CBr \cdot NOH = CO_2 + HBr + N_2O$ . It dissolves in dilute alkali hydroxides, giving a blood-red liquid which rapidly becomes colourless, and is then found to contain only alkali carbonate and bromide in theoretical amount; the same reaction is produced by the alkaline earth hydroxides. It is moderately stable in presence of acids.

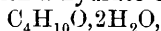
T. H. P.

**Dehydration of Alcohol by Lime.** ANTON KAILAN (*Monatsh.*, 1907, 28, 927—946).—This work was undertaken to obtain exact details as to the proportion of lime, and also the time, necessary for the dehydration of alcohol of 92—93% by weight, as these are not found in



the literature. If 92—93% alcohol is boiled with lime in a reflux apparatus, the velocity of dehydration to 99·5% alcohol is independent of the amount of lime present if the value  $K/A$ , in which  $K$  is the weight of lime in kilograms and  $A$  is the volume of alcohol in litres, remains between 0·25 and 0·41; with  $K/A > 0·4$ , the velocity of the dehydration increases with the proportion of lime, at first rapidly, the velocity with  $K/A = 0·5$  being thrice that with  $K/A = 0·4$ , but thereafter gradually more slowly. With  $K/A > 0·5$ , the value for the velocity constant  $k$ , as calculated by means of the equation for uni-molecular reactions, remains fairly constant throughout each series, but with  $K/A =$  or  $< 0·4$ , the value for  $k$  diminishes rapidly as the concentration of the alcohol increases above 99·5%. The loss of alcohol accompanying this method of dehydration increases rapidly with the proportion of lime employed; it is found most advantageous to add 0·55 kilogram of lime per litre of 92—93% alcohol, when 99·5% alcohol is obtained on boiling for three and a half hours, or 99·9% alcohol in about six hours. Dehydration takes place also at the ordinary temperature, but only slowly; with  $K/A = 0·563$  at 20—22°, the dehydration is complete in about 575 hours. G. Y.

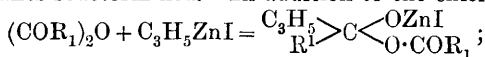
**Mixtures of Trimethylcarbinol and Water.** EMANUELE PATERNÒ and A. MIELI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 153—160).—The curve representing the temperatures of equilibrium between the liquid and solid phases of mixtures of trimethylcarbinol and water exhibits two minima and a horizontal portion the mean position of which corresponds with a hydrate of the composition



m. p. 0°. The density curves of the mixtures for temperatures between 0° and 70° have been determined and those for 0° and 24° confirm the existence of the above hydrate. Moreover, the viscosity at 24° is a maximum for a mixture of the constitution  $\text{C}_4\text{H}_{10}\text{O}, 2\text{H}_2\text{O}$ .

T. H. P.

**Action of Zinc Allyl Iodide on Anhydrides of Monobasic Acids.** ALEXANDER M. SAYTZEFF [with F. PETROFF, N. MUSUROFF, S. CHOWANSKY, G. ANDRÉEFF, B. CHONOWSKY, and ANDREAS LUNJACK] (*J. pr. Chem.*, 1907, [ii], 76, 98—104).—Several diallyl alkyl carbinols have been prepared by the method previously described (*J. Russ. Phys. Chem. Soc.*, 1906, 26, 16), namely, by the action of zinc allyl iodide on the anhydrides of monobasic acids in ethereal solution, and their physical constants redetermined. In addition to the chief reaction:



$\text{C}_3\text{H}_5 \begin{array}{c} \diagup \\ \text{R}_1 \end{array} \text{C} \begin{array}{c} \diagdown \\ \text{O} \cdot \text{COR}_1 \end{array} \text{OZnI} + \text{C}_3\text{H}_5\text{ZnI} = (\text{C}_3\text{H}_5)_2\text{CR}_1 \cdot \text{OZnI} + \text{COR}_1 \cdot \text{OZnI}$ ; the following reaction takes place to a certain extent:  $(\text{C}_3\text{H}_5)_2\text{CR}_1 \cdot \text{OZnI} + (\text{COR}_1)_2\text{O} = (\text{C}_3\text{H}_5)_2\text{CR}_1 \cdot \text{O} \cdot \text{COR}_1 + \text{COR}_1 \cdot \text{OZnI}$ .

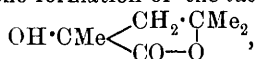
Methyldiallylcarbinol, b. p. 157—159°;  $D_0^\circ$  0·87747,  $D_{20}^\circ$  0·86134 (compare Sorokin, this Journ., 1877, 299). Ethyldiallylcarbinol, b. p. 175—176°/755·6 mm.;  $D_0^\circ$  0·88603,  $D_{20}^\circ$  0·86877 (compare Smirensky, Abstr., 1882, 488). Propyldiallylcarbinol, b. p. 192—194°;

D<sub>0</sub> 0·87939, D<sub>0</sub> 0·86286 (compare A. and P. Saytzeff, Abstr., 1879, 136). *iso*Propyldiallylcarbinol, b. p. 187—188°/759·8 mm.; D<sub>0</sub> 0·88859, D<sub>0</sub> 0·87133 (compare Rjabinin and Saytzeff, Abstr., 1879, 612).

W. H. G.

**Preparation of Glycols from Keto-alcohols by the Action of Organo-magnesium Compounds.** ADOLF FRANKE and MORITZ KOHN [and, in part, J. KOVAČEVIĆ and J. NEMLIČ] (*Monatsh.*, 1907, 28, 997—1015. Compare this vol., i, 171).—The formation of  $\beta$ -glycols by the action of organo-magnesium compounds on  $\beta$ -hydroxy-aldehydes having been described previously, the investigation of the reaction has now been extended to the preparation of glycols by the action of organo-magnesium compounds on keto-alcohols.

When distilled with dilute sulphuric acid,  $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol (Abstr., 1905, i, 111; Zelinsky, Abstr., 1902, i, 593) yields  $\beta\delta$ -dimethyl- $\Delta^{\alpha}$ -pentene- $\delta$ -ol,  $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ , b. p. 132°, which forms an *additive* compound with bromine. The *acetyl* derivative has b. p. 156—158°. Oxidation of the unsaturated alcohol with potassium permanganate leads to the formation of the *lactone*,



which crystallises in white leaflets, m. p. 64°, b. p. 248°/760 mm.

$\beta$ -Methylpentane- $\beta\epsilon$ -diol,  $\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{OH}$ , prepared by the action of magnesium methyl iodide on acetopropyl alcohol ( $\delta$ -keto-*n*-amyl alcohol), is obtained as a viscid, colourless oil, b. p. 118—120°/14 mm., or 218—219°/760 mm. When boiled with 10% sulphuric acid, the diol is converted into 2-methyltetrahydrofuran,  $\text{C}_6\text{H}_{12}\text{O}$ , which forms a colourless oil, b. p. 90—92°, has an odour resembling camphor, and remains unchanged when heated with water at 150°. Oxidation of the diol with potassium permanganate leads to the formation of acetone and a *lactone*,  $\text{C}_6\text{H}_{10}\text{O}_2$ , which is obtained as a mobile liquid, b. p. 200—202°, and has a characteristic odour resembling cinnamon. The corresponding *potassium* and *calcium*,  $(\text{C}_6\text{H}_{11}\text{O}_2)_2\text{Ca}$ , salts are described. A small amount of an acid product formed together with the *lactone* is probably malonic acid.

$\beta$ -Methylhexane- $\beta\zeta$ -diol,  $\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_4\cdot\text{OH}$ , formed from acetobutyl alcohol ( $\epsilon$ -keto-*n*-hexanol) and magnesium methyl iodide, is obtained as a colourless, viscid oil, b. p. 135°/19 mm., and on distillation under atmospheric pressure decomposes, forming an unsaturated alcohol,  $\text{C}_7\text{H}_{14}\text{O}$ , which is a colourless, mobile oil, b. p. 173°/760 mm., and yields an *additive* compound with bromine. When heated with sulphuric acid, the glycol yields dimethylpentamethylene oxide,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2$ , which forms a colourless, mobile oil, b. p. 121°, and has an intense odour of camphor. Oxidation of the glycol with potassium permanganate leads to the formation of acetone and succinic acid.

G. Y.

**Action of Acetic Anhydride on Diisobutylene Glycol.** NICOLAUS A. PRILERZAEFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 759—768. Compare Abstr., 1904, i, 795).—The products obtained by

the interaction of acetic anhydride and  $\alpha$ -glycols depend to a very large extent on the temperature and duration of the experiment. Below  $150^{\circ}$ , almost the only products produced are diacetyl- $\alpha$ -glycols. At higher temperatures, one acetyl group is split off, forming at least two unsaturated monoacetates, which, on saponification, yield the corresponding alcohols, which in their turn can form a variety of compounds, such as aldehydes, ketones, unsaturated hydrocarbons, &c.

The following compounds are formed when acetic anhydride reacts with diisobutylene glycol: (1) a saturated *diacetyl* compound,  $C_8H_{16}O_2(COMe)_2$ , b. p.  $123-125^{\circ}/12.5$  mm., which, on saponification, yielded the *alcohol*,  $C_8H_{16}(OH)_2$ , b. p.  $217-218^{\circ}/760$  mm., m. p.  $59-60^{\circ}$ ; (2) the *monoacetyl* compound of an unsaturated *alcohol*,  $C_8H_{15}O(COMe)$ , b. p.  $190-191^{\circ}/759.8$  mm.,  $D_4^{20}$  0.9067,  $D_4^{20}$  0.8892. On hydrolysis, it yields an *aldehyde* which gives the *silver* salt  $C_8H_{15}O_2Ag$ , and an unsaturated *alcohol*,  $C_8H_{15}OH$ , b. p.  $176-178^{\circ}/762$  mm.,  $D_4^{20}$  0.8652,  $D_4^{20.5}$  0.8512, which easily polymerises, forming a substance with a low b. p. and the properties of an aldehyde; (3) these saponification products and their derivatives. The  $\alpha$ -glycols themselves are quite stable, but when heated in a sealed tube from which the oxygen has not been exhausted, a small quantity of the glycol is oxidised to a hydroxy-acid, which then acts as a catalyst in converting the glycol into aldehyde, but as the quantity of the catalyst is very slight, a high temperature and prolonged heating are necessary to effect the change. Z. K.

**Interaction of Ethyl Bromide and Silver Chromate.** ARTHUR JAKES (*Chem. News*, 1907, 96, 77).—When silver chromate is treated with ethyl bromide in presence of water, silver bromide is obtained together with a red solution containing alcohol and chromic acid. In the absence of water, a brownish-red solid is produced which is probably *ethyl chromate*, but has not yet been obtained pure. On heating this substance, decomposition occurs with formation of chromic acid, carbon dioxide, water, and other products. Sodium hydroxide decomposes it into alcohol and sodium chromate. E. G.

**Symmetrical Dimethylethylene Oxide.** LOUIS HENRY (*Compt. rend.*, 1907, 145, 406—408).—By the action of magnesium methyl bromide on *s*-dimethylethylene oxide,  $O \begin{smallmatrix} \text{CHMe} \\ \diagup \\ \text{CHMe} \end{smallmatrix}$ , *aa*-dimethylpropyl alcohol,  $CH_2Me \cdot CMe_2 \cdot OH$ , is formed exclusively. Since the same tertiary alcohol results from the action of magnesium methyl bromide on methyl ethyl ketone (isomeric with dimethylethylene oxide), whilst the oxide as such would be expected to give  $\alpha\beta$ -dimethylpropyl alcohol,  $CHMe_2 \cdot CHMe \cdot OH$ , it is probable that the magnesium compound causes the oxide to undergo isomeric change into the ketone similar to that induced by dilute sulphuric acid in butylene glycol. E. H.

**Preparation of the Asymmetrical Halohydrins and Properties of the Corresponding Ethylene Oxides.** ERNEST FOURNEAU and MARC TIFFENEAU (*Compt. rend.*, 1907, 145, 437—439).—By the action of organo-magnesium derivatives on chloroacetone

(Tiffeneau) or ethyl chloroacetate and its homologues (Fourneau), unsymmetrical  $\alpha$ -halohydrins are produced together, in some cases, with secondary products of approximately the same boiling point, which are separated from the halohydrins by converting these with alkali into ethylene oxides, or with dimethylamine into aminoalcohols.  $\beta$ -Methyl- $\alpha$ -butylene  $\alpha$ -chlorohydrin,  $\text{CMeEt(OH)·CH}_2\text{Cl}$ , b. p. 152—153°,  $D_0$  1·068 (compare Abstr., 1902, i, 449), is obtained by the action of magnesium ethyl bromide on chloroacetone.

The secondary product is  $\beta$ -methyl- $\alpha$ -ethylbutyl alcohol,  
 $\text{CHMeEt·CHEt·OH}$ ,

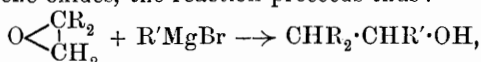
b. p. 149—150° (corr.),  $D_0$  0·8518, which forms a *butyrate*, b. p. 195—198°,  $D_0$  0·883; an *isovalerate*, b. p. 208—209°,  $D_0$  0·837, and a *benzoate*, b. p. 147°/17 mm.,  $D_{16}$  0·987, is oxidised into a *ketone*,  $\text{C}_7\text{H}_{14}\text{O}$ , b. p. 136—138°,  $D_{19}$  0·8248, forming a *semicarbazone*, m. p. 137°, and probably owes its origin to the formation of a *as*-methylethylethylene oxide,  $\text{O} \begin{smallmatrix} \text{CMeEt} \\ | \\ \text{CH}_2 \end{smallmatrix}$ , since this forms the same alcohol when treated with magnesium ethyl bromide.

The secondary product in the formation of  $\beta$ -methyl- $\alpha$ -propylene  $\alpha$ -chlorohydrin,  $\text{CMe}_2(\text{OH})\cdot\text{CH}_2\text{Cl}$ , which with alkali gives a *as*-dimethylethylene oxide,  $\text{O} \begin{smallmatrix} \text{CMe}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , b. p. 51—52°,  $D_0$  0·865, is  $\alpha\beta$ -dimethylpropyl alcohol,  $\text{CHMe}_2\cdot\text{CHMe}\cdot\text{OH}$ . Together with  $\beta$ -ethyl- $\alpha$ -butylene  $\alpha$ -chlorohydrin,  $\text{CH}_2\text{Me}\cdot\text{CEt(OH)·CH}_2\text{Cl}$  (compare Dalebroux and Wuyts, this vol., i, 105), which gives an *oxide*, b. p. 105—106°,  $D_0$  0·837, the alcohol  $\text{C}_8\text{H}_{18}\text{O}$ , b. p. 162—164°,  $D_0$  0·835, which is probably  $\alpha\beta$ -diethylbutyl alcohol,

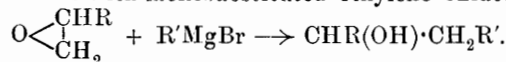
$\text{CH}_2\cdot\text{Me}\cdot\text{CHEt}\cdot\text{CHEt}\cdot\text{OH}$ ,

is formed.  $\alpha\beta$ -Trimethylethylene  $\alpha$ -chlorohydrin,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMeCl}$ , b. p. 141°,  $D_0$  1·053,  $\alpha\beta$ -dimethyl- $\beta$ -ethylethylene  $\alpha$ -chlorohydrin,  $\text{OH}\cdot\text{CMeEt}\cdot\text{CHMeCl}$ , b. p. 160—165°,  $D_0$  1·034, and  $\alpha$ -methyl- $\beta\beta$ -diethylethylene  $\alpha$ -chlorohydrin,  $\text{OH}\cdot\text{CEt}_2\cdot\text{CHMeCl}$ , b. p. 170—174°,  $D_0$  1·021, are prepared by the action of magnesium methyl- or ethylbromide on  $\gamma$ -chloro- $\beta$ -butanone or ethyl- $\beta$ -chloropropionate. With potassium hydroxide, these give trimethylethylene oxide, dimethylethylethylene oxide, and methyldiethylethylene oxide respectively. The secondary products appear to be tertiary alcohols.

When organo-magnesium compounds act on asymmetrical disubstituted ethylene oxides, the reaction proceeds thus:



whilst with monosubstituted ethylene oxides it proceeds as follows:



E. H.

**Binary Solution Equilibrium between Formic Acid and Water, and between Acetic Acid and Water.** ROBERT KREMANN [and, in part, E. BENNESCH, A. FLOOH, and F. KERSCHBAUM] (*Monatsh.*, 1907, 28, 893—900).—According to Roscoe (*Annalen*, 1863, 125, 320), formic acid containing 22·5% of water, corresponding with

a hydrate,  $4\text{CH}_2\text{O}_2, 3\text{H}_2\text{O}$ , boils constantly at  $107^\circ/760$  mm. The existence of such a hydrate, as also of Lorin's hydrate,  $2\text{CH}_2\text{O}_2, 3\text{H}_2\text{O}$ , appeared improbable since the b. p. of the mixtures vary with the pressure, and as a general rule the composition of hydrates is more simple. To establish this point and to investigate the possible existence of a hydrate,  $\text{CH}_2\text{O}_2, \text{H}_2\text{O}$ , corresponding with orthoformic acid, the authors determined the freezing points of a series of mixtures of formic acid and water. The freezing point curve falls to one eutectic point at  $-53.5^\circ$ , corresponding with a mixture of 64% of formic acid and 36% of water, hence formic acid does not form a hydrate.

Acetic acid behaves in the same manner; the freezing point curve for mixtures of acetic acid and water falls to one eutectic point at  $-27.5^\circ$ , corresponding with 57.5% of acetic acid and 42.5% of water. The depressions of the freezing points of formic and acetic acids by addition of water, as calculated from their heats of fusion, approximate to the experimental data only when the water is assumed to be bi- or ter-molecular. G. Y.

**Rôle of Metallic Hydrides in Reduction.** SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 607—609. Compare this vol., i, 10).—An excess of cobalt hydride at  $270^\circ/760$  mm. reduces oleic acid until 28—26% of stearic acid is produced, when the reaction terminates. In sealed tubes the reaction proceeds more readily, 60% of stearic acid being formed. Cobalt, obtained by the reduction of the lower oxide at  $310\text{—}330^\circ$ , when heated with a valeric or butyric acid solution of oleic acid at  $160\text{—}250^\circ$ , a constant stream of hydrogen being sent through the mixture, produces about 31% of stearic acid in one and a half hours. With reduced nickel, a similar result is obtained at  $97\text{—}170^\circ$ , but at the ordinary temperature no reaction takes place in either case. Palladium and platinum black rapidly reduce oleic acid, even at the ordinary temperature. Z. K.

**Mercuric Salts of Organic Acids.** A. D. DONK (*Rec. trav. chim.*, 1907, 26, 214—217).—The author has prepared *mercuric glycollate*,  $\text{C}_4\text{H}_6\text{O}_6\text{Hg}$ , and also the *double salt*,  $\text{C}_4\text{H}_6\text{O}_6\text{Hg}, \text{HgCl}_2$  (compare Schreiber, this Journ., 1876, ii, 398). The addition of silver nitrate to an aqueous solution of the double salt produces a white precipitate, which rapidly becomes yellow and dissolves on the addition of nitric acid; but excess of silver nitrate precipitates silver chloride, which does not re-dissolve. Double salts with mercuric chloride are also formed by mercuric acetate, lactate, propionate, and succinate, but apparently not by mercuric diglycollate. In aqueous solution, mercuric acetate is decomposed on heating, with deposition of mercuric oxide, and the *double salt*,  $\text{Hg}(\text{OAc})_2, \text{HgCl}_2$ , behaves similarly. The double salt formed by mercuric *propionate*,  $(\text{C}_3\text{H}_5\text{O}_2)_2\text{Hg}, \text{HgCl}_2$ , crystallises in mammillary masses of small needles, m. p. about  $87^\circ$ . T. H. P.

**Saponification of the Acetates of Glycerol.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1907, 13, 485—494).—The hydrolysis of the acetates of glycerol is studied in the same way as that of the acetates

of glycol (this vol., i, 462), in order to see whether the velocity constants of the reactions: (1)  $C_3H_5O_3(COMe)_3 + H_2O = C_3H_6O_3(COMe)_2 + Me \cdot CO_2H$ ; (2)  $C_3H_6O_3(COMe)_2 + H_2O = C_3H_7O_3(CO \cdot Me) + Me \cdot CO_2H$ , and (3)  $C_3H_7O_3(COMe) + H_2O = C_3H_8O_3 + Me \cdot CO_2H$ , are in the ratio 3:2:1. The rate of hydrolysis of the three acetates is determined in 0.01 and 0.02*N* hydrochloric acid at 18° and 25.2°, and the three velocity constants calculated from the results in the same way as before. The velocity constants for normal concentration of the hydrogen ions are:

	18°.	25.2°.
Reaction (1).....	0.359	0.650
Reaction (2).....	0.232	0.424
Reaction (3).....	0.132	0.260

The constants are in the ratio 3.10:2.00:1.14 at 18°, and 3.06:2.00:1.25 at 25.2°, that is, in glycerol triacetate the first acetyl group is hydrolysed three times, and the second twice as fast as the third. The experimental results are in good agreement with the view that the hydrolysis takes place in the three stages. T. E.

**Glycerides of Fatty Acids. I. Occurrence of Tristearin in Beef and Mutton Tallow.** ALOIS BÖMER [and, in part, A. SCHEMM and G. HELMSOTH] (*Zeitsch. Nahr. Genussm.*, 1907, 14, 90—117).—The author finds that tristearin is present in both beef and mutton tallow, and that under suitable conditions of crystallisation this triglyceride may be obtained from the fats in a perfectly pure state. In this respect, the results of the authors' experiments do not agree with those of Kreis and Hafner, who state that palmityldistearin is present in these fats (*Abstr.*, 1903, i, 457). The beef tallow examined contained 1.5%, and the mutton tallow 3%, of tristearin, whilst a sample of commercial pressed beef tallow contained from 4—5%. A determination of the melting point of glycerides obtained by crystallisation is of considerable use in ascertaining the purity of the specimens; with a pure glyceride, the first and second melting points (*Abstr.*, 1902, i, 529) coincide exactly. W. P. S.

**Process of Oxidation of Drying Vegetable Oils.** SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 609—615. Compare *Zeitsch. angew. Chem.*, 1906, 51, 2087).—Catalytic reactions of oxidation and of reduction are regarded as being of an essentially similar type, and as conforming to Engler's and Weisberg's theories of molecular autoxidation. The activity of the oxygen depends on its molecular state, thus the oxidation of linseed and other oils in the presence of metallic salts proceeds thus:  $AO_2 + B \rightarrow AO + BO$  (where A is a metal and B an oil). Light affects the process of oxidation both in the presence and absence of a catalyst.

The rate of drying of a layer of oil has been found to be in agreement with Spring's rule, being doubled for every 10° rise in temperature. That the reaction of oxidation of the oil is a catalytic one is shown by (1) the absence of any stoichiometric relation between

the quantity of metal employed and the amount of oxygen absorbed ; (2) the reaction being represented by a logarithmic curve. For the curve representing the first period of the reaction when the absorption of oxygen is proportional to the time, the following equation is proposed:  $k = m/t_1 + 1/t_2 \cdot \lg a/(a-x)$ . The absorption of oxygen seems to be directly proportional to its concentration. When the quantity of the catalyst is diminished, the first period is extended, from which it is deduced that the first phase of the reaction corresponds with molecular autoxidation, and that both molecular and atomic autoxidation can proceed simultaneously.

Old linseed oil, whipped oil, and prepared drying oils dry more quickly than fresh oils because they are already partly oxidised, and for the same reason the former absorb much less oxygen than the latter. The method of preparation of the oil, its freshness, and the material on which the layer is spread all have an important bearing on the mode of the reaction. The following metals act as the strongest catalysts in the process of oxidation : cobalt, manganese, chromium, and nickel, followed by lead, cerium, and barium, the least active being bismuth, mercury, copper, zinc, and uranium. In the process of reduction, the order is reversed. The higher the state of oxidation of the metal employed, the more rapid its effect on the drying up of the layer of oil.

Z. K.

**Cotton-seed Oil.** VICTOR J. MEYER (*Chem. Zeit.*, 1907, 31, 793—794).—By applying Haller's process (fractional distillation under reduced pressure of the fatty methyl esters), the author concludes that cotton-seed oil is largely composed of palmitin.

L. DE K.

**Oil of Myrtle Seeds.** FRANCESCO SCURTI and F. PERCIABOSCO (*Gazzetta*, 1907, 37, i, 483—486).—The seeds of the myrtle (*Myrtus communis*) contain 12—15% of a fatty oil, which, when extracted with ether or carbon disulphide, is obtained as a yellow liquid dissolving readily in turpentine and sparingly in alcohol. Poutet's elaidin test almost completely decolorises it, but does not convert it into a solid mass. The oil readily solidifies and has the following constants :  $D^{15}$  0.9244 ; thermal index by Tortelli's thermo-oleometer, 39 ; acidity, 1.7 c.c. of  $N/10$  alkali per gram ; saponification number, 199.84 ; Reichert-Meissl number, 9.65 ; Hehner's number, 95.31 ; iodine number, 107.45. It contains glycerides of oleic, linoleic, myristic, and palmitic acids, but not of stearic acid.

T. H. P.

**Raspberry-seed Oil.** RICHARD KRŽIŽAN (*Zeitsch. öffentl. Chem.* 1907, 13, 263—267).—A specimen of oil extracted from raspberry seeds gave the following chemical and physical constants :  $D^{15}$  0.9317 ; saponification number, 192.3 ; iodine number, 174.8 ; acid number, 1.0. The seeds yielded about 14.6% of the oil, the unsaponifiable portion of which contained 0.7% of phytosterol. The oil possessed drying properties, but in this respect was inferior to linseed oil. The liquid fatty acids consisted principally of linolic and linolenic acids ; small quantities of oleic and isolinolenic acids were also present.

W. P. S.

**Reactions of Iodine and of Sulphur with Mercurialised Fatty Substances.** ALEXANDRE LEYS (*Bull. Soc. Chim.*, 1907, [iv], 1, 633—640. Compare this vol., i, 582).—The iodine number of a fat can be measured in glacial acetic acid solution as well as in alcohol, iodine being decolorised in the former solvent by sodium thiosulphate with formation of sodium iodide and tetrathionate. If mercuric acetate is also present, titration with thiosulphate must be preceded by addition of a moderately large amount of potassium iodide. A certain amount of the iodine is fixed by the mercuric salt, but as this amount is constant, the results are not vitiated. The mercuric acetate solution must not, however, be heated with the fat. In estimating in this way the iodine number of a fat, the latter is dissolved in chloroform and to the solution is added a mixture of mercuric acetate solution and acetic acid solution of iodine, an equal volume of this mixture being titrated, after addition of potassium iodide, with sodium thiosulphate. After two hours, potassium iodide is added and the excess of iodine estimated by titration with thiosulphate. These observations are in contradiction to the views of Wijs (*Abstr.*, 1898, ii, 412). The above method gives for butter and cocoa-butter the numbers 33.6 and 5.1, Hübl's method giving 32.0 and 4.7.

The fact that the amount of iodine which oleic acid or butter is capable of fixing gradually diminishes when the fat is boiled with an acetic acid solution of mercuric acetate is regarded by the author as evidence supporting the view that oxygen is taken up by the fat (see this vol., i, 582).

When cotton-seed oil is heated with carbon disulphide and sulphur in acetic acid, it gives the characteristic coloration of Halphen's reaction. The changes occurring in this reaction are represented by the following equations:  $\cdot\text{CH}:\text{CH}\cdot + 2\text{CS}_2 = \begin{matrix} \cdot\text{CH}\cdot\text{S}\cdot\text{CS} \\ \cdot\text{CH}\cdot\text{S}\cdot\text{CS} \end{matrix}$ , which, with S,

gives  $\begin{matrix} -\text{CH} \\ | \\ -\text{CH} \end{matrix} > \text{S} + 2\text{CS}_2$ ; finally,  $\begin{matrix} -\text{CH} \\ | \\ -\text{CH} \end{matrix} > \text{S} + \text{CS}_2 = \text{H}_2\text{S} + \text{S} \begin{matrix} \text{C} \\ | \\ \text{C} \end{matrix} > \text{CS}$ .

T. H. P.

**Synthesis and Properties of  $\beta$ -Hydroxy- $\alpha$ -dimethylheptoic Acid.** V. RAICHSTEIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 587—607).—By the action of ethyl  $\alpha$ -bromopropionate on  $\beta$ -methylbutaldehyde in the presence of zinc or zinc-copper, an ester is obtained, b. p. 120—129°/760 mm. The yield of the crude product varies largely with the conditions of the experiment and is better when zinc is employed than with zinc-copper. Owing to decomposition, the ester could not be purified; it is hydrolysed with difficulty, yielding the free  $\beta$ -hydroxy- $\alpha$ -dimethylheptoic acid, a colourless, syrupy liquid, with a pleasant odour, soluble in water, ether, and alcohol. On distillation with sulphuric acid, it yields (1) the lactone,  $\text{CHMe}_2\cdot\text{CH} \begin{matrix} \text{CH}_2 \\ | \\ \text{O} \end{matrix} \begin{matrix} \text{CHMe} \\ | \\ \text{CO} \end{matrix}$ , b. p. 223—225°, with a camphor-like odour; (2) an unsaturated acid,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CMe}\cdot\text{CO}_2\text{H}$ , of which the silver, calcium, and barium salts are described. On dry distillation,  $\beta$ -hydroxy- $\alpha$ -dimethylheptoic acid yields carbon dioxide, water, aldehydes, and an unsaturated acid.



Its salts with the following metals are soluble in water: *sodium, potassium, ammonium, magnesium, calcium, barium, strontium, manganese, zinc, nickel, cobalt, silver, copper, and cadmium*. The following are sparingly soluble: *ferric, mercury, lead, bismuth, and tin*. A detailed comparison is given of the properties of  $\beta$ -hydroxy- $\alpha$ -dimethylheptioic acid and of its homologues (compare Reformatsky, Abstr., 1897, i, 212). Z. K.

**Use of Zinc Chloride in the Esterification of Succinic Acid.** ISAAC K. PHELPS and M. A. PHELPS (*Amer. J. Sci.*, 1907, [iv], 24, 194—196).—Almost the full yield of diethyl succinate is obtained by heating a mixture of 50 grams of pure succinic acid and 1 gram of fused zinc chloride with 40 c.c. of alcoholic hydrogen chloride (10 grams to the litre of absolute alcohol) at 100—110°, and then passing a current of gaseous alcohol (160 c.c.). The product is purified by washing with iced water, neutralisation with sodium carbonate, extraction with ether, and subsequent fractional distillation.

L. DE K.

**Electrolytic Decomposition of Dicarboxylic Acids. Suberic Acid.** B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 79—84, 139—144. Compare Abstr., 1906, i, 624).—The electrolytic decomposition of a 28·8% aqueous solution of potassium hydrogen suberate between platinum electrodes at about 45°, using a current density of about 0·5 ampere and a voltage of 12, proceeds rapidly and gives rise to a vigorous evolution of carbon dioxide together with a little oxygen and about 1% of carbon monoxide. No hydrocarbons, either saturated or unsaturated, are formed, the principal compounds obtained being unsaturated oxidation products, of which the following have been isolated. A mixture of isomeric unsaturated alcohols,  $C_6H_{12}O$ ; isomeric unsaturated acids,  $C_7H_{12}O_2$ , and saturated 7-carbon atom acids; the lactone,  $C_7H_{12}O_2$ , of an acid, the barium salt of which,  $(C_7H_{13}O_3)_2Ba$ , was prepared; neutral aldehydic compounds; keto- and aldo-acids.

T. H. P.

**Oxidisability of Aliphatic Aldehydes, especially Formaldehyde.** V. CERVELLO and A. PITINI (*Gazzetta*, 1907, 37, i, 577—581).—Animal tissues or extracts of them rapidly attack formaldehyde, which is, however, not transformed into formic acid. This action does not take place if the tissues are treated previously with boiling water. It is found that, when submitted to the action of the tissues in presence of hydrogen peroxide, the aldehyde is oxidised to carbon dioxide, the rate of oxidation varying considerably with the tissues of different organs. No action occurs if either the tissue or the aldehyde is omitted. The same action, which is evidently due to an enzyme, is produced with propaldehyde, valeraldehyde or isobutaldehyde.

T. H. P.

**Action of Barium Peroxide and Hydrogen Peroxide on Formaldehyde.** C. ALLAN LYFORD (*J. Amer. Chem. Soc.*, 1907, 29, 1227—1236).—It has been stated by Geisow (Abstr., 1904, i, 289)

that when formaldehyde is oxidised with barium peroxide, hydrogen is evolved and barium carbonate is produced. Experiments are now described which show that barium formate and hydrogen are formed together with small quantities of barium hydroxide and hydrogen peroxide. The changes probably take place as follows. A comparatively slow reaction,  $\text{CH}_2\text{O} + \text{BaO}_2 + \text{H}_2\text{O} = \text{H} \cdot \text{CO}_2\text{H} + \text{Ba}(\text{OH})_2$ , yields formic acid capable of reacting with barium oxide or peroxide. With barium peroxide, it liberates hydrogen peroxide,  $2\text{H} \cdot \text{CO}_2\text{H} + \text{BaO}_2 = \text{Ba}(\text{CO}_2\text{H})_2 + \text{H}_2\text{O}_2$ , and the latter reacts with formaldehyde thus:  $2\text{CH}_2\text{O} + \text{H}_2\text{O}_2 = 2\text{H} \cdot \text{CO}_2\text{H} + \text{H}_2$ . The last two reactions take place much more rapidly than the first, and when combined give the equation  $2\text{CH}_2\text{O} + \text{BaO}_2 = \text{Ba}(\text{CO}_2\text{H})_2 + \text{H}_2$ , which represents the change almost quantitatively. The fact that the first reaction takes place to some extent shows that the yield of hydrogen cannot be quantitative.

Geisow (*loc. cit.*) has also stated that the action of hydrogen peroxide on formaldehyde proceeds thus:  $\text{CH}_2\text{O} + \text{H}_2\text{O}_2 = \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2$ , and that no free formic acid is produced in any stage of the reaction. It is now found that when hydrogen peroxide reacts with formaldehyde, formic acid is produced as an intermediate product and, on prolonged action, is oxidised to carbon dioxide and water. In one experiment, an estimation of the formic acid produced gave a result equivalent to 79.36% of the formaldehyde taken. The reaction is expressed approximately by the equations  $2\text{CH}_2\text{O} + \text{H}_2\text{O}_2 = 2\text{H} \cdot \text{CO}_2\text{H} + \text{H}_2$  and  $2\text{H} \cdot \text{CO}_2\text{H} + 2\text{H}_2\text{O}_2 = 2\text{CO}_2 + 4\text{H}_2\text{O}$ . E. G.

**Preparation of Propaldehyde.** MARIO MARCHIONNESCHI (*Gazzetta*, 1907, 37, ii, 201—204).—To increase the yield of propaldehyde, prepared by the action of chromic acid mixture on propyl alcohol, the author inserts a reflux condenser kept at 30° between the flask in which the reagents are heated and the ordinary condenser. In this way, the yield of aldehyde is approximately quadrupled. If pure propyl alcohol is employed instead of the ordinary alcohol, the process of separating the aldehyde by fractionation is greatly facilitated.

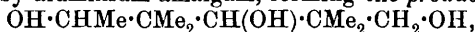
T. H. P.

**Condensation Products of Glyoxal and *iso*Butaldehyde.** HUGO ROSINGER (*Monatsh.*, 1907, 28, 947—960).—The condensation of glyoxal and *isobutaldehyde* has been re-studied as definite results were not obtained by Hornbostel and Siebner (*Abstr.*, 1900, i, 206). When boiled together in alcoholic potassium hydroxide solution, glyoxal and *isobutaldehyde* yield only *isobutyric acid* and Fosseck's octylene glycol, but on condensation in aqueous solution in presence of potassium carbonate at the ordinary temperature form a crystalline substance,  $\text{C}_{10}\text{H}_{18}\text{O}_4$ , a liquid,  $\text{C}_{10}\text{H}_{20}\text{O}_3$ , *isobutaldol*, and *acetisobutaldol*.

The substance  $\text{C}_{10}\text{H}_{18}\text{O}_4$  was isolated by Hornbostel and Siebner; it separates from water in rhombohedra, m. p. 130°, or from ether in crystals, m. p. 55°, b. p. 140°/14 mm., sublimes in needles, reduces ammoniacal silver solutions in the cold, and is considered to have the constitution  $\text{CHO} \cdot \text{CMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CHO}$ . On reduc-

tion with aluminium amalgam and alcohol, it yields the tetrahydroxy-compound,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , which forms transparent crystals, m. p.  $127^\circ$ .

The liquid,  $\text{C}_{10}\text{H}_{20}\text{O}_3$ , b. p.  $114^\circ/14\text{ mm.}$ , is considered to have the constitution  $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CHO}$ ; when distilled under atmospheric pressure, it yields *isobutaldehyde*, and on distillation with dilute sulphuric acid yields a strongly reducing distillate, which has an odour of crotonaldehyde and contains *isobutaldehyde*. It is reduced by aluminium amalgam, forming the *product*,



which is obtained as a slightly green liquid, b. p.  $132^\circ/16\text{ mm.}$

The formation of the liquid product,  $\text{C}_{10}\text{H}_{20}\text{O}_3$ , and of *acetisobutaldehyde* is ascribed to the presence of metaldehyde in the glyoxal prepared by Hornbostel and Siebner's method; in agreement with this view, the glyoxal, when heated at  $150^\circ$  under pressure, has an odour of acetaldehyde, and when distilled into an ethereal solution of ammonia forms aldehydeammonia.

G. Y.

**Isomerism of Aldoximes.** KARL BECK and P. HASE (*Annalen*, 1907, 355, 29—57).—A comparative study of the  $\alpha$ - and  $\beta$ -oximes of benzaldehyde, anisaldehyde, cuminaldehyde, and *m*-nitrobenzaldehyde.

Alcoholic solutions of the  $\beta$ -oximes, but not of the  $\alpha$ -oximes, give intense blood-red colorations with ferric chloride and yellowish-green to olive-green colorations with copper acetate.

The  $\beta$ -oximes of benzaldehyde, anisaldehyde, and cuminaldehyde give at once with silver nitrate in alcoholic solution white, crystalline precipitates. These *additive* compounds decompose at  $98$ — $125^\circ$ , and have the composition 2 mols. oxime + 1 mol. silver nitrate.

These oximes also give crystalline precipitates with mercurous nitrate in alcoholic solution; the *additive* compounds so obtained are not pure; they probably have the composition 1 mol. oxime + 1 mol. mercurous nitrate. The  $\alpha$ -oximes do not give precipitates with mercurous and silver nitrates. It is therefore highly probable that of the two isomeric oximes described by Ratz (*Abstr.*, 1906, i, 238), the one (so-called  $\alpha$ -oxime) which forms an additive compound with silver nitrate really has the  $\beta$ -configuration, and vice versa.

Both  $\alpha$ - and  $\beta$ -oximes combine with chloral and bromal, forming totally different *additive* compounds; all have, however, the general formula: 1 mol. oxime + 1 mol. bromal or chloral. The  $\alpha$ -oxime compounds crystallise in colourless needles, the  $\beta$ -derivatives in large, colourless crystals.

The  $\alpha$ -benzaldoxime and  $\alpha$ -anisaldoxime chloral additive compounds melt at  $57^\circ$  and  $71^\circ$  respectively; a compound with  $\alpha$ -cuminaldoxime could not be obtained. The bromal additive compounds of  $\alpha$ -benzaldoxime,  $\alpha$ -anisaldoxime, and  $\alpha$ -cuminaldoxime melt respectively at  $64^\circ$ ,  $78^\circ$ , and  $75^\circ$ .

The chloral additive compounds of  $\beta$ -benzaldoxime,  $\beta$ -anisaldoxime, and  $\beta$ -cuminaldoxime melt respectively at  $78^\circ$ ,  $90^\circ$ , and  $77^\circ$ , whilst the corresponding bromal derivatives melt at  $95^\circ$ ,  $99^\circ$ , and  $85^\circ$ .

Except in the case of the  $\beta$ -cuminaldoxime chloral compound, which dissociates into the free  $\alpha$ -oxime and chloral, the  $\beta$ -compounds change

into the  $\alpha$ -compounds when kept and in the presence of traces of acid. The  $\beta$ -compounds behave like the  $\beta$ -oximes towards ferric chloride and copper acetate, whilst with silver and mercurous nitrates they give the same compounds as are obtained from the free  $\beta$ -oximes.

The  $\alpha$ -additive compounds do not show any reaction with these four reagents. The  $\alpha$ -oxime chloral compounds may also be prepared by the action of chloralhydroxylamine on the aldehydes. It is remarkable that by this method it is possible to obtain the  $\alpha$ -*cuminaldioxime chloral* additive compound, m. p. 63°.

The isomeric *m*-nitrobenzaloximes and the *N*-benzyl ethers of benzaloxime and anisaloxime do not combine with chloral or bromal.

Corresponding with the two isomeric carbanilido- $\beta$ -benzaloximes obtained by Beckmann (Abstr., 1891, 193), the authors have obtained a second, very labile *carbanilido- $\beta$ -cuminaldioxime*,  $C_{17}H_{14}O_2N_2$ , as a yellow, amorphous powder by adding phenylcarbimide to a solution of the  $\beta$ -oxime in light petroleum; after a time, more quickly on warming, it changes into the white form, m. p. 104° (Goldschmidt, Abstr., 1890, 251). These isomeric carbanilido- $\beta$ -aldoximes behave differently towards ferric chloride and copper acetate. The yellow carbanilido-derivatives of  $\beta$ -benzaloxime, m. p. 74°;  $\beta$ -anisaloxime, m. p. 80°;  $\beta$ -cuminaldioxime and  $\beta$ -*m*-nitrobenzaloxime, m. p. 77° (compare Beckmann, Abstr., 1891, 193, and Goldschmidt and Reitschoten, Abstr., 1893, i, 707), give with ferric chloride in alcoholic solution, at first a red, then a dirty green, and finally an intense blue, coloration, which disappears on long-continued boiling. With copper acetate, is obtained at first a yellowish-green coloration which quickly becomes dirty green, followed by the appearance of a greyish-green, flocculent precipitate. If, however, the alcoholic solution of the substance is heated, or the substance itself is warmed before dissolution, and ferric chloride then added, only a faint red or yellow coloration is obtained. This same faint coloration is obtained by adding ferric chloride to the alcoholic solution of the white carbanilido-derivatives of  $\beta$ -benzaloxime, m. p. 94°, and  $\beta$ -cuminaldioxime, m. p. 104°; these compounds give a yellowish-green coloration with copper acetate, but not a precipitate. The carbanilido- $\alpha$ -oximes do not react with ferric chloride or copper acetate.

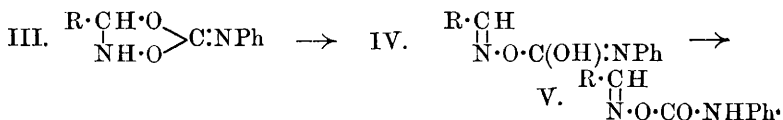
The carbanilido-derivatives obtained synthetically by the action of *s*-phenylhydroxycarbimide on the aldehydes in ethereal solution are identical with the carbanilido- $\alpha$ -oximes prepared by the action of phenylcarbimide on the  $\alpha$ -oximes (Goldschmidt and Reitschoten, *loc. cit.*).

The authors consider that the  $\beta$ -oximes (I) have a different structure from the  $\alpha$ -oximes, the power of reacting in the tautomeric,  $\alpha$ -oxime stereoisomeric, form (II) depending on the ready wandering of the *N*-hydrogen atom :



The yellow carbanilido-derivatives probably have the formula (III) and pass into the colourless form (V) through the intermediate form

(IV); the colorations which the yellow compounds give with ferric chloride are probably due to the formation of this enolic form :



The colourless form would then readily change into the  $\alpha$ -(*anti*-) derivative. It is further argued that since chloralhydroxylamine and phenylhydroxycarbamide combine with aldehydes yielding  $\alpha$ -oxime derivatives, they have the formulæ  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{O} \cdot \text{NH}_2$  and  $\text{NHPH} \cdot \text{CO} \cdot \text{O} \cdot \text{NH}_2$ .  
W. H. G.

### Catalytic Reactions at High Temperatures and Pressures.

**XIII. Reducing Catalysts.** WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 681—692. Compare this vol., i, 5, 6, 457). —The apparatus formerly used for high pressure experiments has been further improved. Acetone when heated in an iron tube in the absence of hydrogen only commences to change at about  $420^\circ$ , when an oil insoluble in and lighter than water is formed, together with a small quantity of carbon dioxide and methane. In the presence of hydrogen at  $400^\circ$ , acetone is reduced to *isopropyl* alcohol, but equilibrium is established when 25% of the acetone has suffered change; a small quantity of the above oil is also formed. *iso*Butaldehyde does not react with hydrogen in the absence of iron. In the presence of iron, but absence of hydrogen, the aldehyde at  $400^\circ$  yields condensation products, carbon monoxide, and small quantities of carbon dioxide and hydrogen. *iso*Butyl alcohol, under the same conditions, yields the same gases, much hydrogen, and *isobutaldehyde*. In an iron tube and in the presence of hydrogen, *isobutaldehyde* is almost wholly converted into the alcohol. *iso*Valeraldehyde behaves similarly, one of the products being amylene. Both ordinary and reduced iron can act as reducing catalysts in all those cases in which reduced nickel can be employed, but the necessary temperature for the latter is much lower. *iso*Propyl alcohol in the presence of reduced nickel at  $200$ — $230^\circ$  reacts thus:  $\text{CHMe}_2 \cdot \text{OH} \cdot \text{Me} \rightleftharpoons \text{H}_2 + \text{COMe}_2$ , the products of the reaction being acetone, *isopropyl* alcohol, hydrogen, and methane. Complete equilibrium is reached only after very prolonged heating. In the presence of an excess of hydrogen, acetone is wholly converted into the alcohol at temperatures not exceeding  $210$ — $220^\circ$ . Above this, the reaction is reversible. Methyl ethyl ketone and the carbinol and *isoamyl* alcohol behave similarly to the *isopropyl* derivatives, under the same conditions, only the corresponding temperatures are higher. Methyl alcohol yields methane, hydrogen, carbon dioxide, and water. Benzene in the presence of iron, without hydrogen, yields hydrogen and diphenyl above  $600^\circ$ . In the presence of hydrogen, the reaction also only commences above  $500^\circ$ , but employing reduced nickel and hydrogen, pure *cyclohexane* is formed at  $255^\circ$ , but above  $300^\circ$  benzene, methane, and carbon are also formed.  
Z. K.

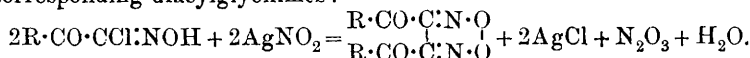
## Catalytic Reactions at High Temperatures and Pressures.

## XIV. Reducing Catalysts in the Presence of Metallic Oxides.

WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 693—702. Compare preceding abstract).—The oxides of nickel have been found to bring about the catalytic reduction of benzene, acetone, isopropyl alcohol, diphenyl, naphthalene, dibenzyl,  $\alpha$ - and  $\beta$ -naphthols, and benzophenone much more quickly than reduced nickel, the pure saturated reduction products being obtained in each case. Nickelic oxide is a better catalyst than nickelous oxide. The reaction proceeds much faster if the oxide is placed at the surface of the liquid than if the latter is poured on to it. The rate of the reaction is considerably diminished by decreasing the amount of catalyst. Time-temperature curves and tables are given. Z. K.

## Action of Silver Nitrite on Chloroisnitrosoketones.

GIACOMO PONZIO and G. CHARRIER (*Gazzetta*, 1907, 37, ii, 65—71).—Chloroisnitrosoketones, when treated with silver nitrite, are not converted into nitrolic acids, as might be expected (compare Piloty and Steinbock, *Abstr.*, 1902, i, 735), but into peroxides of the corresponding diacylglyoximes:



Improved methods are given for the preparation of certain chloroisnitrosoketones (compare Claisen and Manasse, *Abstr.*, 1893, i, 464).

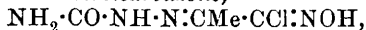
The interaction of chloroisnitrosoacetophenone and silver nitrite yields dibenzoylglyoxime peroxide, which has been prepared by Holleman (*Abstr.*, 1888, 275; 1889, 49) by the action of nitric acid on acetophenone or isonitrosoacetophenone and by Angeli (*Abstr.*, 1893, i, 355) by the action of nitric acid on dibenzoylglyoxime.

Diacylglyoxime peroxide,  $\begin{array}{c} \text{CAc}\cdot\text{N}\cdot\text{O} \\ | \\ \text{CAc}\cdot\text{N}\cdot\text{O} \end{array}$ , prepared from chloroisnitroso-

acetone and silver nitrite, was obtained as a faintly yellow, unstable oil, which could not be purified.

The following new derivatives of chloroisnitrosoacetone have been prepared.

Chloroisnitrosoacetone phenylhydrazone,  $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{CCl}\cdot\text{NOH}$ , crystallises from chloroform in yellowish-brown, shining needles, m. p.  $124^\circ$  (decomp.), and dissolves readily in alcohol or ether, and to a less extent in benzene. The semicarbazone,



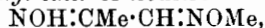
separates in white prisms, m. p.  $158^\circ$  (decomp.), and dissolves in alcohol or water, the latter decomposing it on heating.

Acetylphenylisourethine,  $\text{NOH}\cdot\text{CAc}\cdot\text{NHPh}$ , prepared by the interaction of aniline and chloroisnitrosoacetone in ethereal solution, crystallises from alcohol in faintly yellow plates, m. p.  $119^\circ$ , and dissolves readily in benzene or chloroform and sparingly in ether.

Acetyl-p-tolylisourethine,  $\text{NOH}\cdot\text{CAc}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises from alcohol in white laminæ, m. p.  $130^\circ$ , and dissolves readily in benzene or chloroform and sparingly in ether. T. H. P.

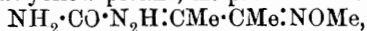
**Derivatives of isoNitrosoketones.** G. CHARRIER (*Gazzetta*, 1907, 37, ii, 145—148).—The best method, giving a yield of 75—80%, of preparing isonitrosoacetone is from ethyl acetoacetate and sodium nitrite. When crystallised from a mixture of ether and light petroleum, it has m. p.  $69^{\circ}$ ; Meyer and Zublin (*Abstr.*, 1878, 659) gave  $65^{\circ}$ .

The oxime of the methyl ether of isonitrosoacetone,



crystallises from light petroleum in long, shining needles, m. p.  $73^{\circ}$ . The corresponding phenylhydrazone,  $\text{N}_2\text{HPh}\cdot\text{CMe}\cdot\text{CH}\cdot\text{NOMe}$ , crystallises from aqueous alcohol in yellow needles, m. p.  $104^{\circ}$ . The semicarbazone,  $\text{CONH}_2\cdot\text{N}_2\text{H}\cdot\text{CMe}\cdot\text{CH}\cdot\text{NOMe}$ , crystallises from water in plates, m. p.  $212\text{--}213^{\circ}$ , and dissolves in alcohol.

The oxime of the methyl ether of isonitrosomethylethylketone,  $\text{NOH}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{NOMe}$ , crystallises from light petroleum in needles, m. p.  $104^{\circ}$ . The phenylhydrazone,  $\text{N}_2\text{HPh}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{NOMe}$ , crystallises from alcohol in yellow prisms, m. p.  $56^{\circ}$ . The semicarbazone,



crystallises from water or alcohol in white prisms, m. p.  $237^{\circ}$  (decomp.).  
T. H. P.

**N-Alkylketoximes.** ERNST BECKMANN and JOHANNES SCHEIBER (*Annalen*, 1907, 355, 235—247).—Acetone reacts with certain  $\beta$ -substituted hydroxylamines to form substances which are presumably N-substituted ketoximes. Phenylhydroxylamine yields a substance,  $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_2$ , m. p.  $136^{\circ}$  (decomp.); p-tolylhydroxylamine yields a mixture of azoxytoluene and a substance,  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$ , m. p.  $157^{\circ}$ ; m-tolylhydroxylamine forms the substance,  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$ , m. p.  $144\cdot5^{\circ}$  (decomp.); naphthylhydroxylamine yields azoxynaphthalene and a substance,  $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_2$ , m. p.  $138^{\circ}$  (decomp.). This behaviour of acetone is not exhibited by its homologues, acetophenone, or aromatic ketones. Ethyl acetoacetate, however, condenses with phenylhydroxylamine and with p-tolylhydroxylamine, yielding substances having m. p.  $120\cdot5^{\circ}$  and  $172^{\circ}$  respectively. These will be described subsequently.

The paper contains a résumé of investigations on the alkylation of oximes.  
C. S.

**The Lævorotation of Mannose.** WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1907, 4, 511—514).—Lævorotatory mannose in solution is partially transformed into another (mutarotatory) modification the dextrorotation of which largely exceeds  $+14\cdot2^{\circ}$  ( $+20\cdot9^{\circ}$ ;  $+23\cdot5^{\circ}$ ), the reaction being unimolecular. The velocity of transformation is greater in aqueous solution than in aqueous alcoholic solution. On treatment with methyl sulphate and potassium carbonate, mannose yields  $\alpha$ -methylmannoside.

A. J. W.

**Action of Ammonium Persulphate Solution on Cellulose.** I. Formation and Properties of Cellulose Peroxide. HUGO DITZ (*Chem. Zeit.*, 1907, 31, 833—834, 844—845, 857—858. Compare Cross and Bevan, *Zeitsch. angew. Chem.*, 1907, 20, 570).—When heated gently with ammonium persulphate solution acidified with

sulphuric acid, filter paper and sulphite cellulose form a peroxide which, after being washed with cold water until free from persulphate, liberates iodine from potassium iodide, but is decomposed by hot water or when dried at  $100^{\circ}$ . The oxidised cellulose contains about 0.015% of active oxygen; the peroxide formation takes place to a smaller extent with potassium persulphate and to only a slight extent in the absence of free sulphuric acid. The peroxide contains an organic acid which is insoluble or only sparingly soluble in water, since after being washed with water it gives an acid reaction with methyl-orange on addition of an aqueous solution of a neutral alkali salt. Stearic acid behaves towards methyl-orange in the same manner (compare Syzskowski, this vol., ii, 238). The active oxygen is not concerned in this acid reaction, as after addition of potassium chloride and neutralisation with an alkali, the product still liberates iodine from potassium iodide.

Cellulose, which has been oxidised with ammonium persulphate, reduces Fehling's solution when heated, and with dilute potassium hydroxide gives a yellow coloration becoming golden-yellow when heated; hence it contains oxycellulose (Nastukoff, Abstr., 1900, i, 540). The acid present in the oxidised cellulose may be Buncke and Wolfenstein's acid cellulose (Abstr., 1899, i, 852). Whilst filter paper, on treatment with ammonium persulphate in absence of sulphuric acid, forms oxycellulose, the acid product, and traces of the peroxide, the product obtained on heating filter paper with dilute sulphuric acid only at  $70^{\circ}$ , contains hydrocellulose and traces of an acid, but not oxycellulose or the peroxide. Similar results are obtained with cotton wool, but the peroxide formation takes place to a smaller extent than with filter-paper, sulphite-cellulose, or linen.

Comparative experiments with filter paper, 20% ammonium persulphate solution, and sulphuric acid (1:4) were performed at  $20-25^{\circ}$ ,  $40^{\circ}$ , and  $65^{\circ}$ . Evolution of gas took place only slowly at the lowest temperature, more quickly at  $40^{\circ}$ , and violently at  $65^{\circ}$ ; only in the last case had the gas the characteristic irritating odour of "active" oxygen. In the first two experiments, the filter paper retained its form, but at the highest temperature it was swollen and partially disintegrated. The amounts of the peroxide and of the acid formed increase with the rise in temperature of the reaction, whilst that of the oxycellulose is slightly greater at  $40^{\circ}$  than at  $20-25^{\circ}$ , but increases only very slightly when the temperature of the reaction is raised to  $65^{\circ}$ .

Cellulose peroxide, when moist, decomposes completely in two to three days, but if washed with alcohol and ether remains unchanged for eighteen days, and after thirty-three days still gives a violet coloration with potassium iodide-starch solution. G. Y.

**Ring Formation of Complex Compounds.** LEO TSCHUGAEFF [and, in part, KARASSEFF] (*J. pr. Chem.*, 1907, [ii], 76, 88—93).—Further evidence is cited in support of the author's views (this vol., i., 17, 392). The stable, bluish-violet *trimethylenediamine nickel sulphate*,  $\text{Ni}(\text{Tr})_2\text{SO}_4$  (Tr = trimethylenediamine), corresponding with the thiocyanate,  $\text{Ni}(\text{Tr})_2(\text{SCN})_2$  (Abstr., 1906, i, 814), has been prepared.



Excess of trimethylenediamine leads to the formation of a very unstable sulphate of the triamine series. However, a stable *platinos-chloride*,  $\text{Ni(Tr)}_3\text{PtCl}_4$ , is readily prepared by adding potassium platinoschloride to the solution obtained by the addition of an excess of trimethylenediamine to an aqueous solution of nickel chloride.

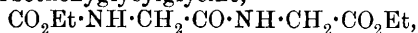
Nickel salts also react with the two stereoisomeric modifications of  $\beta\delta$ -diaminopentane, yielding stereoisomeric complex compounds, in the proportion of 1 atom of nickel to 2 mols. of the amine. These compounds are under investigation.

It is found that  $\alpha$ -oximinoketones behave, in general, like nitroso- $\beta$ -naphthol (Ilinsky and Knorre, Abstr., 1885, 840) in yielding very stable cobalt derivatives. Thus, the brownish-red, crystalline compound,  $(\text{COPh}\cdot\text{CPh}\cdot\text{NO})_3\text{Co}$ , is formed by adding a cobalt salt to a solution of  $\alpha$ -benzilmonoxime in dilute alcohol, in the presence of an excess of ammonium acetate. Analogous iron, nickel, and palladium compounds have also been obtained; they are distinguished by their relatively great stability, abnormal colour, and absence of the ionic reactions of the metals.

The above general formula is proposed for these compounds.

W. H. G.

**Nitration of Glycine Anhydride.** A. D. DONK (*Rec. trav. chim.*, 1907, 26, 207—213).—When dissolved in concentrated nitric acid, glycine anhydride yields a product, m. p. about  $235^\circ$  (decomp.), which the analytical numbers indicate to be a dinitrate of the anhydride, whilst titration with potassium hydroxide gives values in agreement with those for a mononitrate. When treated with acetic anhydride, this compound is transformed into *nitroglycine anhydride*,  $\text{CO}\langle\text{CH}_2\cdot\text{N}(\text{NO}_2)\rangle\text{CO}$ , which crystallises from methyl alcohol in shining, colourless needles or prisms, m. p.  $165^\circ$  (decomp.), and dissolves sparingly in ether, ethyl acetate, acetone, or alcohol; treatment with methyl-alcoholic potassium hydroxide yields *nitroamino-acetylaminooacetic acid*,  $\text{NO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $153^\circ$  (decomp.). An attempt to prepare this acid by the action of nitric acid on ethyl carbethoxyglycylglycine,



resulted in the formation of a nitro-derivative (?) of the latter.

T. H. P.

**Monoamino-Acids from Avenine.** EMIL ABDERHALDEN and YUHO HÄMÄLÄINEN (*Zeitsch. physiol. Chem.*, 1907, 52, 515—520).—When hydrolysed with boiling concentrated hydrochloric acid, avenine gives the following amounts of amino-acids, calculated on 100 parts of avenine dried at  $100^\circ$  free from ash: glycine 1.0, alanine 2.5, valine 1.8, leucine 15.0, proline 5.4, aspartic acid 4.0, glutamic acid 18.4, phenylalanine 3.2, and tyrosine 1.5. The results differ from those obtained for legumin mainly in the amounts of tyrosine and leucine (Abderhalden and Babkin, Abstr., 1906, i, 546).

J. J. S.

**Certain Derivatives of *s*-Diaminoacetone (1:3-Diaminopropanone).** ANTOINE P. N. FRANCHIMONT and HERMANN FRIEDMANN (*Rec. trav. chim.*, 1907, **26**, 223—227).—*Methyl acetone- $\alpha$ -diaminoacetate*,  $\text{CO}(\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Me})_2$ , prepared by the action of methyl chloroformate (1—2 mols.) on 1:3-diaminopropanone hydrochloride (1 mol.) in presence of sodium hydroxide, carbonate, or acetate, crystallises from alcohol in needles, m. p. 154°.

The  *$\alpha$ -dinitro*-compound,  $\text{CO}[\text{CH}_2\cdot\text{N}(\text{NO}_2)\cdot\text{CO}_2\text{Me}]_2$ , prepared by the action of concentrated nitric acid on the preceding compound, crystallises from ether in stellar aggregates of slender needles, m. p. 77°, and dissolves readily in alcohol.

1:3-*Diacetylaminooacetone*,  $\text{CO}(\text{CH}_2\cdot\text{NHAc})_2$ , prepared by acetylating diaminoacetone, crystallises from alcohol in nacreous spangles, m. p. 200°, and dissolves readily in water and sparingly in ether.

T. H. P.

**Preparation of Formamide from Ethyl Formate and Ammonium Hydroxide.** ISAAC K. PHELPS and C. D. DEMING (*Amer. J. Sci.*, 1907, [iv], **24**, 173—175).—Hofmann (Abstr., 1882, 950) has stated that when ethyl formate is left with aqueous ammonia at the ordinary temperature, a large proportion of the formamide produced is converted into ammonium formate, and that for this reason the maximum yield of amide obtainable is not much more than 70%.

It is now found that a theoretical yield of formamide can be obtained by treating ethyl formate, cooled below 0°, with a small quantity of cold aqueous ammonia of D 0.90, and passing dry ammonia into the mixture; or more easily by adding a large quantity of solution of ammonia to the ester, both cooled below 0°. In each case, the mixture is left for about five hours, and then distilled in a vacuum. By keeping the temperature low, the production of ammonium formate is avoided.

E. G.

**Molecular Magnitude of Oxamide.** CONCETTO MASELLI (*Gazzetta*, 1907, **37**, ii, 135—136).—The properties of oxamide, especially its insolubility and high melting point, when compared with those of the corresponding amides of other dibasic acids, would indicate that its molecule is polymerised. Using Bleier and Kohn's apparatus (Abstr., 1899, ii, 643; 1900, ii, 192) heated externally with acetanilide vapour, the author finds that the molecular weight of oxamide at about 300° and under a pressure of a few mm. is 141.21—143.63 instead of 88.

T. H. P.

**New Oxalhydroxamic Acid.** VINCENZO PAOLINI (*Gazzetta*, 1907, **37**, ii, 87—91).—The author has prepared the third oxalhydroxamic acid, isomeric with the two already known (compare Lossen, *Annalen*, 1869, **150**, 314; Hantzsch and Urban, Abstr., 1895, i, 393).

*Oxalhydroxamic acid*,  $\text{NOH}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{NOH}$ , prepared by the action of benzenesulphohydroxamic acid on glyoxal in presence of potassium hydroxide (compare Rimini, Abstr., 1901, i, 450), crystal-

lises from a mixture of alcohol and ether in shining, white, hygroscopic laminæ, m. p. 82—83°, dissolves readily in water giving an acid solution, gives an intense cherry-red coloration with ferric chloride, and yields oxalic acid and hydroxylamine when heated with sulphuric acid. Its *copper* salt,  $C_2O_4N_2Cu_2$ , was analysed. T. H. P.

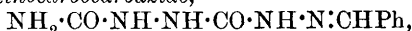
**Reaction between Barium Thiocyanate and Bromoacetic Acid dissolved in Acetone.** HENRI DEMIERRE and MARCEL DUBOUX (*J. Chim. Phys.*, 1907, 5, 340—343. Compare this vol., ii, 75).—The progress of the reaction in question, represented by the equation  $Ba(CNS)_2 + 2CH_2Br \cdot CO_2H = BaBr_2 + 2CNS \cdot CH_2 \cdot CO_2H$ , has been followed by estimating the barium in solution at definite intervals by means of sulphuric acid; the applicability of this method depends on the fact that whilst barium thiocyanate is soluble in acetone, the bromide is insoluble in this medium and can be filtered off. The rate of the reaction is proportional to the concentrations of the thiocyanate and bromoacetic acid respectively, but the constants calculated for a bimolecular reaction diminish somewhat as the initial concentration is increased, and it is therefore suggested that the reaction is ionic. The mean temperature coefficient for 10° between 29.7° and 41.8° is 2.52. G. S.

**Interpretation of the Reaction between Ferric Chloride and Potassium Thiocyanate.** C. BONGIOVANNI (*Gazzetta*, 1907, 37, i, 472—475).—The author shows that no ferrous salt is formed in the interaction of freshly precipitated ferric hydroxide and potassium thiocyanate in an atmosphere of nitrogen. It is also found that a solution containing ferric chloride and potassium oxalate undergoes a continual diminution in acidity, seemingly owing to the formation of complex ions, whilst if potassium thiocyanate is also present, no such diminution in the acidity occurs (compare Tarugi, *Abstr.*, 1905, i, 176). The interpretation of the reaction between ferric chloride and potassium thiocyanate given by Magnanini (*Abstr.*, 1891, 1150), namely,  $FeCl_3 + 3KCNS \rightleftharpoons 3KCl + Fe(CNS)_3$ , best explains the observations. T. H. P.

**Action of Cyanogen Bromide on Hydrazine. II.** GUIDO PELLIZZARI and F. RONCAGLIOLO (*Gazzetta*, 1907, 37, i, 434—446).—The compound, m. p. about 230°, obtained together with diaminoguanidine and guanazine by the interaction of cyanogen haloid and hydrazine in aqueous solution (Pellizzari and Cantoni, *Abstr.*, 1905, i, 576), is shown to be aminocarbocarbazide or hydrazodicarbonamide,  $NH_2 \cdot NH \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH_2$ , which has also been synthesised from carbazide and potassium cyanate. The formation of this compound in the above reaction is probably due to part of the diaminoguanidine formed undergoing transformation in the alkaline liquid to carbazide, whilst some of the cyanogen chloride and potassium hydroxide interact to yield potassium cyanate. If carbazide dihydrochloride is treated with potassium cyanate, the main product is diaminodicarbocarbazide,  $CO(NH \cdot NH \cdot CO \cdot NH_2)_2$ , which can also be obtained by the action of potassium cyanate on aminocarbocarbazide. Certain of the transformation products of the latter compound have also been studied.

*Aminocarbocarbazide*,  $\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , best obtained by the gradual addition of acetic acid to a cold solution containing carbazide (1 mol.) and potassium cyanate (1 mol.) until the liquid becomes acid, separates from water in minute, white crystals, m. p.  $228^\circ$  (decomp.), and is insoluble in organic solvents, but dissolves in mineral acids, from which it is precipitated by addition of ammonia. It reduces energetically Fehling's solution and ammoniacal silver nitrate solution. Aldehydes and ketones react with it in acid aqueous solutions. When heated at  $226^\circ$ , it is converted into ammonia and urazine (dicarbamide).

*Benzylideneaminocarbocarbazide*,



forms a white powder, m. p.  $212^\circ$ .

*Salicylideneaminocarbocarbazide*,  $\text{C}_2\text{H}_5\text{O}_2\text{N}_5 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , forms a yellow, crystalline precipitate, m. p.  $218^\circ$ .

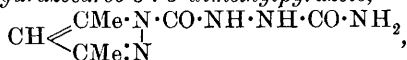
*Phenylethylideneaminocarbocarbazide*,  $\text{C}_2\text{H}_5\text{O}_2\text{N}_5 \cdot \text{CMePh}$ , from acetophenone, forms a white, crystalline precipitate, m. p.  $214^\circ$ .

*Phenylbenzylideneaminocarbocarbazide*,  $\text{C}_2\text{H}_5\text{O}_2\text{N}_5 \cdot \text{CPh}_2$ , from benzophenone, crystallises from alcohol in shining, white needles, m. p.  $222^\circ$ .

*Benzoylbenzylideneaminocarbocarbazide*,  $\text{C}_2\text{H}_5\text{O}_2\text{N}_5 \cdot \text{CPhBz}$ , from benzil, forms a white, crystalline precipitate, m. p.  $240^\circ$ .

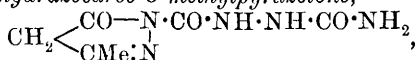
*Diaminodicarbocarbazide*,  $\text{CO}(\text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$ , is deposited from water in minute, white crystals, m. p.  $232^\circ$  (decomp.), and does not react with benzaldehyde or dissolve in dilute acids.

1-*Aminocarbonyldrazocarbonyl-3:5-dimethylpyrazole*,



prepared by the interaction of acetylacetone (1 mol.) and aminocarbocarbazide (1 mol.) in acidified aqueous solution, separates from alcohol in minute, white crystals, m. p.  $166^\circ$ , and is sparingly soluble in water.

1-*Aminocarbonyldrazocarbonyl-3-methylpyrazolone*,



prepared by the action of ethyl acetoacetate on aminocarbocarbazide, forms white crystals, m. p.  $186^\circ$ .

Aminocarbocarbazide also yields crystalline products with alloxan, citral, and chloral.

The action of cyanogen bromide on hydrazine sulphate yields hydrazodicarbonamide and guanazine hydrobromide. T. H. P.

**Constitution of Organo-magnesium Derivatives.** EDMOND É. BLAISE (*Bull. Soc. chim.*, 1907, [iv], 1, 610—612).—Evidence is quoted in support of Baeyer and Villiger's formula for organo-magnesium compounds,  $\text{R} \cdot \text{Mg} \cdot \text{OX} \cdot \text{Et}_2$ . T. H. P.

**Laws of Substitution in Aromatic Compounds. III.** BERNHARD FLÜRSCHHEIM (*J. pr. Chem.*, 1907, [ii], 76, 165—179. Compare Abstr., 1903, i, 79; 1905, i, 614; 1906, ii, 529).—A reply to

Holleman (Abstr., 1906, i, 818) and a criticism of Obermiller's views (this vol., i, 200). G. Y.

**Laws of Substitution in Aromatic Compounds. IV.** BERNARD FLÜRSCHHEIM (*J. pr. Chem.*, 1907, [ii], 76, 185—204. Compare Abstr., 1903, i, 79; 1905, i, 614; 1906, ii, 527, and preceding abstract).—The argument of this theoretical paper is based on the following conceptions of the mode of action of chemical affinity.

(1) Part of the affinity of all atoms remains free when these form chemical compounds, the free affinity being in equilibrium with the combined. The reactivity of the molecule, so far as not determined by electrolytic dissociation, depends on this free or residual affinity.

(2) The chemical affinity of an atom acts uniformly from over its whole surface. Substituents must be arranged in space round the atom so as to utilise their own affinities as fully as possible (compare Claus, Le Bel, Werner), leaving a minimum proportion of free to combined affinity in the molecule.

(3) The affinity value of the hydrogen atoms is approximately one-fourth of that of the carbon atom.

(4) Addition takes place, other things being equal, at that part of the molecule where the free affinity is greatest (compare Armstrong, Thiele, Werner), which holds good also for substitution, since this is preceded always by molecular addition (Armstrong, Kekulé, Werner).

This view of the mode of action of chemical affinity, which is discussed and illustrated in the case of a number of acyclic and cyclic compounds, differs from that of Werner in that the chemical energy is considered to act from the whole surface of the atom and not from its centre of gravity, and, in so far as the equilibrium between the combined and free affinities is concerned, to follow the laws of static electricity, but is in agreement with Traube's view (this vol., ii, 205) that an atom has not individual valons (electrons), but a valon volume filled uniformly with ether, the maximum valency of the atom being determined by the stere of its valon volume. G. Y.

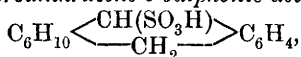
**Hydrolysis of Benzenesulphonic Esters in Alcohol.** ARTUR PRAETORIUS (*Monatsh.*, 1907, 28, 767—802).—The hydrolysis of methyl benzenesulphonate in aqueous acid and alkaline solutions, and in presence of halogen anions, has been studied previously (Abstr., 1905, i, 186; 1906, i, 736), and the results obtained shown to agree with Wegschieder's formula for the hydrolysis of esters (Abstr., 1902, ii, 493). As in these experiments, water was present always in excess, the author has now investigated the hydrolysis of methyl and ethyl benzenesulphonates in alcoholic solutions containing only limited amounts of water. Determinations of the rate of hydrolysis of the sulphonic esters in methyl- and ethyl-alcoholic solutions containing 0—10% of water, show that the action of the alcohol and the water is proportional to their concentrations. Methyl benzenesulphonate reacts with alcohol and water more easily than does the ethyl ester. Both esters are hydrolysed more rapidly by methyl than by ethyl alcohol, and react more easily with water in methyl- than in ethyl-alcoholic

solution. The relation of the action of the water to that of the alcohol is independent of the ester.

The hydrolysis of benzenesulphonic esters by means of alkalis in aqueous-ethyl alcoholic solution is a reaction of the hydroxyl and ethoxyl ions; hence only the dissociated part, termed the "active mass," of the alkali takes part in the reaction. The addition of water, on the one hand, increases this active mass, as is shown by the conductivity, but, on the other, by altering the nature of the medium, leads to changes in the constant of velocity of hydrolysis.

It is found that whilst the rate of hydrolysis may be accelerated by addition of traces of water, it is retarded by the presence of large amounts. The relation between the water-alcohol concentration and the constant of hydrolysis by means of alkalis is represented by the expression:  $K_2 = [e_a.n_a/(n_a + n_w) + e_w.n_w/(n_a + n_w)] [a_a.n_a/(n_a + n_w) + a_w.n_w/(n_a + n_w)]$ , in which  $e_a$  and  $e_w$  are the reactivities of the ester in alcohol and water,  $a_a$  and  $a_w$  those of the alkali in alcohol and water, and  $n_a$  and  $n_w$  the molecular concentrations of the alcohol and water respectively. In consequence of the alteration of the medium by the water, it is not possible to determine if the action of the alkali is accelerated by the addition of water according to the law of mass action. G. Y.

**Octahydroanthracene and its Derivatives.** MARCEL GODCHOT (*Bull. Soc. chim.*, 1907, [iv], 1, 701—710. Compare this vol., i, 308).—When octahydroanthracene is heated with concentrated sulphuric acid, it yields *octahydroanthracene-9-sulphonic acid*,



which could not be prepared in the free state; its *barium* salt,  $(\text{C}_{14}\text{H}_{17}\text{SO}_3)_2\text{Ba} \cdot 2\text{H}_2\text{O}$ , is readily soluble in water. When fused with alkali hydroxide, sodium octahydroanthracenesulphonate yields  $\beta$ -*hexahydroanthracene*,  $\text{C}_6\text{H}_{10} \cdot (\text{C}_2\text{H}_2) \cdot \text{C}_6\text{H}_4$ , which can also be obtained by dehydrating octahydroanthranole,  $\text{C}_6\text{H}_{10} \begin{array}{c} \text{CH}(\text{OH}) \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_4$ .

The action of bromine (2 mols.) on octahydroanthracene (1 mol.) in carbon disulphide or acetic acid at the ordinary temperature yields:

(1) 9:10-*Dibromo-octahydroanthracene*,  $\text{C}_6\text{H}_{10} \begin{array}{c} \text{CHBr} \\ \text{CHBr} \end{array} \text{C}_6\text{H}_4$ , which

may also be obtained by the addition of bromine to  $\beta$ -hexahydroanthracene; it crystallises from ethyl acetate in large, colourless needles, m. p. 194° (corr.), dissolves readily in benzene or chloroform, and sparingly in alcohol or acetic acid, and does not lose its bromine when treated with aqueous or alcoholic potassium hydroxide at 250°.

(2) 9-*Bromo-octahydroanthracene*,  $\text{C}_6\text{H}_{10} \begin{array}{c} \text{CHBr} \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_4$ , which has a yellow colour, gives a red coloration with picric acid, and loses hydrogen bromide with formation of  $\beta$ -hexahydroanthracene when distilled in a vacuum or when heated with aqueous or alcoholic potassium hydroxide at 150°; on oxidation with chromic acid in acetic acid solution, it yields  $\beta$ -dihydro-oxanthranol. (3) 9:10-*Di-*

*bromohexahydroanthracene*,  $C_6H_8 \begin{smallmatrix} \text{CHBr} \\ \text{CHBr} \end{smallmatrix} C_6H_4$ , which crystallises from ethyl acetate in slender, faintly-yellow needles, m. p.  $163^\circ$  (corr.), and gives blue, fluorescent solutions, especially in acetic acid.

The action of chlorine (2 mols.) on octahydroanthracene (1 mol.) in carbon disulphide or acetic acid yields the following chloro-derivatives analogous to the above bromo-compounds: 9:10-*dichloro-octahydroanthracene*,  $C_{14}H_{16}Cl_2$ , crystallises from ethyl acetate in large, colourless needles, m. p.  $192^\circ$  (corr.). 9-*Chloro-octahydroanthracene*,  $C_{14}H_{17}Cl$ , is obtained as a syrupy liquid. 9:10-*Dichlorohexahydroanthracene*,  $C_{14}H_{14}Cl_2$ , crystallises from ethyl acetate in slender, colourless needles, m. p.  $159^\circ$  (corr.). The transformations of these chloro-compounds are similar to those of the corresponding bromo-derivatives.

Oxidation of octahydroanthracene by means of chromic acid yields hexahydroanthrone and a small proportion of  $\beta$ -dihydro-oxanthranol. Concentrated nitric acid attacks octahydroanthracene vigorously, but no crystalline product has been isolated.

T. H. P.

**Action of Bromine in Presence of Aluminium Bromide on Thiophenol and on Phenyl Disulphide.** FÉLIX TABOURY (*Bull. Soc. chim.*, 1907, [iv], 1, 741—742. Compare Bodroux, *Abstr.*, 1898, i, 641).—The action of bromine in presence of aluminium bromide on either thiophenol or phenyl disulphide at  $0^\circ$  yields *s-hexabromophenyl disulphide*,  $C_6H_2Br_3 \cdot S \cdot S \cdot C_6H_2Br_3$ , which crystallises from chloroform in white needles, m. p.  $178$ — $180^\circ$ .

T. H. P.

**Phenyl Chlorothiolicarbonates.** II. HENRI RIVIER (*Bull. Soc. chim.*, 1907, [iv], 1, 733—740. Compare *Abstr.*, 1906, i, 947).—*Phenyl chlorothiolicarbonate*,  $COCl \cdot SPh$ , prepared by the interaction of lead thiophenoxide (1 mol.) and carbonyl chloride (2 mols.) in toluene solution, is a colourless oil with a characteristic odour, b. p.  $104^\circ/13$  mm.,  $150^\circ/22$  mm., and  $225$ — $227^\circ/724$  mm. (decomp.);  $D_4^{15}$  1.285.

Ethyl phenylthiolicarbonate,  $CO_2Et \cdot SPh$ , which was obtained in an impure condition by Otto and Rössing (*Abstr.*, 1886, 692), may be prepared by heating phenyl chlorothiolicarbonate in alcoholic solution, and is a colourless liquid with an ethereal odour, b. p.  $252$ — $253^\circ/740$  mm.,  $130^\circ/16$  mm., and  $135^\circ/20$  mm., m. p.  $6^\circ$ ,  $D_4^{15}$  1.139.

*Phenyl phenylthiolicarbonate*,  $CO_2Ph \cdot SPh$ , prepared by the action of phenyl chlorothiolicarbonate (1 mol.) on a solution of phenol (1 mol.) in the equivalent quantity of sodium hydroxide, crystallises from alcohol in slender, colourless needles, m. p.  $56^\circ$ .

*Phenyl dithioicarbonate*,  $CO(SPh)_2$ , prepared by the action of sodium or lead thiophenoxide on phenyl chlorothiolicarbonate, forms colourless crystals, m. p.  $41^\circ$ , and dissolves readily in alcohol.

*Phenyl thiocarbamate*,  $NH_2 \cdot CO \cdot SPh$ , obtained by gradual addition of an alcoholic solution of ammonia (2 mols.) to an ethereal solution of phenyl chlorothiolicarbonate (1 mol.), crystallises from benzene in colourless needles, m. p.  $91$ — $92^\circ$ , dissolves readily in alcohol or ether, and is hydrolysed by alkali or, to a slight extent, by boiling water into ammonia, carbon dioxide, and thiophenol.

Phenyl phenylthiocarbamate,  $NHPh \cdot CO \cdot SPh$ , obtained by the

interaction of phenyl chlorothiolcarbonate and aniline (2 mols.) in alcoholic solution, has m. p. 122—122·5°; the product, m. p. 125°, prepared by the method of Snape (Trans., 1885, 47, 770), contains carbanilide. Phenyl phenylthiolcarbamate dissociates on heating into phenylcarbimide and thiophenol. When boiled in alcoholic solution or when treated with alkali, it decomposes according to the equation:  $\text{NHPh}\cdot\text{CO}\cdot\text{SPh} + \text{H}_2\text{O} = \text{NH}_2\text{Ph} + \text{CO}_2 + \text{PhSH}$ .

*Phenyl phenylmethylthiolcarbamate*,  $\text{NMePh}\cdot\text{CO}\cdot\text{SPh}$ , obtained by the action of phenyl chlorothiolcarbonate on methylaniline, forms rhombic prisms, m. p. 66—66·5°, and is soluble in alcohol. *Phenyl ethylphenylthiolcarbamate*,  $\text{NEtPh}\cdot\text{CO}\cdot\text{SPh}$ , crystallises in plates, m. p. 96·5—97°. These compounds are not decomposed by boiling with alcohol, or by dilute acid, or alkali.

*Phenyl chlorodithiocarbonate*,  $\text{Cl}\cdot\text{CS}\cdot\text{SPh}$ , prepared by the interaction of thiocarbonyl chloride (1 mol.), thiophenol (1 mol.), and aqueous sodium hydroxide (1 mol.) in chloroform solution, is an orange-red oil with a pungent odour, b. p. 135°/15 mm.,  $D_4^{25}$  1·331, and dissolves in organic solvents. When boiled with alcohol, it is converted into phenyl ethylxanthate, which was prepared by Leuckart (Abstr., 1890, 603) in an impure state and forms a pale yellow liquid having a characteristic odour; b. p. 155°/16 mm. or 171°/35 mm.,  $D_4^{25}$  1·168. The action of phenol in alcoholic potassium hydroxide solution on phenyl chlorodithiocarbonate yields phenyl thionthiolcarbonate,  $\text{SPh}\cdot\text{CS}\cdot\text{OPh}$ , m. p. 51°, described as diphenyl dithiocarbonate in the first portion of this paper (*loc. cit.*). Sodium or lead thiophenoxide converts phenyl dithiocarbonate into *phenyl trithiocarbonate*,  $\text{CS}_3\text{Ph}_2$ , which crystallises from alcohol in deep yellow leaflets, m. p. 95·5—95·7°, and is soluble in ether. The action of alcoholic ammonia on an ethereal solution of phenyl chlorodithiocarbonate proceeds as follows:  $\text{Cl}\cdot\text{CS}\cdot\text{SPh} + 2\text{NH}_3 = \text{NH}_4\text{Cl} + \text{NH}_2\cdot\text{CS}\cdot\text{SPh}$ ;  $\text{NH}_2\cdot\text{CS}\cdot\text{SPh} + \text{NH}_3 = \text{NH}_4\text{CNS} + \text{PhSH}$ ;  $\text{PhSH} + \text{NH}_2\cdot\text{CS}\cdot\text{SPh} = \text{NH}_3 + \text{CS}_3\text{Ph}_2$ .

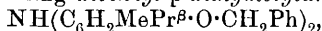
*Phenyl phenyldithiocarbamate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{SPh}$ , obtained by the interaction of phenyl chlorodithiocarbonate (1 mol.) and aniline (2 mols.) in alcoholic solution, separates from alcohol in colourless crystals, m. p. 104—106°; at its melting point it dissociates to a slight extent into thiophenol and phenylthiocarbimide, from which products it may be prepared. *Phenyl phenylmethylthiocarbamate*,  $\text{NMePh}\cdot\text{CS}\cdot\text{SPh}$ , prepared from phenyl chlorodithiocarbonate and methylaniline, forms colourless crystals, m. p. 99·5°, dissolves in alcohol, and is turned yellow by the action of light. Phenyl phenylethylthiocarbamate, similarly prepared, has been described by Billeter and Strohl (Abstr., 1888, 364). T. H. P.

**Structure of Nitrosothymol Dyes. Derivatives of Thymol Benzyl Ether.** BORIS SOLONINA (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 751—759. Compare Abstr., 1905, i, 197).—Thymol benzyl ether, prepared by the action of benzyl chloride on thymol in the presence of sodium ethoxide, is of a pale colour, b. p. 221—223°/35 mm.;  $D_4^{18}$  1·0063,  $n_D^{20}$  1·5511. When dissolved in cold glacial acetic acid and treated



with a cooled solution of nitric acid (D 1.40) in the same solvent, a variety of colours are produced and finally a dark blue solution is formed from which the *oxonium nitrate*,

$\text{CH}_2\text{Ph}\cdot\text{O}(\text{NO}_3)\cdot\text{C}_6\text{H}_2\text{MePr}^\beta\cdot\text{NO}\cdot\text{C}_6\text{H}_2\text{MePr}^\beta\cdot\text{OH}(\text{NO}_3)\cdot\text{CH}_2\text{Ph}$ ,  
m. p.  $-68^\circ$ , separates in bright copper-coloured crystals; when powdered, it appears dark blue and has m. p.  $-62^\circ$ . It is fairly stable in a vacuum, but decomposes when heated, forming a red substance. When an alkali is added to its acid solution, it turns yellow, but becomes blue again on addition of acid, but very soon decomposes, forming a red substance. Hydrogen sulphide, sulphur dioxide, and stannous chloride reduce it, forming *dibenzyl-p-dithymolylamine*,

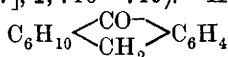


m. p.  $141.5^\circ$ , analogous in properties to its ethyl, methyl, and butyl homologues; the *hydrochloride* has m. p.  $142^\circ$ . When oxidised with ferric chloride, the amine is converted into *p-thymoquinone thymol-imide benzyl ether*,  $\text{O}\cdot\text{C}_6\text{H}_2\text{MePr}^\beta\cdot\text{N}\cdot\text{C}_6\text{H}_2\text{MePr}^\beta\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , m. p.  $81.5^\circ$ , which is similar in properties to the corresponding ethyl compound, and is reduced quantitatively to dithymolylamine,  $\text{C}_{27}\text{H}_{33}\text{O}_2\text{N}$ , by stannous chloride.  
Z. K.

**Preparation and Purification of Hydroxyanthraquinone and Hydroxynaphthaquinone Derivatives and especially of Juglone and Emodin.** R. COMBES (*Bull. Soc. chim.*, 1907, [iv], 1, 800—816).—The reaction with nickel acetate previously described (Abstr., 1906, ii, 118, and this vol., ii, 411) is utilised for the isolation of these hydroxyquinones. The fresh pericarp of the walnut is used as a source of juglone, which is extracted by means of ether, freed from chlorophyll and other impurities by solution in benzene, and finally purified by conversion into the nickel compound, from which it is regenerated by means of acetic acid. From the aqueous solution so obtained, the juglone is extracted by ether or chloroform and finally crystallised from benzene. In old walnut pericarps, which have become brown, the juglone has been transformed into hydrojuglone, so that in preparing the former from such material the crude product recovered from the first solution in benzene is re-dissolved in ether and shaken with chromium mixture as suggested by Bernthsen and Semper (Abstr., 1885, 546). The oxidised product is freed from traces of adherent chromium compounds by repeatedly washing the solution in ether with water and is purified as before. The above methods can be applied generally for the isolation of hydroxynaphthaquinones.

Alder bark collected in May is employed as a source of emodin. The powdered bark is extracted with a dilute solution of sodium hydroxide and the crude emodin, obtained on acidifying this solution with dilute hydrochloric acid, treated with an aqueous solution of nickel acetate, containing calcium carbonate in suspension, whereby the soluble nickel compound of emodin is formed. Dilute hydrochloric acid is added in excess to this solution, when emodin slowly crystallises out, separation being complete after several days. The crystals are purified by washing with 10% hydrochloric acid. This process is a general one for the isolation of hydroxyanthraquinones.  
T. A. H.

**Hexahydroanthrone and its Derivatives.** MARCEL GODCHOT (*Bull. Soc. chim.*, 1907, [iv], 1, 710—719).—Hexahydroanthrone,



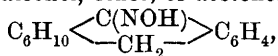
(see this vol., i, 837), crystallises in pale yellow, hard needles, m. p. 45·5°, b. p. 222—225°/25 mm., dissolves readily in ether, alcohol, benzene, or acetic acid, gives a red coloration with concentrated sulphuric acid, and reduces ammoniacal silver nitrate and alkaline copper solutions, but does not combine with sodium hydrogen sulphite. Oxidation with chromic acid in acetic acid solution at 100° converts it into dihydro-9-hydroxyanthranol,  $\text{C}_6\text{H}_6 \begin{array}{c} \diagup \text{C(OH)} \diagdown \\ \text{C(OH)} \end{array} \text{C}_6\text{H}_4$ , and a small proportion of anthraquinone.

*Octahydroanthranol*,  $\text{C}_6\text{H}_{10} \begin{array}{c} \diagup \text{CH(OH)} \diagdown \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_4$ , prepared by reducing hexahydroanthrone with sodium and absolute alcohol, crystallises from aqueous alcohol in rosettes of faintly yellow needles, m. p. 81—82°, dissolves readily in the ordinary solvents, and gives a red coloration with picric acid. On distillation, even in a vacuum, it loses water, forming  $\beta$ -hexahydroanthracene (see below). Its *phenylurethane* derivative,  $\text{C}_{14}\text{H}_{17}\text{O} \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from acetone in colourless needles, m. p. 151—152°.

$\beta$ -Hexahydroanthracene,  $\text{C}_6\text{H}_{10} \begin{array}{c} \diagup \text{CH} \diagdown \\ \text{CH} \end{array} \text{C}_6\text{H}_4$ , also prepared by the action of dehydrating agents on octahydroanthranol, crystallises in colourless plates, m. p. 66·5°, b. p. 303—306°, and dissolves readily in alcohol, acetic acid, or benzene, giving solutions exhibiting blue fluorescence. Oxidation with chromic acid in acetic acid solution converts it into dihydro-9-hydroxyanthranol. It takes up  $\text{Br}_2$  (or  $\text{Cl}_2$ ), yielding  $\text{C}_6\text{H}_{10} \begin{array}{c} \diagup \text{CHBr} \diagdown \\ \text{CHBr} \end{array} \text{C}_6\text{H}_4$ .

*Dibromohexahydroanthrone*,  $\text{C}_6\text{H}_{10} \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{CBr}_2 \end{array} \text{C}_6\text{H}_4$ , prepared by the action of bromine on hexahydroanthrone in acetic acid or carbon disulphide, crystallises from acetone in colourless plates, m. p. 123—124°, dissolves readily in most of the ordinary solvents, and when oxidised with chromic acid in acetic acid solution yields only a small proportion of anthraquinone, most of the compound undergoing complete oxidation. It does not yield an oxime or a semicarbazone.

*Hexahydroanthrone semicarbazone*,  $\text{C}_{14}\text{H}_{16} \cdot \text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , crystallises from aqueous alcohol in faintly yellow needles, m. p. 250°, and dissolves sparingly in alcohol, ether, or acetone. The *oxime*,

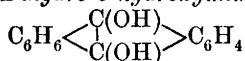


crystallises from alcohol in colourless needles, m. p. 143°.

$\gamma$ -Octahydroanthramine,  $\text{C}_6\text{H}_{10} \begin{array}{c} \diagup \text{CH(NH}_2) \diagdown \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_4$ , prepared by reducing the preceding oxime, is a yellow, strongly basic liquid, b. p.

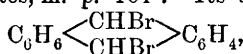
182°/12 mm. The *hydrochloride*,  $C_{14}H_{19}N \cdot HCl$ , m. p. 188°; *picrate*,  $C_{14}H_{19}N \cdot C_6H_3O_7N_3$ , m. p. 212°, and *acetyl* derivative,  $C_{14}H_{17} \cdot NHAc$ , m. p. 183°, were prepared. T. H. P.

**Dihydro-9-hydroxyanthranol and its Derivatives.** MARCEL GODCHOT (*Bull. Soc. chim.*, 1907, [iv], 1, 719—724. Compare preceding abstracts).—*Dihydro-9-hydroxyanthranol*,



(compare Schulze, *Abstr.*, 1886, 247), crystallises from ethyl acetate in golden-yellow, prismatic needles, m. p. 158·5°, dissolves readily in benzene or its homologues or alcohol, gives a red coloration with sulphuric acid, and a deep red colour with a trace of alkali. Its *diacetyl* derivative,  $C_{14}H_{10}(OAc)_2$ , m. p. 220°, gives solutions exhibiting a blue fluorescence, and its *dibenzoyl* compound,  $C_{14}H_{10}(OBz)_2$ , has m. p. 255° (partially decomp.). When subjected to the prolonged action of chromic acid, it yields a small proportion of anthraquinone.

*γ-Tetrahydroanthracene*,  $C_6H_6 \begin{array}{c} \diagup CH_2 \\ \diagdown CH_2 \end{array} C_6H_4$ , prepared by reducing dihydro-9-hydroxyanthranol with hydriodic acid, crystallises from alcohol in colourless plates, m. p. 101°. Its *dibromo*-derivative,



crystallises from ethyl acetate in large, faintly yellow needles, m. p. 169°, dissolves readily in benzene, does not give up its bromine to aqueous or alcoholic potassium hydroxide at 200°, and gives dihydro-9-hydroxyanthranol when treated with chromic acid in acetic acid solution. T. H. P.

**Electrolytic Reduction of the Three Isomeric Nitrobenzylsulphonic Acids.** L. WEISS and K. REITER (*Annalen*, 1907, 355, 175—195).—The experiments have been performed in aqueous, alcoholic, or aqueous-alcoholic solutions in a divided cell with lead, nickel, or platinum cathodes, the completion of the reduction being ascertained by comparing the indications of a water-voltameter in the circuit with the amount of gas collected in a eudiometer at the cathode. In alkaline solution, sodium *o*- and *p*-nitrobenzylsulphonates are converted into the corresponding azobenzylsulphonates; the *m*-isomeride does not give definite results. In faintly acid solution, the three isomerides are reduced through the hydroxylamine derivatives to the aminosulphonic acids. In strongly acid solution, the *o*- and *m*-nitrosulphonates are converted into the hydroxylamine derivatives, which are then transformed into the isomeric aminohydroxysulphonic acids; *p*-hydroxylaminobenzylsulphonic acid, which cannot undergo the preceding transformation, is reduced to the aminosulphonic acid by the addition of alcohol or by the prolonged action of the electric current.

A table is given which states the composition of the solution, the nature and area of the cathode, the current strength, the voltage, and the yield. C. S.

**Piperidides.** ANTOINE P. N. FRANCHIMONT, WILLEM VAN RIJN, and HERMANN FRIEDMANN (*Rec. trav. chim.*, 1907, **26**, 228—239).—The authors have prepared various piperidides and have subjected them to the action of concentrated nitric acid. It is found that the piperidides of the nitrobenzoic acids and of 2:4- and 3:5-dinitrobenzoic acids are not attacked by nitric acid at the ordinary temperature, whilst those of succinic and sulphuric acid yield nitropiperidine (compare Franchimont and Erp, *Abstr.*, 1896, i, 602; Franchimont and Taverne, *ibid.*).

*Malonylpiperidide*,  $C_{13}H_{22}O_2N_2$ , prepared by the action of ethyl malonate (1 mol.) on piperidine (rather more than 2 mols.), separates from light petroleum in crystals, m. p.  $57^\circ$ .

*Succinylpiperidide*,  $C_{14}H_{24}O_2N_2$ , prepared by the interaction of succinyl chloride (1 mol.) and piperidine (4 mols.), separates from light petroleum in crystals, m. p.  $70^\circ$ .

*o-Nitrobenzoylpiperidide*,  $C_{12}H_{14}O_3N_2$ , prepared by the action of *o*-nitrobenzoyl chloride on piperidine, crystallises from alcohol in pale yellow, rectangular, triclinic plates [F. M. JAEGER,  $a:b:c = 1.3444:1.09672$ ;  $\alpha = 101^\circ 34'$ ,  $\beta = 95^\circ 59\frac{1}{3}'$ ,  $\gamma = 70^\circ 36'$ ], m. p.  $56^\circ$ ,  $D^{15} 1.345$ .

*p-Nitrobenzoylpiperidide*,  $C_{12}H_{14}O_3N_2$ , separates from alcohol in faintly yellow, rhombic crystals [F. M. JAEGER,  $a:b:c = 1.1128:1.09620$ ], m. p.  $120.5^\circ$ ,  $D^{15} 1.310$ .

The molecular volumes of *o*-, *m*-, and *p*-nitrobenzoylpiperidides are 173.97, 176.70, and 179.40 respectively, the differences being 2.73 and 2.70; the molecular volume is hence greatest for the crystals exhibiting the lowest symmetry.

2:4-Dinitrobenzoylpiperidide,  $C_{12}H_{13}O_5N_3$ , crystallises from alcohol in slender, pale yellow needles, m. p.  $159^\circ$ .

3:5-Dinitrobenzoylpiperidide,  $C_{12}H_{13}O_5N_3$ , crystallises from alcohol in shining scales, m. p.  $147^\circ$ . T. H. P.

**Arylanthranilic Acids.** FRITZ ULLMANN (*Annalen*, 1907, **355**, 312—358).—In connexion with work previously published with Sponagel (*Abstr.*, 1905, i, 644), the author observed that phenylanthranilic acid is formed when copper powder is added to a boiling solution of *o*-chlorobenzoic acid in aniline. This action has now been further studied. The condensation between *o*-chlorobenzoic acid and aniline takes place the more readily the higher the temperature; it is noted, however, that at high temperatures the phenylanthranilic acid formed is decomposed into diphenylamine and carbon dioxide, so that the heating must not be continued too long. Better results are obtained when potassium carbonate is added to the reaction mixture, since not only is potassium phenylanthranilate stable at high temperatures, but the hydrogen chloride formed is neutralised. In some cases, where vessels of copper or of iron were used, the addition of copper powder was not necessary.

The action of various catalysts in promoting the condensation was studied. Salts of iron, nickel, platinum, and zinc act as catalysts, whilst salts of manganese and tin do not. The best catalyst is copper, a trace of which suffices.

The condensation between aniline and *o*-bromobenzoic acid or *o*-iodobenzoic acid takes place without the addition of a catalyst.

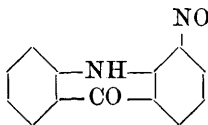
The action was extended to the preparation of substituted phenylanthranilic acids and is general for the preparation of arylanthranilic acids, since other aromatic amines may be substituted for aniline. In order to obtain good yields of the latter acids, the addition of amyl alcohol or nitrobenzene to the mixture of amine and acid is of service.

The arylanthranilic acids described are of interest on account of the ease with which they are converted into acridone derivatives; they may also be used for the preparation of unsymmetrical diphenylamine derivatives. The acridone derivatives prepared were examined with respect to their fluorescent properties; halogen acridones fluoresce like acridone itself, but, when a nitro-group is present in the acridone, there is no fluorescence. 2- and 4-Aminoacridones exhibit strong fluorescence in alcoholic solution, whilst 1-aminoacridone does not fluoresce in the same solvent. When hydrochloric acid is added to the alcoholic solution of each one of these aminoacridones, the solution of the 1-amino-compound fluoresces and the others do not. The alcoholic solutions of 2- and 4-hydroxyacridones exhibit a blue fluorescence, whilst the yellow solutions in dilute alkalis exhibit a green fluorescence.

[With PAUL DIETERLE.]—The preparation of phenylanthranilic acid and the influence of various catalysts are described in detail.

[With WALTER BADER.]—*o*-Tolylanthranilic acid, obtained from *o*-chlorobenzoic acid, *o*-toluidine, potassium carbonate, and copper powder, crystallises from benzene in colourless leaflets, m. p. 185° (Locher, Abstr., 1894, i, 530, gives 179°). When heated at 230–250°, it is converted into phenyl-*o*-toluidine. *m*-Tolylanthranilic acid, prepared from *o*-chlorobenzoic acid and *m*-toluidine in a similar manner, separates from benzene in colourless leaflets, m. p. 139°, and, when distilled, is converted into phenyl-*m*-toluidine. *p*-Tolylanthranilic acid was similarly prepared, m. p. 196° (Kahn gives 191.5°); it is readily converted into phenyl-*p*-toluidine. 2:4-Xylylanthranilic acid was also prepared, m. p. 187° (Kaufmann gives 182°); phenyl-2:4-xylylamine has m. p. 44° (Girard and Vogt give m. p. 52°).

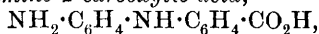
2'-Nitrodiphenylamine-2-carboxylic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , prepared from potassium *o*-chlorobenzoate, *o*-nitroaniline, copper acetate, potassium carbonate, and amyl alcohol, crystallises from benzene in dark yellow, glistening needles, m. p. 219°. Its solution in concentrated sulphuric acid is yellow and becomes green on the addition of nitric acid. When heated at 100° with concentrated sulphuric acid, it forms 1-nitroacridone, which separates from toluene in glistening, orange-red needles, m. p. 262°; its solution in concentrated sulphuric acid is yellowish-brown and, when its alcoholic solution is boiled with sodium sulphide, 1-aminoacridone,  $\text{C}_{13}\text{H}_{10}\text{ON}_2$ , is formed, which



crystallises from alcohol in dark yellow needles, m. p. 355° (decomp.). The solution of the latter compound in concentrated sulphuric acid is yellowish-green and exhibits a blue fluorescence.

*3'-Nitrodiphenylamine-2-carboxylic acid*,  $C_{13}H_{10}O_4N_2$ , obtained by the condensation of *m*-nitroaniline with *o*-chlorobenzoic acid, crystallises from alcohol in yellow needles, m. p.  $218^\circ$ . Its solution in concentrated sulphuric acid is yellow and, on the addition of nitric acid, becomes brown and then green. On reduction, it forms *3'-aminodiphenylamine-2-carboxylic acid*,  $C_{13}H_{12}O_4N_2$ , which crystallises from toluene in colourless needles, m. p.  $166^\circ$  (decomp.); when warmed with concentrated sulphuric acid, a green fluorescence is observed and, on the addition of nitric acid, the solution becomes first brownish-red and then dirty green. When heated at  $215\text{--}220^\circ$ , *3'-nitrodiphenylamine-2-carboxylic acid* forms *3-nitrodiphenylamine*, which separates from dilute alcohol in red leaflets, m. p.  $114^\circ$ , and forms an almost colourless solution in concentrated sulphuric acid which, on the addition of nitric acid, assumes first a violet and then a brown tint. Concentrated sulphuric acid converts *3'-nitrodiphenylamine-2-carboxylic acid* into *4-nitroacridone*, which separates from nitrobenzene in yellow needles and with concentrated sulphuric acid forms a yellow solution which does not fluoresce. *4-Aminoacridone* crystallises from alcohol in yellow needles, m. p.  $285^\circ$ ; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence.

*4'-Aminodiphenylamine-2-carboxylic acid*,



prepared by the condensation of *o*-chlorobenzoic acid with *p*-phenylenediamine, separates from xylene in yellow needles, m. p.  $205^\circ$  (decomp.). Its solution in dilute hydrochloric acid assumes a faintly violet tint on exposure to the air. *3-Aminoacridone* crystallises from alcohol in yellow needles, which melt indefinitely at  $298^\circ$ . Its solution in alcohol or in acetone is yellow and exhibits a green fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

[With ERNST TEDESCO.]—Monohalogen-anilines condense readily with *o*-chlorobenzoic acid. The less basic dichloroaniline also condenses, but tribromoaniline does not.

*2'-Chlorodiphenylamine-2-carboxylic acid*,  $C_6H_4Cl \cdot NH \cdot C_6H_4 \cdot CO_2H$ , prepared by heating a mixture of potassium *o*-chlorobenzoate, *o*-chloroaniline, amyl alcohol, and copper powder, crystallises from benzene in white needles, m. p.  $192^\circ$ . *1-Chloroacridone* crystallises from glacial acetic acid in bright yellow needles, m. p. over  $360^\circ$ . Its alcoholic solution exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid has a bluish-green fluorescence. *3'-Chlorodiphenylamine-2-carboxylic acid* crystallises from benzene in colourless needles, m. p.  $167^\circ$ , and when heated at  $250\text{--}260^\circ$  until the evolution of carbon dioxide ceases it forms *3-chlorodiphenylamine*, an oil, b. p.  $335\text{--}336^\circ/724\text{ mm.}$

*4-Chloroacridone* crystallises from glacial acetic acid or nitrobenzene in yellow needles, m. p. over  $360^\circ$ . Its alcoholic solution exhibits a weak blue fluorescence.

*4'-Chlorodiphenylamine-2-carboxylic acid*, obtained by the usual method from *p*-chloroaniline, forms yellow needles, m. p.  $177^\circ$ . *3-Chloroacridone* forms yellow needles, m. p. over  $360^\circ$ . Its alcoholic solution is faintly yellow with a bluish-violet fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

4-Chlorodiphenylamine, obtained from 4'-chlorodiphenylamine-2-carboxylic acid as usual, has m. p. 74° and b. p. 334—335°/726 mm.

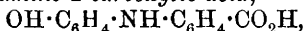
2':4'-Dichlorodiphenylamine-2-carboxylic acid, prepared by the condensation of dichloroaniline with potassium *o*-chlorobenzoate, separates from glacial acetic acid in yellow needles, m. p. 249°.

1:3-Dichloroacridone crystallises from glacial acetic acid in yellow needles, m. p. over 360°. Its solution in glacial acetic acid is yellow and exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid is yellow and exhibits a blue fluorescence.

2:4-Dichlorodiphenylamine separates from dilute alcohol in needles, m. p. 64°; its solution in concentrated sulphuric acid is colourless, but, on the addition of nitric acid, becomes first violet and then reddish-brown. 4'-Bromodiphenylamine-1-carboxylic acid separates from a mixture of benzene and light petroleum in glistening leaflets, m. p. 185°. 3-Bromoacridone crystallises from glacial acetic acid in bright yellow needles, m. p. over 360°; its alcoholic solution is faintly yellow and exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

[With HERMANN KIPPER.]—The condensation of potassium *o*-chlorobenzoate with *o*-aminophenol gives only a 40% yield. With *o*-anisidine, the yield is 85% when amyl alcohol is used as the solvent. Good yields are also obtained with *m*-anisidine and *p*-phenetidine respectively.

2-Hydroxydiphenylamine-2-carboxylic acid,



crystallises from dilute alcohol in glistening needles, m. p. 190°.

2-Methoxydiphenylamine-2-carboxylic acid, obtained from *o*-anisidine, crystallises from benzene in colourless needles, m. p. 176°. 2-Methoxydiphenylamine, obtained by heating the preceding compound at 240—260°, is a colourless liquid, b. p. 325—326°/732 mm.; it becomes brown on exposure to the air. 1-Methoxyacridone separates from 50% acetic acid in faintly yellow needles, m. p. 293°; its alcoholic solution is faintly yellow and exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

1-Hydroxyacridone, obtained either by the usual method from 2'-hydroxydiphenylamine-2-carboxylic acid or by the action of aluminium chloride on 1-methoxyacridone, using xylene as solvent, crystallises from dilute acetic acid in yellow needles, which sinter at 290° and melt at 300°. Its alcoholic solution exhibits a blue fluorescence; its solution in dilute aqueous sodium hydroxide is yellow; its solution in concentrated sulphuric acid is yellowish-brown and exhibits a green fluorescence.

3'-Methoxydiphenylamine-2-carboxylic acid, obtained from *m*-anisidine, separates from a mixture of benzene and light petroleum in colourless needles, m. p. 132°. 4'-Ethoxydiphenylamine-2-carboxylic acid, obtained from *p*-phenetidine, crystallises from dilute acetic acid in colourless needles, m. p. 209°. 3-Hydroxyacridone, obtained from the preceding compound, crystallises from alcohol in yellow needles, m. p. 345—350° (indefinite); its solution in alcohol is yellow and exhibits a bluish-green fluorescence; its solution in concentrated sulphuric acid is faintly yellow and exhibits a green fluorescence.

[With GEORGES RASSETTI.]—The condensation of  $\beta$ -naphthylamine with *o*-chlorobenzoic acid proceeds better than that of  $\alpha$ -naphthylamine. The corresponding naphthacridones cannot readily be obtained by the sulphuric acid method, since the naphthalene nucleus undergoes sulphonation; the aluminium chloride method, however, may conveniently be used.

*$\alpha$ -Naphthylaniline-2-carboxylic acid*,  $C_{10}H_7 \cdot NH \cdot C_6H_4 \cdot CO_2H$ , separates from a mixture of benzene and light petroleum in colourless, glistening leaflets, m. p.  $208^\circ$ . When its solution in concentrated sulphuric acid is warmed, it becomes yellow and exhibits a bluish-green fluorescence.

*2:1-Naphthacridone* is prepared by adding phosphorus pentachloride to a solution of the preceding acid in thiophen-free benzene, warming until the solution of hydrogen chloride ceases and then heating with aluminium chloride; it crystallises from pyridine in faintly yellow needles, m. p. over  $360^\circ$ ; its solution in concentrated sulphuric acid exhibits a blue fluorescence. When distilled with zinc dust, it forms the corresponding naphthacridine.

*$\beta$ -Naphthylaniline-2-carboxylic acid* crystallises from acetone in white, glistening needles, m. p.  $212^\circ$ . *1:2-Naphthacridone* forms orange-yellow needles, m. p. over  $360^\circ$ ; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence; on reduction with zinc dust, the corresponding naphthacridine is formed.

[With HEINRICH HOZ.]—*o*-Chlorobenzoic acid readily condenses with aminobenzoic acids to form diphenylaminedicarboxylic acids, which may be converted into acridonecarboxylic acids.

*Diphenylamine-2:2'-dicarboxylic acid*,  $CO_2H \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot CO_2H$ , obtained either from *o*-chlorobenzoic acid and anthranilic acid or by the action of ammonia on *o*-chlorobenzoic acid, in which case anthranilic acid is the primary product, crystallises from alcohol in colourless crystals, m. p.  $295^\circ$  (decomp.).

*Acridone-1-carboxylic acid*,  $C_{14}H_9O_3N$ , separates from alcohol in dark yellow needles, m. p.  $325^\circ$  (decomp.); its solution in alkalis is yellow and exhibits a blue fluorescence; its solution in concentrated sulphuric acid exhibits a green fluorescence. Its *methyl ester* crystallises from methyl alcohol in yellow needles, m. p.  $172^\circ$ ; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

*Diphenylamine-2:3'-dicarboxylic acid* crystallises from alcohol in faintly brown needles, m. p.  $296^\circ$  (decomp.); its solution in concentrated sulphuric acid exhibits a blue fluorescence. *Diphenylamine-2:4'-dicarboxylic acid* forms colourless needles, m. p.  $290^\circ$  (decomp.).

*Acridone-3-carboxylic acid* forms a faintly yellow, crystalline powder, m. p. above  $350^\circ$ ; its alcoholic solution exhibits a blue fluorescence; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence. Its *methyl ester* forms almost colourless needles, m. p.  $339^\circ$ ; its solution in alcohol is faintly yellow and exhibits a blue fluorescence.

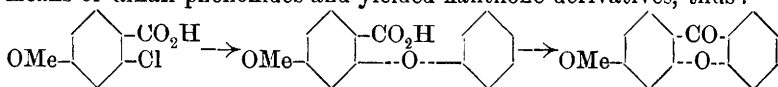
A. MCK.

**Transformations of Substituted *o*-Chlorobenzoic Acids in the Presence of Copper.** FRITZ ULLMANN and CARL WAGNER (*Annalen*, 1907, 355, 359—371. Compare preceding abstract).—The authors have studied the interaction of substituted *o*-chlorobenzoic



acids and amines in the presence of copper, when substituted diphenylamine-*o*-carboxylic acids were formed, which were then converted into the corresponding acridones.

Derivatives of salicylic acid phenyl ether were also formed by means of alkali phenoxides and yielded xanthone derivatives, thus :



2-Chloro-4-nitrotoluene was prepared by the action of antimony pentachloride on *p*-nitrotoluene and from 4-nitro-2-toluidine by Sandmeyer's method. When oxidised by potassium permanganate, it is converted into 2-chloro-4-nitrobenzoic acid, which, when heated with soda lime, water, and a trace of copper powder at 160–170° for six hours, is converted into 4-nitrosalicylic acid; the latter crystallises from water in almost colourless, felted needles, m. p. 226°, and gives a red coloration with ferric chloride.

When 2-chloro-4-nitrobenzoic acid is heated with sodium phenoxide and methyl alcohol at 180° in the presence of a trace of copper, it is converted into 5-nitrodiphenyl ether-2-carboxylic acid [4-nitro-2-phenoxybenzoic acid],  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OPh}$ , which crystallises from benzene in almost colourless leaflets, m. p. 156°.

3-Nitroxanthone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$ , is obtained from the preceding acid either by means of sulphuric acid or by treatment of the chloride with aluminium chloride; it crystallises from dilute alcohol in faintly yellow needles, m. p. 176°; its solution in concentrated sulphuric acid is yellow and exhibits a green fluorescence. When reduced by stannous chloride, it is converted into 3-aminoxanthone, which separates from alcohol or toluene in faintly yellow, feathery needles, m. p. 232°; its alcoholic solution is almost colourless and exhibits a blue fluorescence which, on the addition of hydrochloric acid, becomes green.

5-Nitrodiphenylamine-2-carboxylic acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NHPh}$ , obtained by the condensation of 2-chloro-4-nitrobenzoic acid with aniline, crystallises from toluene in orange-yellow needles, m. p. 230°.

2-Nitroacridone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$ , obtained by the aluminium chloride method, crystallises from nitrobenzene or acetic acid in yellow needles, m. p. above 350°.

2:4-Dichlorobenzoic acid was prepared by the oxidation of 2:4-dichlorotoluene with potassium permanganate. 5-Chlorodiphenylamine-2-carboxylic acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NHPh}$ , obtained from 2:4-dichlorobenzoic acid and aniline, crystallises from benzene or dilute alcohol in yellow needles, m. p. 207°. 2-Chloroacridone, prepared by the aluminium chloride method, crystallises from glacial acetic acid in faintly yellow needles, m. p. over 360°; its alcoholic solution is yellow and exhibits a blue fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

5-Chlorodiphenyl ether-2-carboxylic [4-chloro-2-phenoxybenzoic] acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{OPh}$ , prepared from 2:4-dichlorobenzoic acid and sodium phenoxide, crystallises from dilute alcohol in colourless, glistening

needles, m. p. 115°. 3-Chloroxanthone, obtained by the sulphuric acid method, separates from alcohol or a mixture of benzene and light petroleum in white, silky needles, m. p. 171°; its solution in concentrated sulphuric acid is faintly yellow and exhibits a bluish-green fluorescence.

2-Chloro-4-toluidine was converted, through the diazonium salt, into 2-chloro-*p*-cresol,  $C_7H_7OCl$ , which forms colourless needles, m. p. 55°, b. p. 229°/735 mm. When methylated by methyl sulphate, it forms 2-chloro-4-methoxytoluene, a colourless liquid, b. p. 212°. When the latter compound is oxidised with potassium permanganate, it is converted into *o*-chloroanisic acid, m. p. 208°, identical with the acid obtained by Tiemann by the oxidation of chloroanisaldehyde. It reacts with potassium phenoxide in the presence of a trace of copper to form 4-methoxy-2-phenoxybenzoic acid, glistening needles, m. p. 177°, which, with sulphuric acid, forms 3-methoxyxanthone, m. p. 129° (Dreher and Kostaneki, Abstr., 1893, i, 217, give 128.5°); the solution of the latter compound in concentrated sulphuric acid is faintly yellow and exhibits a blue fluorescence. By the action of aluminium chloride, 3-methoxyxanthone is converted into 3-hydroxyxanthone, m. p. 243°, the solution of which in concentrated sulphuric acid exhibits a greenish-blue fluorescence.

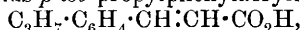
5-Methoxydiphenylamine-2-carboxylic acid separates from benzene in faintly yellow, glistening leaflets, m. p. 178°. By the action of sulphuric acid, it is converted into 3-methoxyacridone, which separates from dilute acetic acid in faintly yellow needles, m. p. 290°; the alcoholic solution of the latter compound exhibits a blue fluorescence.

A. McK.

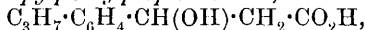
**Constitution of Greiff's Dibromoanthranilic Acid.** PAUL FRIEDLÄNDER and V. LASKE (*Monatsh.*, 1907, 28, 987—989).—Greiff's dibromoanthranilic acid, formed by the action of bromine on *o*-nitrotoluene (Abstr., 1880, 648), must be 3:5-dibromo-2-aminobenzoic acid, as if diazotised and boiled with alcohol it yields 3:5-dibromobenzoic acid, whilst its silver salt when heated decomposes, forming 2:4-dibromoaniline. The same constitution must be ascribed to the dibromoanthranilic acid obtained from dibromoisatin by Dorsch (Abstr., 1886, 359).

G. Y.

**Synthesis of  $\beta$ -*p*-iso-Propylphenyl  $\beta$ -Hydroxypropionic Acid.** G. BRONSTEIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 578—587).—When cuminaldehyde reacts with ethyl bromoacetate in the presence of a zinc-copper couple, an ester is obtained which on hydrolysis with hot barium hydroxide yields *p*-iso-propylphenylacrylic acid,



of which the barium,  $(C_{12}H_{13}O_2)_2Ba \cdot 7H_2O$ , and silver salts are described. On saponifying the ester with cold barium hydroxide, the barium salt,  $(C_{12}H_{16}O_3)_2Ba \cdot 8.5H_2O$ , is obtained, which with dilute acid yields  $\beta$  hydroxy- $\beta$ -*p*-isopropylphenylpropionic acid,



m. p. 95°. The following salts have been obtained: silver, sodium, copper, zinc, magnesium, cobalt, nickel, and mercury. When distilled

with sulphuric acid, the acid loses water and yields *p*-isopropylphenyl acrylic acid; but the derivatives obtained by the substitution of alkyl groups for the hydrogen in the  $\text{CH}_2$  group, when similarly treated, yield water, carbon dioxide, and an unsaturated hydrocarbon. These derivatives, like the parent substance, form colourless needles, more soluble in hot than in cold water. Z. K.

**Formation of Phthalide.** MARCEL GODCHOT (*Bull. Soc. chim.*, 1907, [iv], 1, 829—830).—When Sabatier and Senderens' method of catalytic reduction by means of nickel is applied to phthalic anhydride at  $200^\circ$ , phthalide is formed quantitatively. It was found to be impossible to obtain hydrophthalides by this process (compare Eykman, this vol., i, 378). T. A. H.

**Esterification of Anisic and Gallic Acids by means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Monatsh.*, 1907, 28, 965—986. Compare Abstr., 1906, ii, 659; this vol., ii, 158, 242, 243).—A study of the rate of esterification of anisic and gallic acids by means of hydrogen chloride in alcoholic solutions containing varying amounts of water, at  $25^\circ$ . The method employed is that described previously (*loc. cit.*). The constant for the velocity of esterification, when calculated with the aid of the equation for unimolecular reactions, is found to increase more rapidly than the concentration of the hydrogen chloride in the case of anisic acid in all aqueous-alcoholic concentrations or of gallic acid in presence of much water, but more slowly than the hydrogen chloride concentration in the case of gallic acid in concentrated alcohol.

The relations of the velocity constants to the concentrations of the water and hydrogen chloride are represented by the expressions, for anisic acid:  $1/k = -6.11 + 40.16/c - 0.6127/c^2 + (-138.9 + 101.6/c + 15.25/c^2)w + (-58.1 + 128.4/c + 1.163/c^2)w^2$ , and for gallic acid:  $1/k = -3.33 + 49.07/c - 2.916/c^2 + (61.1 - 23.40/c + 25.02/c^2)w + (-276.6 + 260.6/c - 10.02/c^2)w^2$ . These expressions apply to solutions having the concentration of water,  $w = 0.03$  to  $1.3$ , and of the hydrogen chloride,  $c = 0.16$  to  $0.67$ .

Anisic acid is esterified more rapidly than is *p*-hydroxybenzoic acid. The esterification of gallic acid takes place more slowly than would be the case if the introduction of a hydroxyl group into a 3:4- or 3:5-dihydroxybenzoic acid had the same influence on the reaction as the substitution of hydroxyl for a hydrogen atom in benzoic or *m*- or *p*-hydroxybenzoic acid. The behaviour of anisic and gallic acid on esterification is compared with and shown to be analogous to that of the acids previously studied. G. Y.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.** XVI. **Derivatives of Aminoterephthalic Acid.** PAUL CAHN-SPEYER (*Monatsh.*, 1907, 28, 803—817. Compare Abstr., 1906, i, 86; this vol., i, 60).—The action of an excess of hydrogen chloride on aminoterephthalic acid in boiling methyl-alcoholic solution leads to the formation of the dimethyl ester, m. p.  $133$ — $134^\circ$  ( $126^\circ$ : Ahrens, Abstr., 1886, 801), but of a limited amount of hydrogen chloride to

that of 4-methyl 1-hydrogen 2-aminoterephthalate, m. p. 213°, which is formed also on prolonged heating of the acid with methyl alcohol at 100° under pressure, or by partial hydrolysis of the dimethyl ester by means of potassium hydroxide or hydrogen chloride in methyl alcoholic solution. On diazotisation and boiling in dilute sulphuric acid, this yields 4-methyl 1-hydrogen 2-hydroxyterephthalate (Wegscheider and Bittner, Abstr., 1900, i, 658). The dimethyl ester is obtained in a yield of 70% of the aminoterephthalic acid, together with small amounts of the 4-monomethyl ester, when the acid is heated with methyl alcohol and concentrated sulphuric acid. The action of boiling methyl iodide on silver aminoterephthalate leads to the formation of a mixture of the dimethyl and 4-monomethyl esters; at the ordinary temperature, only traces of the monomethyl ester are formed, whilst in the complete absence of water, the reaction does not take place (compare Wegscheider and Frankl, this vol., i, 373).

The product, m. p. 265°, obtained on treating aminoterephthalic acid with silver oxide and methyl iodide, or the potassium hydrogen salt with methyl iodide, is found now to be a mixture of methylamino- and dimethylamino-terephthalic acids (compare Süß, Abstr., 1906, i, 86).

Acetylamino-terephthalic acid crystallises in yellow needles, decomp. 355°, is not fluorescent, and is hydrolysed readily by boiling dilute sulphuric acid; the *silver*,  $C_{10}H_7O_5NaAg_2$ , and *potassium hydrogen*,  $C_{10}H_8O_5NK$ , salts are described. The *dimethyl* ester has m. p. 167°; the 4-methyl hydrogen ester, m. p. 163°, or after a year, 196—199°. Another preparation of the monomethyl ester had m. p. 208°.

Acetylmethylaminoterephthalic acid has m. p. 255° (decomp.)

The action of methyl iodide on silver hemipinate leads to the formation of the dimethyl and  $\alpha$ -methyl hydrogen esters. G. Y.

**Esterification of Unsymmetrical Di- and Poly-basic Acids. XVII. Aminoterephthalic Esters.** RUDOLF WEGSCHEIDER (*Monatsh.*, 1907, 28, 819—824).—As only one of the two possible monomethyl esters of aminoterephthalic acid can be prepared directly (compare preceding abstract), the author has prepared both isomerides by reduction of the corresponding methyl hydrogen nitroterephthalates by means of tin and hydrochloric acid. The product obtained from  $\beta$ -methyl hydrogen nitroterephthalate is identical with the ester already described, and when pure has m. p. 216—217° (corr.).

*1-Methyl 4-hydrogen 2-aminoterephthalate*, obtained from  $\alpha$ -methyl hydrogen nitroterephthalate, forms yellow crystals, m. p. 216—217° (corr.), and has a violet-blue fluorescence in solution. A mixture of this with the monomethyl ester, formed by esterification of aminoterephthalic acid, has m. p. 192—199°. G. Y.

**Sodium Hyposulphite as a Reducing Agent for Organic Substances.** EUGÈNE GRANDMOUGIN (*J. pr. Chem.*, 1907, [ii], 76, 124—142).—An account of the author's work on the reduction of organic substances by means of sodium hyposulphite. Part of the work has been published previously (Abstr., 1906, i, 716, 967; this vol., i, 166); the following details are new.

The reaction takes place most easily when the substance to be

reduced is soluble in aqueous alkalis; *p*-hydroxyazobenzene is readily reduced to aniline and *p*-aminophenol.

1-Amino- $\beta$ -naphthol-3:6-disulphonic acid, formed by reduction of Ponceau 2R, is more stable, and reduces silver nitrate more slowly than the product obtained on reduction with stannous chloride (Witt, Abstr., 1889, 273). The following substances are obtained on reduction in the same manner of the dyes named: aniline and 1-amino- $\beta$ -naphthol-3:6-disulphonic acid from Ponceau 2G; aniline and 1-amino- $\beta$ -naphthol-6:8-disulphonic acid from Orange G;  $\alpha$ -naphthylamine and 1-amino- $\beta$ -naphthol-6:8-disulphonic acid from Crystal Ponceau; naphthionic acid and 1-amino- $\beta$ -naphthol-3:6-disulphonic acid from Bordeaux S; naphthionic acid and 2-amino- $\alpha$ -naphthol-4-sulphonic acid from Azo Rubin; aniline and 2-amino- $\alpha$ -naphthol-4-sulphonic acid from anilineazo- $\alpha$ -naphthol-4-sulphonic acid.

Acetylated azo-compounds may be hydrolysed during the reduction; thus the acetyl derivatives of benzeneazo- $\alpha$ -naphthol and benzeneazo- $\beta$ -naphthol yield 2-amino- $\alpha$ - and 1-amino- $\beta$ -naphthols, and not the corresponding acetoxy-compounds.

Whilst azobenzene is reduced almost quantitatively to hydrazobenzene, *p*-ethoxyazobenzene yields a mixture of the hydrazo-compound with aniline and *p*-phenetidine.

*o*-Nitrobenzeneazosalicylic acid is reduced to hydroxyphenylbenzotriazolecarboxylic acid.

*p*-Nitrophenol is reduced readily in alkaline solution, forming *p*-aminophenol.

*o*-Nitroazobenzene is reduced to aniline, *o*-phenylenediamine, benzeneazoiminobenzene, and benzeneazoiminobenzene oxide.

Reduction of nitroso- $\beta$ -naphthol in alkaline solution leads to the formation of 1-amino- $\beta$ -naphthol-4-sulphonic acid (compare Böniger, Abstr., 1894, i, 199).

Tetramethyldiaminobenzophenone is not reduced by sodium hyposulphite.

Quinizarin is reduced in alcoholic or alkaline solution, forming dihydroquinizarin, which must be 1:4-dihydroxyoxanthranol. When heated with aniline and glacial acetic acid, this forms a *monoanilide*,  $C_{20}H_{13}O_3N$ , which crystallises in dark violet needles, m. p. 153°, gives with concentrated sulphuric acid a green coloration becoming blue on addition of boric acid, and dissolves sparingly in hot alkalis or alcohol, more readily in chloroform or glacial acetic acid, forming violet to blue solutions. The *dianilide*,  $C_{26}H_{18}O_2N_2$ , formed by heating dihydroquinizarin with aniline, boric acid, and glacial acetic acid at 120–125°, separates in dark, glistening crystals, m. p. 218°, is dichroic in concentrated sulphuric acid solution, and forms blue solutions in alcohol, chloroform, and glacial acetic acid. Both anilides form dyes on sulphonation; that from the monoanilide dyes wool in an acid bath a bluish-violet. The dye from the dianilide dyes wool bluish-green.

Reduction of alizarin with sodium hyposulphite leads to the formation of a *product* which is not identical with Römer's deoxyalizarin (Abstr., 1881, 823), and may be 1:2-dihydroxyoxanthranol.

Indigotin is reduced readily by sodium hyposulphite in hot alcoholic solution, forming indigo-white. G. Y.

**Menthane-1 : 8-dicarboxylic Acid and a New Dicyclic Ketone.** PHILLIPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1907, 145, 255—257).—By the action of magnesium on an ethereal solution of dipentene dihydrochloride, a mixture of two monomagnesium and one dimagnesium compounds is obtained together with a small quantity of dipentene. When the mixture of organomagnesium compounds is submitted to the action of carbon dioxide, two unsaturated monobasic acids, and *menthane-1 : 8-dicarboxylic acid*,  $\text{CO}_2\text{H} \cdot \text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , are formed. The two possible stereoisomeric modifications of the latter acid have both been isolated. The *cis*-form is a microcrystalline powder, m. p. 192°, the *cis-trans*-form, m. p. 174—175°, is more soluble in water. The former when boiled with acetic anhydride gives the *anhydride*,  $\text{C}_{10}\text{H}_{18} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ , m. p. about 145—148°, which on distillation at atmospheric pressure (compare Blanc, this vol., i, 220) evolves carbon dioxide and hydrogen, and forms the ketone,  $\text{C}_{11}\text{H}_{16}\text{O}$ . For the latter, the authors propose the formula  $\text{CMe} \begin{smallmatrix} \text{CO} \cdot \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} = \text{CH} \end{smallmatrix} \text{CH}$ , and assign to it the name 1 : 3 : 3-trimethyl 1 : 7 : 8 : 4-dicyclo- $\Delta^5$ -hexene-2-one. It forms a greenish-yellow liquid, b. p. 93—95°/13 mm.,  $D_0$  0.9886,  $n_D$  1.49018. E. H.

**Reaction of Organic Magnesium Compounds with Cinnamylidene Esters. I. Reactions with Methyl Cinnamylidenemalonate.** MARIE REIMER (*Amer. Chem. J.*, 1907, 38, 227—237).—Experiments on the behaviour of Grignard's reagent towards  $\alpha$ -cyanocinnamylidenemalonate showed that the reaction was much more complex than in the case of  $\alpha$ -cyanocinnamic acid (Kohler and Reimer, *Abstr.*, 1905, i, 347). Since both these compounds contain the system,  $\text{C}:\text{C}:\text{C}:\text{O}$   $\begin{smallmatrix} \diagup \\ \text{C}:\text{N} \end{smallmatrix}$ , it seemed likely that the complexity of the reaction was due to the influence of the additional double linking in the system,  $\text{C}:\text{C}:\text{C}:\text{C}:\text{O}$ , rather than to the presence of the cyano-group, although Kohler (*Abstr.*, 1906, i, 427) has shown that this group does react with Grignard's reagent. The object of the investigation, now being carried out, is to study the effect of the double linking on the reactivity of the system  $\text{C}:\text{C}:\text{C}:\text{O}$ . The results described in the present paper show that the compounds produced by the action of both aromatic and aliphatic magnesium compounds on methyl cinnamylidenemalonate are formed by 1 : 4-addition.

*Methyl  $\beta$ -phenyl- $\gamma$ -benzylidene-ethylmalonate,*  
 $\text{CHPh}:\text{CH} \cdot \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Me})_2$ ,

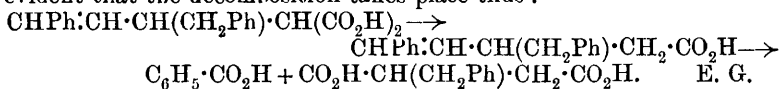
m. p. 94°, obtained by the action of magnesium phenyl bromide on methyl cinnamylidenemalonate, crystallises in white prisms.  *$\beta$ -Phenyl- $\gamma$ -benzylidene-ethylmalonic acid*, m. p. 166° (decomp.), separates from hot water in slender, white needles. On heating this acid at 175°, it is converted into  *$\beta$ -phenyl- $\gamma$ -benzylidenemalonic acid*,

$\text{CHPh}:\text{CH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ,

m. p. 118°, which forms long, slender needles.

By the action of magnesium methyl iodide on the ester, *methyl  $\gamma$ -benzylidene- $\beta$ -methylethylmalonate*, b. p.  $210^{\circ}/30$  mm., is produced. The acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{H})_2$ , m. p.  $120-121^{\circ}$ , crystallises in small, white needles, and, when heated at  $160^{\circ}$ , is converted into  *$\gamma$ -benzylidene- $\beta$ -methylbutyric acid*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $51-52^{\circ}$ , which forms hard needles.

Magnesium benzyl chloride reacts with the ester with formation of an acid, probably  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CH}(\text{CO}_2\text{H})_2$ , which crystallises in white needles. On heating this acid at  $180^{\circ}$  and oxidising the product, benzoic and benzylsuccinic acids are obtained, whence it is evident that the decomposition takes place thus :



**Action of Methylamine on Salicylic Acid and Methyl *o*-Ethoxybenzoate.** FRANCESCO NICOLA (*Chem. Zentr.*, 1907, ii, 49—50; from *Giorn. Farm. Chim.*, 1907, 56, 193—197).—A 33% solution of methylamine acts on methyl salicylate in the same way as ammonia, but only yields salicylmethylamide after heating at  $100^{\circ}$  for four hours. Methyl *o*-ethoxybenzoate is hydrolysed forming *o*-ethoxybenzoic acid. *Salicylmethylamide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHMe}$ , m. p.  $91^{\circ}$ , forms white leaflets and is very readily soluble in alcohol or ether, rather soluble in boiling water, but very sparingly so in cold water. When ferric chloride is added to the aqueous solution, a violet coloration is formed, and by the action of potassium hydroxide, methylamine and potassium salicylate are obtained. E. W. W.

**Observations on Aldehydes.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 199—204).—The author has examined certain aldehydes to ascertain whether they are in accord with the classification of aldehydes into : (I.) true aldehydes, which give all the reactions of aldehydes, including those of Angeli and Marchetti (this vol., i, 551), and Doebner (Abstr., 1894, i, 261, 532), and are comparable with true nitroso-derivatives. (II.) Aldehydes, which are not sugars, which give all the reactions of aldehydes with the exception of that of Angeli and Marchetti, and are analogous to isonitroso-derivatives and are hence termed isomaldehydes. (III.) The aldoses, which give neither Angeli and Marchetti's reaction nor that of Doebner and are called pseudo-aldehydes.

Pyrrole-2-aldehyde, when heated with pyruvic acid and  $\beta$ -naphthylamine in absolute alcoholic solution, yields 2-pyrryl-2-naphthacinchonic acid,  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_2$ , which is a yellow substance, m. p.  $300^{\circ}$  (decomp.).

Similarly, *o*-nitrobenzaldehyde yields 2-*o*-nitrophenylnaphthacinchonic acid,  $\text{C}_{20}\text{H}_{12}\text{O}_4\text{N}_2$ , which crystallises from alcohol in microscopic needles, m. p.  $265^{\circ}$  (decomp.), and glycollaldehyde gives 2-methoxy-naphthacinchonic acid,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$ , which separates from alcohol in crystals, m. p.  $255^{\circ}$ .

Glycollaldehyde also gives Angeli and Marchetti's reaction.

T. H. P.

**Spontaneous Oxidation in Presence of Hydramides.** MARIO BETTI (*Gazzetta*, 1907, 37, ii, 91—99).—The oxidation of 1-phenyl-3-methyl-5-pyrazolone in alcoholic ammonia solution to rubazonic acid (*Abstr.*, 1906, i, 985) takes place when the benzaldehyde is replaced by another aromatic aldehyde. With salicylaldehyde, the rubazonic acid is accompanied by 4-salicylidene-bis-1-phenyl-3-methyl-5-pyrazolone; with anisaldehyde, by 4-anisylidene-bis-1-phenyl-3-methyl-5-pyrazolone, and so on; the hydramide derivatives formed by these aldehydes with ammonia accelerate the oxidation more than the aldehydes themselves. The oxidation also occurs in presence of formaldehyde, but not with other aliphatic aldehydes or acetone; formaldehyde has a strong tendency to react with ammonia, yielding hexamethylenetetramine, a compound which, in some ways, is analogous to the aromatic hydramides.

The conclusion is drawn that the oxidation is not effected by those aldehydes having the characteristic property of giving, with ammonia, additive products of the type  $R\cdot CH(OH)\cdot NH_2$ , in the formation of which no oxygen becomes detached. On the other hand, aldehydes which react with ammonia, forming compounds of the type  $R\cdot CH:NX$ , and liberating oxygen in the form of water, act energetically in bringing about the oxidation. The action may, indeed, be a catalytic one, depending on this detachment of oxygen from the aldehyde molecule.

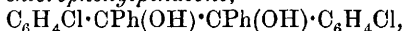
In anhydrous solutions, the reaction proceeds very slowly at first, but rapidly after an hour or so. The presence of a small quantity of water hence appears to exert an influence on the reaction. The oxidation is, however, not affected by the bis-pyrazolone compounds formed with the rubazonic acid. T. H. P.

**Intramolecular Atomic Transpositions. VII. Influence of Substituents of the Phenyl Group on the Transformation of Benzopinacones into Benzopinacolins.** P. J. MONTAGNE (*Rec. trav. chim.*, 1907, 26, 253—272. Compare this vol., i, 140, 141).—When treated with acetyl chloride, benzopinacone and its derivatives are converted into benzopinacolins, the transformation being accompanied by the migration of a phenyl group. When, however, not only phenyl groups but also substituted phenyl groups are attached to the  $:C(OH)\cdot C(OH):$  residue, migration of either of these two kinds of groups may occur. The author proposes to examine this migration for pinacones containing differently substituted phenyl radicles, so as to ascertain, in each case, whether these radicles migrate more easily or more difficultly than phenyl itself. Thörner and Zincke (*Abstr.*, 1878, i, 223) have shown that, when heated with acetyl chloride, *s*-diphenyldi-*p*-tolylpinacone is converted into  $\beta$ -di-*p*-tolyldiphenylpinacolin, and Acree (*Abstr.*, 1905, i, 216) states that this transformation is quantitative. *p*-Tolyl hence migrates more readily than phenyl. In the case of *s*-diphenyldi-*p*-chlorophenylpinacone, the author finds that both the phenyl and *p*-chlorophenyl radicles migrate, but the former (60%) to a greater extent than the latter (40%). The influence of the chlorine atom on the migration of phenyl is hence opposed to, and weaker than, that exerted by the methyl group. This result is not in



accord with the general law laid down by Tiffeneau (Abstr., 1902, i, 666) to the effect that the tendency of the phenyl group to migrate according to the scheme  $\cdot\text{CPh}:\text{CH}_2 \rightarrow \text{R}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$  is greatly enhanced when the phenylic hydrogen is replaced by substituents which increase its molecular magnitude and hence also its ability to migrate.

*s*-Diphenyl-di *p*-chlorophenylpinacone,



prepared by reducing *p*-chlorobenzophenone either by the action of sunlight on its alcoholic solution or by means of zinc dust and acetic acid, separates from alcohol in white crystals, m. p.  $168^\circ$  (decomp.).

*p*-Chlorobenzhydrol,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHPh}\cdot\text{OH}$ , prepared by reducing *p*-chlorobenzophenone either by zinc dust and acetic acid or by sodium amalgam and alcohol, crystallises from light petroleum in long needles, m. p.  $62^\circ$ , and has the normal molecular weight in boiling benzene.

4-Chlorodiphenylmethane,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\text{Cl}$ , prepared by reducing *p*-chlorobenzophenone by means of phosphorus and hydriodic acid in acetic acid solution, has b. p.  $298^\circ/742\cdot5$  mm., and has the normal molecular weight in boiling benzene.

T. H. P.

**Intramolecular Atomic Transpositions. VIII. Preparation of 2:4:6-Trichlorobenzophenone and of Phenyl  $\alpha$ - and  $\beta$ -Naphthyl Ketones.** P. J. MONTAGNE (*Rec. trav. chim.*, 1907, 26, 273—284).—2:4:6-Trichlorobenzophenone,  $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{COPh}$ , prepared by the interaction of benzoyl chloride and 1:3:5-trichlorobenzene in presence of aluminium chloride, separates from light petroleum in shining, prismatic crystals belonging to the triclinic system [F. M. JAEGER,  $a:b:c=1\cdot3908:1\cdot1\cdot1537$ ;  $\alpha=129^\circ56\frac{3}{4}'$ ,  $\beta=123^\circ21\frac{2}{3}'$ ,  $\gamma=60^\circ26'$ , m. p.  $103\cdot5^\circ$ , b. p.  $356^\circ/763$  mm.

2:4:6-Trichlorobenzamide, already prepared (Abstr., 1903, i, 169), separates from a mixture of absolute alcohol, light petroleum, and benzene in shining, rhombic crystals [F. M. JAEGER,  $a:b:c=0\cdot5380:1\cdot1\cdot15180$ ].

The interaction of benzoyl chloride and naphthalene in carbon disulphide solution in presence of aluminium chloride yields a mixture of phenyl  $\alpha$ -naphthyl ketone (78·5%), m. p.  $75\cdot5^\circ$ , b. p.  $386^\circ/764$  mm. or  $225^\circ/12$  mm., and phenyl  $\beta$ -naphthyl ketone (14%), m. p.  $82^\circ$ , b. p.  $398^\circ/754$  mm., which were separated by crystallising from alcohol, the  $\alpha$ -derivative being deposited first.

T. H. P.

**2:4:2':4'-Tetramethylbenzophenone.** JACOB BÖESEKEN (*Rec. trav. chim.*, 1907, 26, 285—288).—The tetramethylbenzophenone, obtained by the interaction of *m*-xylene and an excess of carbon tetrachloride in presence of aluminium chloride (Abstr., 1905, i, 423), does not yield an oxime or a hydrazone. It is, however, found to be identical with the ketone obtained by distillation of calcium 2:4-dimethylbenzoate, and is hence 2:4:2':4'-tetramethylbenzophenone,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Me}_2$ . The constants for the compound are: (1) prepared from *m*-xylene and carbon tetrachloride, b. p.  $185^\circ/5$  mm.,  $D^{12}_4$  1·0506,  $D^{15}_4$  1·0477,  $n^{20}_D$  1·5876; (2) prepared from calcium 2:4-dimethylbenzoate, b. p.  $188^\circ/7$  mm.,  $D^{15}_4$  1·043,  $n^{15}_D$  1·5869.

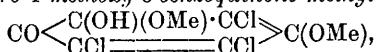
When the ketone is boiled with zinc in a faintly alkaline alcoholic solution, no reduction takes place, only 2:4-dimethylbenzoic acid being formed. T. H. P.

**Some Derivatives of Tetrachloro-*o*-benzoquinone.** C. LORING JACKSON and ROBERT D. MACLAURIN (*Amer. Chem. J.*, 1907, **38**, 127—175. Compare Abstr., 1906, i, 97).—Jackson and Porter (Abstr., 1903, i, 266; 1904, i, 254) have shown that by the action of methyl alcohol on tetrabromo-*o*-benzoquinone, two substances are formed, namely, the compound  $4\text{C}_6\text{O}_2\text{Br}_4\cdot\text{MeOH}$  and the  $\alpha$ -compound (octabromo-1'-hydroxy-1-methoxy-*o*-benzoquinone-1-monoxide). By the action of various reagents on the  $\alpha$ -compound, the isomeric  $\beta$ -compound (octabromo-1'-hydroxy-1-methoxy-*o*-benzoquinone-1:2:2-trioxide) is produced. Further work on these substances has been carried out by Jackson and Carlton (Abstr., 1905, i, 907), Jackson and Russe (Abstr., 1906, i, 288), and by Jackson and MacLaurin (this vol., i, 223).

The action of methyl alcohol on tetrachloro-*o*-benzoquinone has now been studied and the following six products have been isolated. The  $\beta$ -compound (octachloro-1'-hydroxy-1-methoxy-*o*-benzoquinone-1:2:2-trioxide),  $3:5:6$ -trichloro-4-methoxy-*o*-benzoquinone methylhemiacetal,  $3:5:6$ -trichloro-2-hydroxy-*p*-benzoquinone, chloroanilic acid, hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether, and hexachloro-*o*-benzoquinodimethylhemiacetalcatechol ether. The difference in the products obtained from the tetrabromo- and tetrachloro-*o*-quinones is chiefly ascribed to the fact that in the former compound the action is confined to the oxygen atoms, whilst in the latter compound the chlorine also takes part in the reaction.

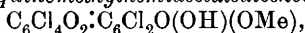
The  $\beta$ -compound (octachloro-1'-hydroxy-1-methoxy-*o*-benzoquinone-1:2:2-trioxide),  $\text{OMe}\cdot\text{C}_6\text{Cl}_4:\text{O}_3:\text{C}_6\text{Cl}_4\cdot\text{OH}$ , m. p.  $157^\circ$ , forms rhombic plates, and has a structure corresponding with that of the  $\beta$ -compound obtained from tetrabromo-*o*-quinone (this vol., i, 223).

*3:5:6-Trichloro-4-methoxy-*o*-benzoquinone methylhemiacetal,*



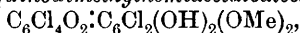
m. p.  $138$ — $140^\circ$ , crystallises in thick, white, rhombic plates; its *acetyl* derivative has m. p.  $149$ — $150^\circ$ , and its *phenylhydrazone*, m. p.  $235^\circ$ . By the action of concentrated hydrochloric acid on this compound, it is converted into  $3:5:6$ -trichloro-2-hydroxy-*p*-benzoquinone (Zincke and Schaum, Abstr., 1894, i, 233).

*Hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether,*



m. p.  $198^\circ$ , crystallises in yellow needles and yields an *acetyl* derivative, m. p.  $215^\circ$ . The *diacetyl* derivative of hexachlorodihydroxycatechol ether, m. p.  $290^\circ$ , forms white, lustrous leaflets.

*Hexachloro-*o*-benzoquinodimethylhemiacetalcatechol ether,*



m. p.  $218^\circ$ , crystallises in white plates, and when gently heated with strong sulphuric acid is converted into hexachloro-*o*-benzoquinocatechol ether, whilst on reduction or by the action of hydrochloric acid it is converted into hexachlorodihydroxycatechol ether.

The remarkable observation was made during the course of these

experiments that when 3:5:6-trichloro-2-hydroxy-*p*-benzoquinone is left with methyl alcohol and hydrochloric acid, hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether is produced, a *p*-quinone thus being converted into a derivative of an *o*-quinone.

By the action of ethyl alcohol on tetrachloro-*o*-benzoquinone, four compounds are formed, namely, 3:5:6-trichloro-2-hydroxy-*p*-benzoquinone, chloroanilic acid, a *compound*, m. p. 115°, and, as principal product, a *compound*,  $C_{28}H_{12}O_{10}Cl_{12}$ , m. p. 210°, which forms yellow, rhombic plates and probably consists of hexachloro-*o*-benzoquinocatechol ether (2 mols.) combined with ethyl alcohol (2 mols.).

*n*-Propyl and *iso*amyl alcohols react with tetrachloro-*o*-benzoquinone with formation of 3:5:6-trichloro-2-hydroxy-*p*-benzoquinone and chloroanilic acid. *iso*Propyl alcohol yields only chloroanilic acid, whilst *tert*.-butyl alcohol furnishes a product, m. p. 250°, which may be the *β*-*compound*, octachloro-1-*tert*.-butyloxy-1'-hydroxy-*o*-benzoquino-1:2:2-trioxide. Benzyl alcohol gives a yellow *substance*, m. p. 215°.

When tetrachloro-*o*-benzoquinone is treated with ordinary undried toluene, the following four products are obtained. Tetrachloro-*o*-benzoquinone with 1 mol. toluene of crystallisation; the *α*-water *compound*,  $OH \cdot C_6Cl_4 \cdot O_2 \cdot C_6Cl_4 \cdot OH$ , m. p. 172°, which crystallises in needles; a small quantity of a brown *compound*, m. p. 182—183°; and a *substance*,  $C_{24}H_8O_8Cl_{13}$ , m. p. 290°, which is probably composed of the hexachloro-*o*-benzoquinocatechol ether (1 mol.) with heptachloro-*o*-benzoquinocatechol hemiether (1 mol.), but the way in which these ethers are united in the substance has not yet been ascertained.

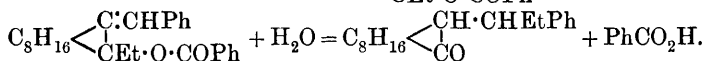
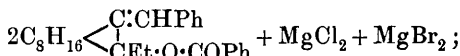
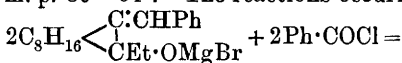
By the action of glacial acetic acid on tetrachloro-*o*-benzoquinone, the *α*-*compound*, octachloro-1-acetoxy-1'-hydroxy-*o*-benzoquino-1-monoxide,  $OAc \cdot C_6Cl_4 \cdot O_3 \cdot C_6Cl_4 \cdot OH$ , m. p. 250—252°, is produced, which crystallises in white needles.

When tetrachloro-*o*-benzoquinone is warmed with water for a few minutes, it is converted into hexachloro-*o*-benzoquinocatechol ether. If this ether is treated with methyl alcohol, it yields hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether, whilst if a little water is added to the methyl alcohol, hexachloro-*o*-benzoquinodimethylhemiacetalcatechol ether and chloroanilic acid are produced. Ethyl alcohol reacts with the ether with formation of chloroanilic acid and a *compound*, m. p. 210°, identical with that obtained by the action of ethyl alcohol on tetrachloro-*o*-benzoquinone. *n*-Propyl alcohol yields a *compound*, m. p. 210°. Phenylhydrazine reduces the ether to hexachlorodihydroxycatechol ether.

E. G.

**Derivatives of Menthone.** EYVIND BÖDTKER (*Compt. rend.*, 1907, 145, 329—331).—Organo-magnesium compounds do not act on ethylmenthone (compare Haller and Bauer, *Abstr.*, 1906, i, 440, 441). When an ethereal solution of benzylidenementhone is added to a solution of magnesium ethyl bromide, *phenylmenthyl ethyl methane*,  $C_8H_{16} \begin{matrix} \diagup CH \cdot CHPhEt \\ | \\ CO \end{matrix}$ , which forms white needles, m. p. 102·5—103·5°,  $[\alpha]_D - 79^\circ 34'$ , in benzene solution, and a *substance* crystallising in fine needles in quantity insufficient for analysis, m. p. 83—84°, are formed. If before treating with water, benzoyl chloride (1 mol.) is added to the

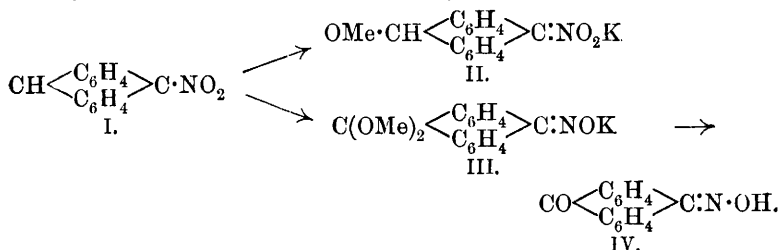
reaction-product a further reaction occurs and the viscous substance obtained, after saponification with alcoholic potash, gives white needles, m. p. 102·5—103·5°, identical with the above, and a stereoisomeride, m. p. 89—91°. The reactions occurring in the latter case are probably



If bromobenzene is used instead of ethyl bromide, the product consists of *diphenylmenthylmethane*,  $\text{C}_8\text{H}_{16} \begin{array}{c} \text{CH}\cdot\text{CHPh}_2 \\ \diagup \quad \diagdown \\ \text{C}=\text{O} \end{array}$ , slender needles,

m. p. 139—140°, feebly dextrorotatory in benzene solution. By means of the benzoyl chloride reaction, two stereoisomerides are obtained, one having m. p. 160·5—161·5°,  $[\alpha]_D -158^\circ 30'$ , the other m. p. 136—137°, and inactive. A mixture of the latter with the substance, m. p. 139—140°, has m. p. 130°, whilst alcoholic potash transforms the substance, m. p. 139—140°, into its isomeride, m. p. 136—137°. E. H.

**Reactions of Unsaturated Nitro-compounds.** JAKOB MEISENHEIMER (*Annalen*, 1907, 355, 249—311).—The transformation of 9-nitroanthracene into the isomeric anthraquinoneoxime has already been interpreted by the author (*Abstr.*, 1902, i, 795), thus :

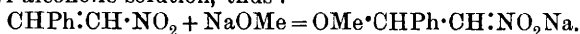


(I) is converted into (II) by 5% cold methyl-alcoholic potassium hydroxide and into (III) by 10% boiling methyl-alcoholic potassium hydroxide; (II) is converted into (III) by 10% boiling methyl-alcoholic potassium hydroxide, and (III) into (IV) by dilute mineral acids. The mechanism of those changes was clear, with the exception of the change of (II) into (III) and, with the object of elucidating this particular phase, the work recorded in the present paper was undertaken. Evidence is submitted for the formation of nitrosomethoxyanthracene,  $\text{OMe}\cdot\text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}\cdot\text{NO}$ , as intermediate between (II) and (III).

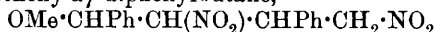
A large number of nitro-compounds has been investigated from the same standpoints.

[With FRIEDRICH HEIM.]—The action of alkalis on phenylnitroethylene has already been studied by Meisenheimer and Heim (*Abstr.*,

1905, i, 269). Phenylnitroethylene interacts with sodium methoxide in methyl-alcoholic solution, thus :

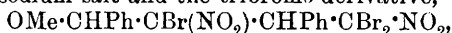


The resulting solution quickly changes with production of resins. With dilute methoxide at the ordinary temperature, from 20—30% of  $\beta\delta$ -dinitro- $\alpha$ -methoxy- $\alpha\gamma$ -diphenylbutane,



(*loc. cit.*), was isolated together with appreciable amounts of the corresponding benzoic ester, the bulk of the nitroethylene resinifying. Accordingly, 2 mols. of nitroethylene react with 1 mol. of alcohol, and the acetaloxime anticipated was not formed.

The molecular weight of  $\beta\delta$ -dinitro- $\alpha$ -methoxy- $\alpha\gamma$ -diphenylbutane was determined in ethylene dibromide solution. Further details regarding the sodium salt and the tribromo-derivative,

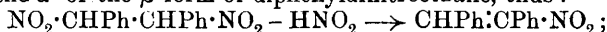


are given. The *dibromo*-derivative,  $\text{C}_{17}\text{H}_{16}\text{O}_5\text{N}_2\text{Br}_2$ , obtained as a by-product in the preparation of the tribromo-derivative, separates from acetone in prisms, m. p.  $186^\circ$  (decomp.). Another *bromide*,  $\text{C}_9\text{H}_9\text{O}_3\text{NBr}_2$ , obtained by the action of bromine (4 atoms) on the sodium salt, crystallises from methyl alcohol in glistening leaflets, m. p.  $156^\circ$ .

The behaviour of  $\beta\delta$ -dinitro- $\alpha$ -methoxy- $\alpha\gamma$ -diphenylbutane towards concentrated methyl-alcoholic potassium hydroxide was studied. The acetaloxime anticipated was, however, not obtained, disruption taking place with the formation of benzoic acid and a brown resin. It is supposed that the acetaloxime is not stable under the conditions employed.

Phenylnitroethylene is converted by exposure to light into a compound, which is not *isophenyl*nitroethylene, as Priebis supposes, but is the *polymeride*,  $(\text{C}_8\text{H}_7\text{O}_2\text{N})_2$ ; it dissolves in alkalis, but is reprecipitated by acids.

Better results were obtained by the authors with  $\alpha$ -nitrostilbene. This compound may be prepared according to Knoevenagel and Walter (*Abstr.*, 1905, i, 65) by the condensation of phenylnitromethane with benzaldehyde by aid of aliphatic bases or by the action of alkali on either the  $\alpha$ - or the  $\beta$ -form of diphenyldinitroethane, thus :



the same compound is formed, no matter whether the  $\alpha$ - or  $\beta$ -form referred to is used, although two  $\alpha$ -nitrostilbenes are theoretically possible.

$\alpha$ -Nitrostilbene readily acts on sodium methoxide to form  $\beta$ -nitro- $\alpha$ -methoxy- $\alpha\beta$ -diphenylethane, which, by the action of concentrated methyl-alcoholic potassium hydroxide, gives the anticipated acetal.

The stilbene, necessary for the preparation of the diphenyldinitroethanes, was prepared from benzyl chloride by means of Grignard's reaction, but the method, although the best of those attempted, does not give a satisfactory yield.  $\beta$ -Nitro- $\alpha$ -methoxy- $\alpha\beta$ -diphenylethane( $\alpha$ ),  $\text{OMe}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NO}_2$ , obtained by the addition of sodium methoxide to ( $\alpha$ )-diphenyldinitroethane dissolved in methyl alcohol, separates from methyl alcohol in colourless needles, m. p.  $130$ — $131^\circ$ . It is not changed when boiled for half an hour with 28% methyl-alcoholic

potassium hydroxide. The corresponding  $\beta$ -nitro- $\alpha$ -methoxy- $\alpha\beta$ -diphenylethane( $\beta$ ) crystallises in prisms, m. p. 97—98°; when carbon dioxide is passed into its alkaline solution, the  $\alpha$ -form is precipitated.

7-Nitrostilbene is readily obtained from either form.  $\beta$ -Nitro- $\alpha$ -ethoxy- $\alpha\beta$ -diphenylethane,  $C_{16}H_{17}O_3N$ , obtained from  $\alpha$ -nitrostilbene and ethyl-alcoholic potassium hydroxide, forms colourless needles, m. p. 92°.

syn.-Benzilmonoximedimethylacetal, 
$$\begin{array}{c} \text{CPh}(\text{OMe})_2 \cdot \text{C} \cdot \text{CPh} \\ | \qquad \qquad | \\ \text{OH} \cdot \text{N} \end{array}$$
, obtained by

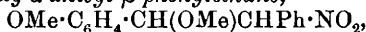
the action of 28% methyl-alcoholic potassium hydroxide on nitromethoxydiphenylethane at 150°, forms silky needles, m. p. 208° (decomp.). Its benzyl ether,  $C_{23}H_{25}O_3N$ , crystallises from methyl alcohol in colourless prisms, m. p. 71—72°, and is converted by concentrated hydrochloric acid into  $\alpha$ -benzilmonoxime benzyl ether, m. p. 94—95°. syn.-Benziloximedimethylacetal was also defined by its direct conversion into  $\beta$ -benzilmonoxime by means of concentrated hydrochloric acid.

[With LEO JOCHELSON.]—The behaviour of  $\alpha$ -nitro-4'-methoxy-stilbene towards alkali is similar to that of  $\alpha$ -nitrostilbene itself. In methyl-alcoholic solution, it combines with alkali methoxides very readily with the formation of  $\beta$ -nitro- $\alpha$ -methoxy- $\alpha$ -anisyl- $\beta$ -phenylethane. The latter compound is very stable towards alkali in methyl-alcoholic solution, but at 160—170° is converted into 4'-methoxybenzilmonoxime- $\beta\beta$ -dimethylacetal, which is saponified by cold concentrated hydrochloric acid with the formation of 4'-methoxybenzilmonoxime. The following phases may thus be realised:

$$\begin{array}{l} \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CPh} \cdot \text{NO}_2 \longrightarrow \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OMe}) \cdot \text{CPh} \cdot \text{NO}_2\text{K} \longrightarrow \\ \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe})_2 \cdot \text{CPh} \cdot \text{N} \cdot \text{OH} \longrightarrow \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CPh} \cdot \text{N} \cdot \text{OH}. \end{array}$$
These reactions proceed quantitatively with the exception of the formation of the acetaloxime.

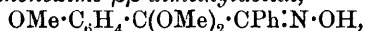
$\alpha$ -Nitro-4'-methoxystilbene was prepared by the condensation of phenylnitromethane with anisaldehyde.

$\beta$ -Nitro- $\alpha$ -methoxy- $\alpha$ -anisyl- $\beta$ -phenylethane,



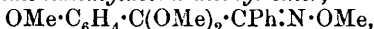
crystallises from methyl alcohol in silky needles, m. p. 139°.

4'-Methoxybenzilmonoxime- $\beta\beta$ -dimethylacetal,



separates from methyl alcohol in colourless needles, m. p. 206—208° (decomp.). Its solution in concentrated sulphuric acid is blood-red, and when poured into water it yields anisic acid. As by-products in its preparation, anisic acid, benzoic acid, benzaldehyde, and benzaldoxime (in an impure state) were isolated.

Methoxybenziloximedimethylacetal methyl ether,

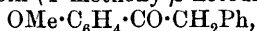


obtained by the action of methyl iodide on a solution of the acetaloxime in a mixture of methyl alcohol and concentrated methyl-alcoholic potassium hydroxide, crystallises from methyl alcohol in colourless needles, m. p. 82—83°.

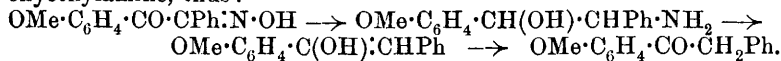
4'-Methoxybenziloxime,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CPh} \cdot \text{N} \cdot \text{OH}$ , crystallises from

methyl alcohol in colourless, prismatic needles, m. p. 130—131°. Its solution in concentrated alkali is yellow. Its *methyl ether* separates from methyl alcohol in colourless crystals, m. p. 93—94°; sometimes a *stereoisomeride* is formed, which crystallises from methyl alcohol in glistening, silvery needles, m. p. 79·5°, and is the less stable of the two forms; it is not decided which modification is *syn*- and which *anti*-.

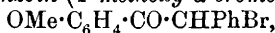
*p*-Methoxydeoxybenzoin (4'-methoxy- $\beta$ -ketodibenzyl),



obtained by the reduction of 4'-methoxybenziloxime, or of the acetaldoxime with zinc dust and acetic acid, crystallises from methyl alcohol in colourless, stellate needles, m. p. 77—78°. The formation from the benziloxime is probably accompanied by the transient existence of an oxyethylamine, thus:



When acted on by bromine, the preceding deoxybenzoin forms *p* methoxybromodeoxybenzoin (4'-methoxy- $\alpha$ -bromo- $\beta$ -ketodibenzyl),



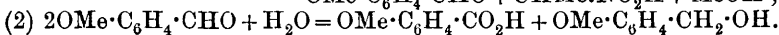
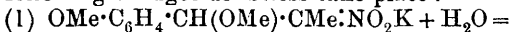
which crystallises from methyl alcohol in colourless needles, m. p. 73—74°, and, by treatment with sodium carbonate, yields *p*-methoxybenzoin, m. p. 108°.

The next section of the work deals with the behaviour of derivatives of  $\beta$ -nitroanethole, which readily acts on alkali methoxide; by the action of carbon dioxide, 1-anisyl-2-nitropropane-1-oxymethane is formed.

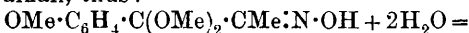
$\beta$ -Nitroanethole was prepared by the action of alcoholic ammonia on anethole*pseudonitrosite*.

$\beta$ -Nitro- $\alpha$ -methoxy- $\alpha$ -anisylpropane,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OMe}) \cdot \text{CHMe} \cdot \text{NO}_2$ , is a yellow liquid, b. p. 172—174·5°/12—14 mm. When acted on by bromine water, it forms  $\beta$ -bromo- $\beta$ -nitro- $\alpha$ -methoxy- $\alpha$ -anisylpropane,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OMe}) \cdot \text{CBrMe} \cdot \text{NO}_2$ , which crystallises from petroleum in silvery needles, m. p. 76°.

$\beta$ -Nitro- $\alpha$ -methoxy- $\alpha$ -anisylpropane is very stable towards alkali, differing in this respect from the behaviour of the methyl alcohol additive product derived from phenylnitroethylene and resembling the corresponding products from the nitrostilbenes described. After boiling for ten hours with very concentrated methyl-alcoholic potassium hydroxide, it is partly unchanged; the bulk is resinified, whilst from 10% to 20% yields anisic acid, anisaldehyde, and anisyl alcohol. The following changes doubtless take place:



It is probable that an acetaldoxime is produced as an intermediate product which undergoes decomposition in the presence of the strong alkali, thus:

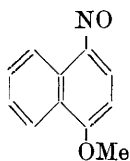


The author next gives the experimental details accumulated by himself with 1-nitronaphthalene and 9-nitrophenanthrene respectively. 1-Nitronaphthalene is very sensitive towards hot alcoholic alkali;

when boiled with alkali, it is converted into a black mass, which could not be crystallised, but small amounts of products which were soluble in alkali were obtained. At 22—24°, the action is slower, but it was not possible to detect in the filtrate the nitro-dihydronaphthol methyl ether which might be anticipated to result from the action of potassium methoxide. The filtrate contained 4-nitroso-1-naphthol methyl ether,  $C_{11}H_9O_2N$ , which crystallises from methyl alcohol in yellowish-green needles, m. p. 64—65°. When water is added to the green methyl-alcoholic solution of the preceding compound, a green oil is precipitated which, on the addition of a trace of dilute hydrochloric acid, is converted into naphthaquinoneoxime, the potassium salt of which was analysed. 1:4-Naphthaquinoneoxime methyl ether,  $C_{11}H_9O_2N$ , obtained by the addition of methyl-alcoholic potassium hydroxide to a methyl-alcoholic solution of naphthaquinoneoxime, and subsequent addition of methyl iodide to the resulting potassium salt, separates from methyl alcohol in bright yellow needles, m. p. 80—82°.

When alkali is added to the green solution of 4-nitroso-1-naphthol methyl ether in methyl alcohol, a change of tint to yellow occurs, and this solution contains without doubt the potassium salt of 1:4-naphthaquinoneoxime dimethylacetal, although the salt could not be isolated.

The colour of these compounds is of interest. The nitrosonaphthol ether is green in accordance with the annexed structure. The naphthaquinoneoxime, on the other hand, is faintly yellow and almost colourless, a fact which is not in accordance with a quinonoid structure, especially when one considers that the corresponding quinone is intensely yellow. The potassium salt, obtained from the naphthaquinoneoxime, is, however, dark yellowish-brown, and its solutions are reddish-brown.



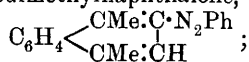
The author is inclined to assign a quinonoid structure to the potassium salt, and a non-quinonoid structure to the free oxime.

9-Nitrophenanthrene is attacked by methyl-alcoholic potassium hydroxide with comparative difficulty; there is no action in the cold, but, on heating, action takes place, although the primary product, nitro-dihydrophenanthrol methyl ether, could not be isolated. When the product, obtained by boiling for  $\frac{1}{2}$  hour, is poured into an excess of water, a slight precipitate, probably consisting of azo- and azoxy-phenanthrene, is formed. When the aqueous solution is extracted with ether, phenanthrenequinoneoxime dimethylacetal,  $C_{16}H_{15}O_3N$ , is obtained as colourless prisms, m. p. 166—167° (decomp.). The alkaline mother liquors, from which the preceding compound had been isolated, gave an appreciable amount of phenanthraquinoneoxime, m. p. 158°. A. McK.

1:4-Dimethyl-2-naphthaquinol. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 205—214).—By the action of nitrous acid on 1:4-dimethyl-2-naphthol in ethereal solution, the author obtains the dimethylnaphthaquinonitrole,  $C_6H_4$   $\begin{matrix} \text{OMe(NO}_2) \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CMe} = \text{CH} \end{matrix}$  (compare Zincke, Abstr., 1903, i, 756), which is converted by the action of ether and



acetic acid into the dimethylnaphtha- $\psi$ -quinol<sup>1</sup> (compare Bamberger, Abstr., 1901, i, 141),  $C_6H_4 \begin{smallmatrix} \text{CMe(OH)CO} \\ \text{CMe} \text{---} \text{CH} \end{smallmatrix}$ . This latter compound is found to be identical with the compound, m. p. 104—105°, prepared by Cannizzaro and Carnelutti (Abstr., 1883, 77; compare also Cannizzaro and Andreocci, Abstr., 1896, i, 488), and termed by them oxydimethylnaphthol. The compound described as the phenylhydrazone of the latter (Cannizzaro and Andreocci, *loc. cit.*) must, in the light of Bamberger's researches (Abstr., 1902, i, 509), be regarded as benzeneazodimethylnaphthalene,



with this formula, Cannizzaro and Andreocci's analytical results are in better accord than with that of the phenylhydrazone.

*Dimethylnaphthaquinonitrole*,  $C_{12}H_{11}O_3N$ , separates from ether as an oil which subsequently changes to yellow crystals, m. p. 99—100°.

*Dimethylnaphthylazocarbonamide*,  $C_6H_4 \begin{smallmatrix} \text{CMe:C} \cdot N_2 \cdot CO \cdot NH_2 \\ \text{CMe:CH} \end{smallmatrix}$  (compare Bamberger, *loc. cit.*), prepared by the action of semicarbazide on dimethylnaphtha- $\psi$ -quinol, is deposited from aqueous alcohol as a pale orange-yellow, crystalline powder, m. p. 167—168° (decomp.), dissolves in hydrochloric acid giving a green coloration, and in concentrated sulphuric acid forming a green solution which changes to red, and is readily soluble in ether, acetic acid, or chloroform.

T. H. P.

*d*-Phellandrene in the Oil of *Abies Siberica*. IWAN SCHINDELMEISER (*Chem. Zeit.*, 1907, 31, 759—760. Compare Abstr., 1903, i, 267; Bertram and Walbaum, Abstr., 1893, i, 659).—*d*-Phellandrene and dipentene have now been found, in addition to camphene and pinene previously observed, in the oil of *Abies sibirica*. The phellandrene nitrite, obtained from the fraction b. p. 169—172°, had m. p. 106—107°,  $[\alpha]_D - 46.16^\circ$ ,  $D_{20}^{21} 1.478$ , and may have contained *l*-phellandrene nitrite (compare Wallach, Abstr., 1887, 967; Schreiner, Abstr., 1901, i, 600).

G. Y.

**Presence of Amygdonitrile Glucoside [*l*-Mandelonitrile Glucoside] in *Cerasus Padus*.** HENRI HÉRISSEY (*J. Pharm. Chim.*, 1907, [vi], 26, 194—198).—From 1000 grams of young branches of *Cerasus Padus* covered with opening buds, the author has isolated about 0.3 gram of *l*-mandelonitrile glucoside, which was identified by its rotatory power, by its conversion into prulaurasin by means of a small quantity of baryta (compare Caldwell and Courtauld, Trans., 1907, 91, 671), and by hydrolysis with hydrochloric acid which yields *l*-phenylglycolic acid.

T. H. P.

**Production of Prulaurasin by the Action of a Soluble Enzyme on *iso*Amygdalin.** HENRI HÉRISSEY (*J. Pharm. Chim.*, 1907, [vi], 26, 198—201).—When yeast is mixed with 40 times its weight of distilled water and, after five or six hours, separated by

filtration under pressure, washed with water, and dried at 33–34°, it is found to be capable of transforming *isoamygdalin* into *prulaurasin* (compare Caldwell and Courtauld, this vol., ii, 809).

Contrary to the statement of Caldwell and Courtauld (Trans., 1907, 91, 673), *isoamygdalin* is stable and non-hygroscopic and can be dried in the air.

T. H. P.

**Taxicatin, a New Glucoside from *Taxus baccata*.** CHARLES LEFEBVRE (*J. Pharm. Chim.*, 1907, [vi], 26, 241–254. Compare Chevallier and Lassaigue, *ibid.*, 1818, [ii], 4, 558; Lucas, *Arch. Pharm.*, 1856, [ii], 85, 145; Marmé, *Chem. Centr.*, 1876, [iii], 7, 166; Hilger and Brandes, *Abstr.*, 1890, 650; Thorpe, *Trans.*, 1902, 81, 874).—*Taxicatin*,  $C_{13}H_{22}O_7$ , crystallises from alcohol in colourless needles, m. p. 169–170° (corr). Crystals obtained from aqueous solutions contain  $2H_2O$ . In 95% alcoholic solution,  $\alpha_D = -67.25^\circ$ . It is decomposed by emulsin or by 2% sulphuric acid into dextrose and a substance readily soluble in ether and chloroform. When the glucoside is treated with a drop of nitric acid, a blue coloration is produced.

The yield of taxicatin was 35 grams from 70 kilos. of fresh substance. Twigs of *Taxus baccata* were found to contain both invertin and emulsin.

N. H. J. M.

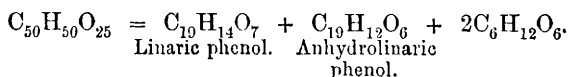
**Presence of Aucubin in Different Species of *Plantago*.** L. BOURDIER (*J. Pharm. Chim.*, 1907, [vi], 26, 254–266).—The glucoside aucubin obtained by Bourquelot and Hérissé (Abstr., 1905, i, 364) from *Aucuba japonica* was found to be present in *Plantago major*, *P. media*, and *P. lanceolata*, and it probably occurs in *P. arenaria*, in *P. cynops*, and in *P. psyllium*. All varieties of *Plantago* were found to contain invertin and emulsin.

N. H. J. M.

**Two New Glucosides, Linarin and Pectolarin.** TIMOTHÉE KLOBB (*Compt. rend.*, 1907, 145, 331–334).—It has already been shown (this vol., ii, 123) that the substance “linarinic acid,” isolated from *Linaria vulgaris*, is a glucoside which has been named linarin. It is now shown that the gelatinous substance, *pectolarin*, discovered by Schlagdenhauffen in the same plant, is also a glucoside, differing in composition from linarin by a molecule of water. Linarin is very difficultly, pectolarin easily, hydrolysed by hydrochloric acid. Both glucosides, on hydrolysis, give a reducing sugar and a mixture of *linarinic* and *anhydrolinaric phenols*. Linarin is laevorotatory; when dissolved in hydrochloric acid to a 1.2% solution, it has  $\alpha = -61.8^\circ$ .

*Pectolarin* is a straw-yellow, amorphous substance, m. p. 188–190° (on Maquenne block), which is transformed into crystallised linarin by prolonged boiling with water. Both linarin and pectolarin, when dissolved in normal alkali, are, in twenty-four hours, transformed into  $\beta$ -modifications.  $\beta$ -Linarin, on hydrolysis with hydrochloric acid, gives *anhydrolinaric phenol* in straw-yellow needles, m. p. 267–268°, which dissolves in sodium hydroxide solution giving a golden-yellow liquid, but no green flakes, and forms an *acetyl* derivative,  $C_{19}H_{19}O_6Ac_3$ .  $\beta$ -Pectolarin, by similar treatment,

gives *linarinic phenol* in lemon-yellow crystals, m. p. 245°. This dissolves in sodium hydroxide to a solution which gives a deep green, flocculent precipitate in contact with air (difference from anhydrolinaric phenol). Assuming that the sugar formed is a hexose, the author suggests, provisionally, that the hydrolysis of  $\alpha$ -linarin should be represented by the equation :



E. H.

**Rhinanthin.** MARCEL MIRANDE (*Compt. rend.*, 1907, 145, 439—442).—The glucoside rhinanthin,  $\text{C}_{58}\text{H}_{52}\text{O}_{40}$ , which is relatively rare in *Rhinanthus*, *Euphrasia*, and *Odontites*, occurs abundantly in the *Orobanches* and *Phelipæa*. A detailed description is given of the microchemical reactions of the glucoside, and also of the parts of *Orobanchehederæ* and *Pedicularis comosa* in which it is found.

In the *Orobanches*, the quantity of rhinanthin diminishes as the seed ripens and as the stem dries. When the stem is dry, it appears no longer to contain the glucoside.

Rhinanthin is interesting as a glucoside, which is localised specially in the wood of certain generally parasitic plants. E. H.

**Chlorophyll. IV. Yellow Substances which accompany Chlorophyll.** RICHARD WILLSTÄTTER and WALTER MIEG (*Annalen*, 1907, 355, 1—28. Compare this vol., i, 784).—An investigation of two yellow pigments, carrotene and xanthophyll, which occur together with chlorophyll in green leaves.

Carrotene, obtained by extracting stinging-nettle leaves with light petroleum, crystallises in copper-coloured leaflets which appear red by transmitted light, and is undoubtedly identical with the carrotene obtained from carrots. The results of analysis and molecular weight determinations show that it has the formula  $\text{C}_{40}\text{H}_{56}$ , and not  $\text{C}_{26}\text{H}_{38}$  as assigned to it by Arnaud (Abstr., 1885, 670 ; 1886, 711 ; 1887, 859). It is probable that erythrophyll (Bongarel, this Journ., 1877, ii, 790) and chrysophyll (Schunck, Abstr., 1889, 279) are identical with carrotene, and that Husemann's caroten (*Annalen*, 1861, 117, 200) is a definite oxidation product of carrotene,  $\text{C}_{40}\text{H}_{56}\text{O}_2$ , isomeric with xanthophyll.

Carrotene absorbs oxygen to the extent of 34.3% of its weight, being converted into a colourless substance (compare Arnaud, Abstr., 1890, 285). It likewise combines with iodine, forming *carrotene iodide*,  $\text{C}_{40}\text{H}_{56}\text{I}_2$ , which crystallises in rosettes of dark violet prisms and sinters and decomposes at 140—170°.

*Xanthophyll*, which accompanies chlorophyll in the alcoholic extract of leaves, is similar to carrotene in appearance, but differs from it in that the crystals appear yellow by transmitted light. Molecular weight determinations and analysis show that it has the formula  $\text{C}_{40}\text{H}_{56}\text{O}_2$ . It combines with methyl and ethyl alcohols, forming the *substances*  $\text{C}_{40}\text{H}_{56}\text{O}_2\cdot\text{CH}_3\text{O}$  and  $\text{C}_{40}\text{H}_{56}\text{O}_2\cdot\text{C}_2\text{H}_5\text{O}$ ; the alcohol is slowly given off in a vacuum. Xanthophyll is an indifferent substance, and

reacts neither as an alcohol, acid, nor ketone. Like carotene, it readily absorbs oxygen to the extent of 36.55% of its weight. From the oxidised material, the compound,  $C_{40}H_{56}O_{18}$ , was isolated in the form of a white, crystalline powder, which swells up at  $100^{\circ}$  and melts slowly at  $140^{\circ}$ .

Xanthophyll readily unites with iodine, forming *xanthophyll iodide*,  $C_{40}H_{56}O_2I_2$ , which crystallises in tufts of thin, dark violet prisms with a metallic lustre.

The authors maintain that it is impossible by the methods of Kraus, Sorby (*Proc. Roy. Soc.*, 1873, 21, 442), and Marchlewski and Schunck (*Trans.*, 1900, 77, 1080) to obtain chlorophyll free from carotene, and they show, further, that Kraus's method is superior to that of Sorby for the separation of xanthophyll from chlorophyll.

W. H. G.

**Studies in the Chlorophyll Group.** T. KÓZNIEWSKI and LEON MARCHLEWSKI (*Annalen*, 1907, 355, 216—234. Compare Willstätter and Hocheder, this vol., i, 784; Tsvett, *ibid.*, 787).—Phylloxanthin, extracted from *Ficus repens* and carefully freed from phyllocyanin, is dissolved in 90% alcohol, and potassium hydroxide added to make a 6% solution. After being heated for thirty minutes, the products are isolated and examined by Willstätter's method (this vol., i, 69). The ethereal solution is extracted with 2%, 5%, 10%, and 25% solutions of hydrochloric acid. The 10% extract has a reddish-brown colour; the ethereal extract of the diluted solution is red and strongly fluorescent, whilst the residual hydrochloric acid solution is dark green and non-fluorescent, and on evaporation leaves a dark green substance which is called *phylloxanthrubin*, the spectrum of which is very similar to that of the original phylloxanthin. From the 25% extract is obtained a neutral substance, called *phylloxantverdin*, the spectrum of which in ethereal solution shows two absorption bands in the red, a faint one in the orange, and a stronger one in the bluish-green.

Alkachlorophyll is converted by alcoholic hydrogen chloride into the so-called phyllotaonin ethers, which yield on hydrolysis a phyllotaonin which should be identical with that obtained by Schunck by the action of alkalis on phyllocyanin. Schunck's results of the spectroscopic examination of his phyllotaonin in ethereal solution, according to which the substance shows five absorption bands which become six after treatment with acid, have been criticised adversely by Marchlewski, who found that crystalline phyllotaonin in ethereal solution yields a six-banded spectrum without treatment by acids. The authors have reinvestigated the subject, working on larger quantities of materials. A mixture of methyl and ethyl phyllotaonin (0.67 gram) is heated for twenty-five minutes with 3% alcoholic sodium hydroxide, and the products of hydrolysis are isolated, dissolved in ether, and extracted with 2%, 4%, 7%, 11%, and 15% hydrochloric acid. The phyllotaonin produced by the hydrolysis is present mainly in the 4% extract, and is obtained in the form of a steel-blue mass (0.55 gram). The spectrum of its ethereal solution, which is olive-green with red fluorescence, contains, before evaporation, five bands

and recalls that of phyllocyanin; by the evaporation of its ethereal solution, phyllotaonin is changed incompletely into another substance called *allophyllotaonin*, the change being complete when phyllotaonin is evaporated repeatedly with chloroform. From the incompletely transformed product, a substance can be obtained the six-banded spectrum of which is identical with that of Schunck's crystalline phyllotaonin.

*alloPhyllotaonin* is a feebly basic substance, dissolves sparingly in ether forming a non-fluorescent solution the spectrum of which is identical with that of crystalline ethylphyllotaonin, from which substance *allophyllotaonin* differs by its solubility in very dilute aqueous sodium hydroxide. When its solution in sodium hydroxide is acidified immediately, the substance is recovered unchanged; if some time elapses before acidifying, a substance is obtained the spectrum of which is identical with that of Schunck's crystalline phyllotaonin; if the alkaline solution is boiled before acidifying, the *allophyllotaonin* is converted into the phyllotaonin obtained as above by the hydrolysis of the phyllotaonin ethers.

These results indicate that Schunck's crystalline phyllotaonin, the spectrum of which shows six bands, is a mixture of *allophyllotaonin* and the authors' phyllotaonin, the spectrum of which has five absorption bands. This deduction is supported by the facts that a mixture of the dilute ethereal solutions of *allophyllotaonin* and phyllotaonin has the same spectrum as Schunck's crystalline phyllotaonin, and that from the latter in ethereal solution 7% hydrochloric acid extracts the authors' phyllotaonin, 11% and 15% hydrochloric acid a mixture of phyllotaonin and *allophyllotaonin*, whilst *allophyllotaonin* alone remains in the residual ethereal solution.

Little can be said concerning the nature of the change of phyllotaonin into *allophyllotaonin*, and vice versa. Acids alone do not cause the former change. The fact that phyllotaonin changes into *allophyllotaonin* after prolonged keeping in a dry atmosphere indicates that the change may be one of anhydride formation.

C. S.

**Chlorophyll.** LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1907, 5, 344—345).—Largely a polemical reply to Tsvett (this vol., i, 787). It is pointed out that  $\beta$ -chlorophyllan cannot be identical with phylloxanthin, as the absorption spectra of the two substances are different.

J. J. S.

**The Dye of Antique Purple from Murex brandaris.** PAUL FRIEDLÄNDER (*Monatsh.*, 1907, 28, 991—996).—A short account is given of the work of various authors on the purple of the ancients. The dyes obtained by Schunck (*Trans.*, 1879, 35, 589; 1880, 37, 613) and Letellier (*Abstr.*, 1889, 1207; 1890, 1452) cannot be the purple of the Romans, as *Purpura lapillus* does not occur in the Mediterranean.

A small amount of a pure purple dye has been obtained now from *Murex brandaris*; it contains nitrogen, but not sulphur, forms dark violet crystals, and in its appearance, the colour of its vapour, and ab-

sorption spectrum resembles indigotin, but is distinguished from this by its more sparing solubility, by giving with cold concentrated sulphuric acid a reddish-violet coloration, becoming brownish-violet when heated, and yielding a reddish-violet precipitate on addition of water. When treated with fuming sulphuric acid, the purple dye yields a blue, soluble *sulphonic acid*, and on reduction in alkaline solution forms a slightly yellow solution from which it separates as a reddish-violet, flocculent precipitate on exposure to air. These properties show that the purple dye, whilst closely resembling indigotin and thioindigotin, is not identical with either (compare Abstr., 1906, i, 378; this vol., i, 334). G. Y.

**Monocarboxylic Acids of Thiophen.** GERARDUS L. VOERMAN (*Rec. trav. chim.*, 1907, 26, 293—310).—The author has made various physico-chemical measurements of thiophen-2- and 3-carboxylic acids, and of the isomeric *a*-acid of Meyer (V. Meyer, "Die Thiophengruppe," Brunswick, 1888), in order to ascertain the relation of the *a*-acid to the 2- and 3-acids.

The melting-point curve for mixtures of the 2- and 3-acids shows that the two acids form two series of homogeneous mixed crystals, with a gap between 25% and 60.5% of the 3-acid. The electrical conductivity of the mixtures was also determined.

[F. M. JAEGER.—Crystals of the 2-acid have only rudimentary ends and cannot be defined morphologically, but those of the 3-acid are monoclinic. The acids form a series of isodimorphous mixtures, with a gap from 22.5% to 61—62% of the 3-acid.]

Meyer's *a*-acid represents one term in the series of mixed crystals, and contains 82—83% of the 2-acid and 17—18% of the 3-acid. Preliminary experiments indicate that it can be separated into its components by crystallisation. T. H. P.

**Crystalline Double Iodide of Bismuth and Strychnine.** EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, 12, 357).—Bismuth and strychnine form a crystalline *double iodide* which is well suited for the microchemical identification of strychnine. The reagent is prepared by adding a large excess of potassium iodide to a very dilute solution of bismuth chloride, containing a small amount of alcohol, and acidifying with hydrochloric acid. If this is added to a solution of a strychnine salt, there is formed a chocolate-brown precipitate, which rapidly becomes crystalline, and glistens when agitated. Under the microscope, the precipitate appears as a matted mass of needles together with isolated, flame-coloured, dichroic, prismatic crystals. G. Y.

**Double Iodide of Bismuth and Cocaine.** EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, 12, 358).—The *double iodide* of bismuth and cocaine is obtained usually as a brick-red, amorphous precipitate, but if precipitated by means of the reagent described in the preceding abstract and heated becomes crystalline after some hours. Under the microscope, the precipitate appears as matted, fiery-red needles, and serves for the microchemical identification of cocaine.

The precipitate dissolves in alcohol forming an orange-yellow solution ; it does not crystallise from this solution on evaporation, but does so after some hours from an aqueous solution in presence of an excess of bismuth.

G. Y.

**Picrolonates of Certain Alkaloids.** WILLIAM H. WARREN and R. S. WEISS (*J. Biol. Chem.*, 1907, 3, 327—338).—The following numbers give the number of grams of picronic acid (4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone) which dissolve in 1 c.c. of the respective solvents : water, 0.0017 ; alcohol, 0.0209 ; ether, 0.005 ; benzene, 0.0024 ; chloroform, 0.015 ; ethyl acetate, 0.041 ; amyl alcohol, 0.0056. An alcoholic solution of the acid may be used for precipitating alkaloids, and the reaction is more delicate than that with picric acid, but not to a very marked extent. The picrolonates of the following alkaloids are described : coniine, pale yellow, large rhombohedra, m. p. 195.5° (decomp.) ; nicotine, long prismatic needles, m. p. 213° ; strychnine, crystalline plates, or rectangular prisms, m. p. about 275° (decomp.) ; brucine, cubical crystals, m. p. 256° (decomp.) ; morphine, broad, flat needles, readily soluble in alcohol, m. p. 186.5° ; codeine, deep yellow rosettes of short prisms, m. p. 219° ; atropine, pointed crystals, m. p. 194° ; quinine, hair-like needles, m. p. 225° ; hydrastine, long, flat needles, m. p. 220°. All the salts contain 1 mol. of the base combined with one of picronic acid, with the exception of the quinine salt, which contains 2 mols. of the acid.

Picrolonates of cocaine, aconitine, and caffeine have not been obtained.

Brucine picrate exists in two modifications, a yellow and an orange-red ; the former is transformed into the latter when heated at 213°. J. J. S.

**Bebeerine.** HERMANN HILDEBRANDT (*Archiv. exp. Path. Pharm.*, 1907, 57, 279—284).—Scholtz has shown that bebeerine and pelosine, formerly known only in the amorphous state, may be crystallised from methyl alcohol and that they may be recovered again in the amorphous condition by means of chloroform. Buxine, from *Buxus sempervirens*, does not show these properties, and is therefore distinct from the two former compounds. The chemical constitution of the crystalline and the amorphous bebeerine is the same,  $\text{OH} \cdot \text{C}_{16}\text{H}_{14}\text{O}(\text{OMe})\text{NMe}$ . It is levorotatory. Recently in investigating the alkaloidal constituents of the roots of *Pareira brava* he obtained a dextrorotatory, crystalline substance having the same specific rotation and constitution as bebeerine, and the same m. p. as the latter when crystalline. By admixture in chloroform, the racemic compound, m. p. 300°, which could also be isolated from the plant, was obtained. The physiological action of the following compounds was investigated. The amorphous and crystalline forms of *d*- and *l*-bebeerine, the racemic modification in small quantities, the methiodide, and commercial bebeerine sulphate. The latter substance contains other alkaloidal constituents besides bebeerine. In frogs, no results could be obtained bearing on the differences of effect between the various bases. The general effect was that of curare. In white mice, subcutaneous injection of a 3% solution of the chloride gave

results dependent on the direction of rotation of the alkaloid. The racemic compound behaved as a molecular mixture.

With dogs, using the *d*-base, a dose of the crystalline form, equivalent to a lethal dose of the amorphous form, has no effect. The dextro-crystalline base is much more toxic to cats than dogs. The amorphous form of the *l*-base is much more toxic than the crystalline form to dogs. Bebeerine was recovered from the urine of the animals experimented upon partly as an easily decomposed combination with glycuronic acid. Molecular weight determinations point to the simple molecular formula  $C_{18}H_{21}O_3N$  for both the amorphous and the crystalline modifications.

G. S. W.

[Carnosine.] WLADIMIR VON GULEWITSCH (*Zeitsch. physiol. Chem.*, 1907, 52, 527—528).—The reactions of carnosine with silver nitrate and alkalis are as previously described by Gulewitsch and Amiradžibi (Abstr., 1900, i, 516). When equivalent amounts of carnosine and silver nitrate are used, the addition of ammonia, either in large or small amounts, produces no precipitate (compare Kutscher, this vol., i, 337).

J. J. S.

**Chemical Properties of Amanita-toxin.** HERMANN SCHLESINGER and WILLIAM W. FORD (*J. Biol. Chem.*, 1907, 3, 279—283).—When the aqueous extract of *Amanita phalloides* is mixed with alcohol, the hæmolytic glucoside, phallin (this vol., ii, 192), is precipitated, and the heat-resistant amanita-toxin is found in the alcoholic filtrate. This toxin can produce in animals the lesions found in man, including hæmorrhage, necrosis, and especially fatty degeneration. The toxin is readily soluble in water, but only sparingly so in hot absolute alcohol; its solutions may be boiled for some time without losing its toxic properties. It is slowly affected by dilute acids at the ordinary temperature and rapidly by boiling acids. It does not react with any of the ordinary reagents for alkaloids with the exception of phosphotungstic acid. It appears to be neither glucoside, alkaloid, nor protein in the generally accepted sense of these terms. It contains both nitrogen and sulphur, the latter in the form of conjugate sulphuric acid. When heated with solid potassium hydroxide, it yields indole and pyrrole.

J. J. S.

**Aporeine and other Alkaloids of Papaver dubium. II.** VITTORIO PAVESI (*Gazzetta*, 1907, 37, i, 629—636).—Contrary to what was previously stated (Abstr., 1905, i, 368), aporeine is deposited from solvents as an amorphous, resinous, almost colourless mass, showing a faint, whitish-blue fluorescence, and is readily soluble in ether, chloroform, carbon disulphide, ethyl acetate, light petroleum, or alcohol, in the last of which it has a slight alkaline reaction towards litmus. The crystalline salts formed with the mineral acids have an acid reaction. The hydrochloride,  $C_{18}H_{16}O_2N, HCl$ , *sulphate*, *nitrate*, *acetate*, and *platinichloride*,  $(C_{18}H_{16}O_2N)_2, H_2PtCl_6$ , have been prepared. Aporeine salts are precipitated by most of the general alkaloid reagents, to some of which they are extremely sensitive. A number of reactions of aporeine are given.



On exposing a solution of aporeine hydrochloride to the action of sunlight for a fortnight and extracting with ether, another base, *aporegenine*, is obtained, which crystallises in masses of white needles, but could not be obtained in a pure state.

Aporeine is accompanied, in the latex of *Papaver dubium*, by another base, *aporeidine*, which crystallises from ether in bundles of minute, white needles, m. p. 124—125° (somewhat impure). Various reactions of aporeidine are described. T. H. P.

**The Poison Plants of Western Australia.** EDWARD A. MANN and WALTER H. INCE (*Proc. Roy. Soc.*, 1907, **79**, B, 485—491).—The authors have investigated the poisonous plants of Western Australia and have isolated the new alkaloids, *cygnine*, from the "York Road" poison plant, *Gastrolobium calycinum*, and *lobine* from the "Box" poison plant, *Oxylobium parviflorum*. In the preparation of cygnine, the material obtained by alcoholic extraction when treated with lead acetate and then tannic acid, gives a residue which crystallises from hydrochloric acid and alcohol as a mixture of needle-shaped and cubical crystals. The former are very toxic; the latter appear to be a degradation product of the alkaloid, and have an acid reaction. Their composition would indicate the formula  $C_{12}H_{19}O_3$ .

The acicular crystals are the hydrochloride of an alkaloid  $C_{12}H_{22}O_3N_2$ . They are unstable, undergoing spontaneous decomposition if left moist or heated above 30°. One hundred c.c. of water dissolve 1.932 grams at 15°. The aqueous solution gives the usual alkaloidal reactions. Physiological experiments showed the alkaloid to be a powerful poison, belonging to that group of which the principal member is strychnine.

*Lobine* was obtained in a similar way and is a very similar substance. It is slightly more stable, and has the composition  $C_{23}H_{31}O_4N_3$ . Like cygnine, its hydrochloride when heated yields a non-nitrogenous substance, crystallising in cubes, and a nitrogenous uncrystallisable compound. The form in this case has the composition  $C_9H_{14}O_3$ .

Some other substances were obtained from the "York Road" poison plant besides cygnine.

*Cygnic acid*,  $C_{10}H_{10}O_4$ , was recovered from the lead precipitate obtained during the clearing of the alcoholic extracts. It gives a stable ammonium salt which is precipitated as a crystalline powder by addition of alcohol, and when analysed gives figures corresponding with  $C_{10}H_8O_4(NH_4)_2$ . The lead, silver, and barium salts are insoluble.

*Gastrolobic acid*,  $C_7H_{10}O_5 \cdot H_2O$ , is obtained from the same source as cygnic acid, and forms a stable sodium salt.

*Gastrolobin* is a vegetable gelatinoid. When the lead acetate precipitate is suspended in water and decomposed by passing hydrogen sulphide, the filtrate has a viscous character. The addition of absolute alcohol brings about the precipitation of a flocculent substance, insoluble in water. It does not reduce Fehling's solution, and is precipitated by tannic acid, dilute sulphuric acid, and sodium carbonate. An analysis shows its composition to be in accordance with the formula  $C_6H_{10}O_5$ . The oxidation product resulting from treatment with nitric acid gives the pyrrole test for mucic acid. The substance probably belongs to that ill-defined family of vegetable

carbohydrate gelatinoids of which agar-agar is the best known member.

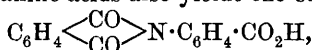
*Cygnose*,  $C_6H_{12}O_6$ , is isolated from the solution, after removal of the gastrolobin by means of lead acetate, by means of its *osazone*, which crystallises from alcohol in yellow needles, m. p.  $179^\circ$ . The sugar is optically inactive, both before and after inversion. It is not fermented by yeast. G. S. W.

**Constitution of Tripyridinechromium Trichloride.** PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1907, 55, 97—100).—The ordinary method for determining constitutions cannot be applied to tripyridinechromium trichloride,  $CrCl_3 \cdot 3Py$ , previously prepared by the author (Abstr., 1900, i, 559) on account of its complete insolubility in water. As, however, it is soluble in concentrated nitric acid and precipitated unchanged by water, it is considered improbable that any of the chlorine atoms are ionised, and, since it is soluble in such organic solvents as pyridine and glycol, its constitution is probably represented by the formula  $\left[ Cr \begin{smallmatrix} Cl_3 \\ Py_3 \end{smallmatrix} \right]$ .

The behaviour of this compound towards nitric acid and water may be taken advantage of to obtain it in a pure condition. G. S.

**Condensation Products of Phthalonic Acid with Anthranilic Acid.** ROSARIO SPALLINO (*Gazzetta*, 1907, 37, ii, 151—154).—When phthalonic acid is heated with anthranilic acid, it decomposes with formation of benzaldehyde-*o*-carboxylic acid, which condenses with the anthranilic acid yielding the compound  $\begin{array}{c} N-C_6H_4 \cdot CO \\ | \\ CH \cdot C_6H_4 \cdot CO \end{array} > O$ , crystallising

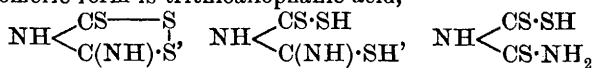
from alcohol in slender, white needles, m. p.  $215^\circ$ , and having the normal molecular weight in boiling alcohol. When heated with alcoholic ammonia in a closed tube at  $100^\circ$ , this substance is converted into the compound  $\begin{array}{c} N-C_6H_4 \cdot CO \\ | \\ CH \cdot C_6H_4 \cdot CO \end{array} > NH$ , which separates in long, white needles, m. p.  $240^\circ$ , and is soluble in alcohol. The interaction of phthalonic and anthranilic acids also yields the compound



which owes its presence to the action on the anthranilic acid of the phthalic anhydride produced in the decomposition of phthalonic acid.

T. H. P.

**Derivatives of Perthiocyanic Acid and of Cyanoimido-dithiocarbonic Acid. Synthesis of New Triazoles.** EMIL FROMM and D. VON GÖNCZ (*Annalen*, 1907, 355, 196—215).—Hantzsch and Wolvekamp's perthiocyanic acid (Abstr., 1904, i, 718) may be regarded as the disulphide of a dihydric mercaptan, which in its tautomeric form is trithioallophanic acid,



Benzyl trithioallophanate has been prepared by Fromm (Abstr.,

1895, i, 605) from *as*-phenylmethyldithiobiuret, which, in its turn, is obtained from perthiocyanic acid. This relationship between perthiocyanic acid and trithioallophanic acid is supported by the following results.

*Dibenzyl cyanoiminodithiocarbonate*,  $(C_7H_7 \cdot S)_2C:N \cdot CN$ , m. p.  $82^\circ$ , is obtained by the reaction in alcoholic solution between benzyl chloride and the potassium salt, which Hantzsch and Wolvekamp have prepared by the action of potassium hydroxide on perthiocyanic acid (*loc. cit.*). The successive action of hydrogen sulphide and of dry ammonia on a cold alcoholic solution of the dibenzyl ester leads to the formation of benzyl mercaptan and benzyl trithioallophanate.

Dibenzyl cyanoiminodithiocarbonate is converted by cold alcoholic ammonia into benzyl mercaptan and *amino-ψ-benzylthiocarbamide cyanide* (*benzyl cyanoiminothiocarbamate*),  $C_7H_7S \cdot C(NH_2):N \cdot CN$ , m. p.  $158^\circ$ , which is decomposed by boiling concentrated hydrochloric acid forming benzyl thioallophanate (compare Fromm, *Abstr.*, 1895, ii, 461). Aniline and *o*- and *p*-toluidines react in a similar manner with dibenzyl cyanoiminodithiocarbonate in hot alcohol, forming benzyl esters of cyanoiminothiocarbamates in which a hydrogen atom of the amino-group is replaced by the aryl group of the amine; these compounds have been already prepared by Fromm by the action of sodium hydroxide and benzyl chloride on substituted thiobiurets. Benzidine and dibenzyl cyanoiminodithiocarbonate react to form the compound  $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH \cdot C(SC_7H_7):N \cdot CN$ , which begins to decompose at  $190^\circ$ , but is not fused at  $280^\circ$ .

Phenylhydrazine and dibenzyl cyanoiminodithiocarbonate react energetically to form Fromm and Schneider's 5-amino-3-thiobenzyl-1-phenyl-1:2:4-triazole (*Abstr.*, 1906, i, 714), the *diacetyl* derivative of which has m. p.  $228-229^\circ$ .

Ammonia or aniline reacts with benzyl cyanoiminophenylthiocarbamate,  $C_7H_7S \cdot C(NHPh):N \cdot CN$ , at  $110-120^\circ$ , with the elimination of benzyl mercaptan, but a pure product has not been isolated. At the same temperature, phenylhydrazine in excess reacts to form a *base*, m. p.  $148^\circ$ , together with a small quantity of an *isomeride*, m. p.  $166^\circ$ ; at  $180^\circ$ , the latter is the main product. These bases, which are stable towards boiling hydrochloric acid, are guanazole derivatives; the former is regarded as 5-amino-3-anilino-1-phenyl-1:2:4-triazole,

$$NPh \begin{array}{c} \text{NH} \text{---} \text{C} \text{---} \text{NHPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}) \text{---} \text{N} \end{array}$$
, the *acetyl* derivative of which has m. p.  $189^\circ$ ,

and the *hydrochloride* has m. p.  $275^\circ$ . The latter is sparingly soluble, and changes by heating with phenylhydrazine at  $180^\circ$  to the very soluble *hydrochloride* of the isomeric base, m. p.  $166^\circ$ , which is regarded as 3-amino-5-anilino-1-phenyl-1:2:4-triazole; the *acetyl* derivative has m. p.  $166^\circ$ .  
C. S.

**Action of Cyanogen Halides on Phenylhydrazine.** GUIDO PELLIZZARI (*Gazzetta*, 1907, 37, i, 611-623).—In ethereal solution, cyanogen chloride reacts with phenylhydrazine to form anilcyanamide or phenylaminocyanamide,  $NHPh \cdot NH \cdot CN$  (*Abstr.*, 1892, 1323). The author now finds that, in aqueous solution, these two compounds interact in two ways, a small proportion of phenylaminocyanamide

being formed, but the main product being aminophenylcyanamide formed according to the equation:  $2\text{NH}_2\cdot\text{NPh} + \text{CNBr} = \text{NH}_2\cdot\text{NPh}\cdot\text{CN} + \text{NH}_2\cdot\text{NPh}\cdot\text{HBr}$ . The phenylaminocyanamide formed undergoes transformation, yielding (1) phenylsemicarbazide, formed by the reaction  $\text{NPh}\cdot\text{NH}\cdot\text{CN} + \text{H}_2\text{O} = \text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , and (2) diphenyldiaminoguanidine hydrobromide, formed by the addition of phenylhydrazine hydrobromide,  $\text{NPh}\cdot\text{NH}\cdot\text{CN} + \text{NH}_2\cdot\text{NPh}\cdot\text{HBr} = \text{NH}\cdot\text{C}(\text{NH}\cdot\text{NPh})_2\cdot\text{HBr}$ .

*Aminophenylcyanamide* or  $\alpha$ -cyanophenylhydrazide,  $\text{NH}_2\cdot\text{NPh}\cdot\text{CN}$ , crystallises from alcohol in shining, white plates, m. p.  $89^\circ$ , dissolves in water, benzene, or ether, has the normal molecular weight in boiling alcohol or benzene, and reduces ammoniacal silver nitrate or Fehling's solution. It has, however, no basic properties, and does not dissolve in acids or form a salt with picric acid.

*Diphenyldiaminoguanidine hydrobromide*,  $\text{NH}\cdot\text{C}(\text{NH}\cdot\text{NPh})_2\cdot\text{HBr}$ , is deposited from alcohol in round masses of reddish crystals, m. p.  $178\text{--}180^\circ$  (decomp.), and dissolves in water with a red coloration which disappears on the addition of an acid. The picrate,  $\text{C}_{13}\text{H}_{15}\text{N}_5\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises from alcohol in minute needles, m. p.  $170^\circ$  (decomp.).

*Benzylideneaminophenylcyanamide*,  $\text{CN}\cdot\text{NPh}\cdot\text{N}\cdot\text{CHPh}$ , prepared by the interaction of aminophenylcyanamide and benzaldehyde in water containing a small quantity of hydrochloric acid, separates from alcohol in shining crystals, m. p.  $103^\circ$ , and dissolves sparingly in water.

*Aminophenylcarbamide* ( $\alpha$ -phenylsemicarbazide),  $\text{NH}_2\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$ , obtained by hydrolysing aminophenylcyanamide by means of boiling 10% potassium hydroxide, is deposited from alcohol in shining crystals, m. p.  $120^\circ$ , has the normal molecular weight in boiling alcohol, and reduces Fehling's solution and ammoniacal silver nitrate solution containing potassium hydroxide. It has basic properties, and dissolves in acids in the cold.

*Benzylideneaminophenylcarbamide*,  $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$ , prepared by the action of benzaldehyde on aminophenylcarbamide in presence of an acid, crystallises from alcohol in white needles, m. p.  $154^\circ$ , and is moderately soluble in alcohol.

*Aminophenylthiocarbamide*,  $\text{NH}_2\cdot\text{NPh}\cdot\text{CS}\cdot\text{NH}_2$ , obtained by the interaction of aminophenylcyanamide and ammonium hydrosulphide, crystallises from water in striated laminae, m. p.  $153^\circ$ , dissolves to a moderate extent in alcohol, and combines with aldehydes and ketones, forming readily crystallisable compounds.

*Benzylideneaminophenylthiocarbamide*,  $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{CS}\cdot\text{NH}_2$ , separates from benzene in large transparent crystals containing  $1\frac{1}{2}\text{C}_6\text{H}_6$ , m. p.  $65\text{--}70^\circ$ , or, when free from benzene,  $163^\circ$ ; it is readily soluble in alcohol and sparingly so in water.

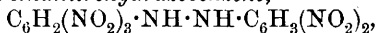
T. H. P.

**Aromatic Nitro-derivatives.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 133—138).—In continuation of his previous investigations (Ciusa and Agostinelli, *Abstr.*, 1906, i, 891), the author has studied the action of picryl chloride on acetoneazine, and on acetone-*s*-trinitrophenylhydrazone, -2:4-dinitrophenylhydrazone, and

-*p*-nitrophenylhydrazone. Picryl chloride acts on acetone liberating 1 mol. of acetone and forming acetone-trinitrophenylhydrazone, on which it exerts no further action; with the dinitro- and mononitrophenylhydrazones of acetone, it reacts readily, liberating acetone and forming 2:4:6:2':4'-pentanitrohydrazobenzene and 2:4:6:4'-tetranitrohydrazobenzene respectively. The behaviour of 1-chloro-2:4-dinitrobenzene is quite analogous to that of picryl chloride.

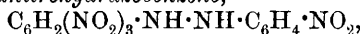
Acetonetrinitrophenylhydrazone, prepared from picryl chloride and acetone, has m. p. 130° and not 125° as was stated by Purgotti (Abstr., 1895, i, 27) and Curtius and Dedichen (Abstr., 1895, i, 29).

2:4:6:2':4'-Pentanitrohydrazobenzene,



crystallises from a mixture of ethyl acetate, alcohol, and a few drops of acetic acid in microscopic, golden-yellow plates, m. p. 226° (decomp.), and gives an intense violet coloration with even a trace of alkali.

2:4:6:4'-Tetranitrohydrazobenzene,



is deposited from a mixture of ethyl acetate and alcohol in yellow, acicular crystals, m. p. 210°, and gives an intense coloration with a trace of alkali.

The action of 1-chloro-2:4-dinitrobenzene on acetone yields acetone-2:4-dinitrophenylhydrazone, m. p. 128° (compare Curtius and Dedichen, Abstr., 1895, i, 29; Fischer and Ach, Abstr., 1890, 40; and Purgotti, Abstr., 1895, i, 27).

The action of 1-chloro-2:4-dinitrobenzene on benzylideneazine yields benzaldehyde-2:4-dinitrophenylhydrazone.

2:4-Dinitrodiphenylamine,  $\text{NHPh} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ , obtained by the action of 1-chloro-2:4-dinitrobenzene on benzylideneaniline, separates from alcohol in red crystals, m. p. 156°. T. H. P.

**Condensation Products of Aminophenylcyanamide with Aldehydes and Ketones.** LUIGI ROLLA (*Gazzetta*, 1907, 37, i, 623—629. Compare preceding abstract).—Aminophenylcyanamide,  $\text{NH}_2 \cdot \text{NPh} \cdot \text{CN}$ , reacts with aldehydes and ketones and even with compounds such as quinone and alloxan, yielding derivatives analogous to phenylhydrazones and having the structure  $\text{R} \cdot \text{N} \cdot \text{NPh} \cdot \text{CN}$ . The reaction proceeds best in alcoholic solution and in presence of a small quantity of hydrochloric acid.

*Ethylideneaminophenylcyanamide* (acetaldehydecyanophenylhydrazone),  $\text{CHMe} \cdot \text{N} \cdot \text{NPh} \cdot \text{CN}$ , separates from alcohol in white crystals, m. p. 45°, and dissolves in ether, benzene, or water.

*Salicylideneaminophenylcyanamide* (salicylaldehydecyanophenylhydrazone),  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{NPh} \cdot \text{CN}$ , separates from alcohol as a white, indistinctly crystalline substance, m. p. 132°, and is readily soluble in benzene or ether.

*Nitrobenzylideneaminophenylcyanamide* (nitrobenzaldehydecyanophenylhydrazone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}_2 \cdot \text{Ph} \cdot \text{CN}$ , crystallises from alcohol in white, opaque leaflets, m. p. 163°, and dissolves in benzene.

*Vanillideneaminophenylcyanamide* (vanillincyanophenylhydrazone),

$\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{N}_2\text{Ph} \cdot \text{CN}$ , forms white crystals, m. p.  $118^\circ$ , and dissolves in alcohol or ether.

*Furfurylideneaminophenylcyanamide* (*furfuraldehydecyanophenylhydrazone*),  $\text{C}_6\text{OH}_3 \cdot \text{CH} : \text{N}_2\text{Ph} \cdot \text{CN}$ , is deposited from alcohol in minute, white crystals, m. p.  $98^\circ$ , and is soluble in ether or benzene.

*Acetophenonecyanophenylhydrazone*,  $\text{CPhMe} : \text{N}_2\text{Ph} \cdot \text{CN}$ , separates from alcohol as a felted mass of minute, white crystals, m. p.  $67^\circ$ , and dissolves in ether or benzene.

*Isatincyanophenylhydrazone*,  $\text{N} \begin{smallmatrix} \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} : \text{N}_2\text{Ph} \cdot \text{CN}$ , separates from alcohol as a voluminous, yellow mass, m. p.  $191^\circ$ , and is readily soluble in ether or benzene.

*Benzil-monocyanophenylhydrazone*,  $\text{COPh} \cdot \text{CPh} : \text{N}_2\text{Ph} \cdot \text{CN}$ , separates from alcohol in pale yellow crystals, m. p.  $168^\circ$ .

*Benzoquinonedi-cyanophenylhydrazone*,  $\text{C}_6\text{H}_4(\text{N}_2\text{Ph} \cdot \text{CN})_2$ , crystallises from alcohol in red scales with golden-yellow lustre, m. p.  $178^\circ$ , and dissolves readily in ether or benzene.

*Alloxancyanophenylhydrazone*,  $\text{C}_4\text{H}_2\text{O}_3\text{N}_2 : \text{N}_2\text{Ph} \cdot \text{CN}$ , separates as a voluminous, straw-yellow precipitate, m. p.  $286^\circ$ .

With ethyl acetoacetate, benzophenone, and tetramethyldiaminobenzophenone, aminophenylcyanamide yields oily products, whilst with the sugars no compounds could be prepared. T. H. P.

**Preparation of Quinazoline Derivatives.** HERMANN FINGER (*J. pr. Chem.*, 1907, [ii], 76, 97. Compare Abstr., 1906, i, 901).—Acetiminioethyl ether and benziminioethyl ether condense with isatoic acid with the elimination of carbon dioxide and alcohol, and the formation of 4-keto-2-methyldihydroquinazoline,  $\text{C}_9\text{H}_8\text{ON}_2$ , and 4-keto-2-phenyldihydroquinazoline,  $\text{C}_{14}\text{H}_{10}\text{ON}_2$ , respectively. W. H. G.

**Action of Imino-ethers on Amino-esters.** HERMANN FINGER [and, in part, SCHUPP and W. ZEH] (*J. pr. Chem.*, 1907, [ii], 76, 93—97. Compare Abstr., 1906, i, 901).—*Phenylglyoxalidone*,  $\text{C}_9\text{H}_8\text{ON}_2$ , is formed by the interaction of glycine ethyl ester and benziminioethyl ether. It is oxidised in acetic acid solution by atmospheric oxygen with the formation of a red substance, probably identical with glyoxaline-red (Ruhemann and Stapleton, *Trans.*, 1900, 77, 804).

*Methylglyoxalidone*,  $\text{CMe} \begin{smallmatrix} \text{N} - \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix}$  or  $\text{CMe} \begin{smallmatrix} \text{N} - \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH} \end{smallmatrix}$ , is formed when acetiminioethyl ether and glycine ethyl ester are mixed in molecular proportions; it forms white crystals, m. p.  $140$ — $141^\circ$ , is decomposed on boiling with alkalis, and combines in alkaline solution with diazonium compounds with the formation of azo-dyes.

The *hydrochloride*,  $\text{C}_4\text{H}_6\text{ON}_2 \cdot \text{HCl}$ , crystallises in small, brown needles.

The compound,  $\text{CMe} \begin{smallmatrix} \text{N} - \text{CH} \cdot \text{CH} - \text{N} \\ \diagup \quad \diagdown \\ \text{NBz} \cdot \text{CO} \quad \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CMe}$ , glistening, white leaflets, m. p.  $216$ — $218^\circ$  (decomp.), is obtained by the benzylation of methylglyoxalidone by the Schotten-Baumann method. The action of benzoyl chloride on the base in pyridine solution leads to the formation

of *methylglyoxalidone dibenzoate*,  $C_{18}H_{14}O_3N_2$ , crystallising in small, slender, white needles, m. p.  $128^\circ$ . The *dibenzylidene* derivative,  $CHPh:CH:C \begin{smallmatrix} \nwarrow N-C:CHPh \\ \nearrow NH-CO \end{smallmatrix}$ , m. p.  $218^\circ$ , is prepared by heating methylglyoxalidone with an excess of benzaldehyde, or by shaking an alkaline solution of the base with benzaldehyde.

Attempts to prepare *N*-alkylglyoxalidones by employing sarcosine ethers in place of glycine ethyl ester were unsuccessful.

*Monochloroacetiminoethyl ether*,  $C_4H_8ONCl$ , prepared by Pinner's method, is a liquid which decomposes when boiled under atmospheric pressure; it has a pyridine-like odour and produces inflammation of the mucous membrane.

W. H. G.

**Action of Concentrated Nitric Acid on Trimethyleneureine and on Hydrouracil.** ANTOINE P. N. FRANCHIMONT and HERMANN FRIEDMANN (*Rec. trav. chim.*, 1907, **26**, 218—222).—Donk (this vol., i, 831) finds that the action of nitric acid on glycine anhydride does not conform to the law laid down by Franchimont (*Abstr.*, 1889, 1145) concerning the action of concentrated nitric acid on cyclic derivatives containing a NH group situated between the carbonyl group and the residue of a saturated hydrocarbon. The law is supported by the course of the action of nitric acid on trimethyleneureine and on hydrouracil.

*Nitrohydrouracil*,  $CO \begin{smallmatrix} \nwarrow CH_2 \cdot CH_2 \\ \nearrow NH-CO \end{smallmatrix} N \cdot NO_2$ , prepared by dissolving hydrouracil in concentrated nitric acid, is deposited from ethyl acetate in shining crystals, decomposing at  $155-158^\circ$ , and dissolves readily in water or methyl alcohol and sparingly in ether, light petroleum, benzene, chloroform, or carbon tetrachloride. When boiled with water, nitrohydrouracil (1 mol.) yields carbon dioxide (1 mol.) and  $\beta$ -nitroaminopropionamide,  $NO_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$ , which separates from water or alcohol in large, colourless crystals, m. p.  $122^\circ$ .

$\beta$ -Nitroaminopropionic acid,  $NO_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , prepared by the action of sodium hydroxide solution on the corresponding amide, crystallises from alcohol in long needles, m. p.  $73^\circ$ , and is readily soluble in ether. The formulæ of the *barium*,  $C_3H_4O_4N_2Ba \cdot H_2O$ , and *silver* salts,  $C_3H_4O_4N_2Ag_2$ , show that the acid behaves as a dibasic acid.

*Dinitrotrimethyleneureine*,  $CH_2 \begin{smallmatrix} \nwarrow CH_2 \cdot N(NO_2) \\ \nearrow CH_2 \cdot N(NO_2) \end{smallmatrix} CO$ , prepared by the action of concentrated nitric acid on trimethyleneureine, crystallises from alcohol in whitish-yellow needles and yields carbon dioxide and trimethylenedinitroamine when boiled with water.

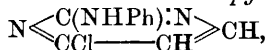
T. H. P.

**Pyrimidines. XXI. Action of Methyl Iodide on 6-Oxy-2-anilinopyrimidine and Synthesis of 2-Anilinopyrimidine.** TREAT B. JOHNSON and FREDERICK W. HEYL (*Amer. Chem. J.*, 1907, **38**, 237—249).—It has been shown previously (this vol., i, 728) that by the action of methyl iodide or ethyl iodide on 6-oxy-2-ethylthiopyrimidine in presence of alkali hydroxide, the corresponding 1-alkyl derivatives are produced, but neither the corresponding oxygen ethers nor the 3-alkyl derivatives are formed. The action of methyl iodide

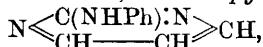
on 6-oxy-2-anilinopyrimidine (Johnson and Johns, Abstr., 1906, i, 456) in presence of potassium hydroxide has now been studied, and it is found that a mixture of 2-anilino-6-methoxypyrimidine and 6-oxy-2-anilino-1-methylpyrimidine is produced.

2-Anilino-6-methoxypyrimidine,  $N \begin{smallmatrix} \diagup C(NHPh):N \\ \diagdown C(OMe)-CH \end{smallmatrix} > CH$ , m. p. 119°, best prepared by the action of methyl iodide on the silver derivative of 6-oxy-2-anilinopyrimidine, forms transparent prisms. 6-Oxy-2-anilino-1-methylpyrimidine,  $NMe \begin{smallmatrix} \diagup C(NHPh):N \\ \diagdown CO-CH \end{smallmatrix} > CH, H_2O$ , m. p. 149—150°, crystallises in slender prisms. This compound can also be obtained by heating 6-oxy-2-ethylthiol-1-methylpyrimidine (Johnson and Heyl, *loc. cit.*) with aniline at 150°. The isomeric 6-oxy-2-methylanilinopyrimidine,  $NH \begin{smallmatrix} \diagup C(NPhMe):N \\ \diagdown CO-CH \end{smallmatrix} > CH$ , m. p. 187°, obtained by heating 6-oxy-2-ethylthiolpyrimidine with methylaniline, forms large, prismatic crystals.

6-Oxy-2-anilinopyrimidine reacts smoothly with phosphorus oxychloride with formation of 6-chloro-2-anilinopyrimidine,



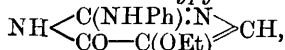
m. p. 134°, which crystallises in plates. When this substance is digested with water and zinc dust, 2-anilinopyrimidine,



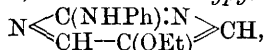
m. p. 116°, is produced, which forms prismatic crystals; its *hydrochloride*, decomp. 125°, *sulphate*, m. p. 140—142°, and *platinichloride*, m. p. 218—221° (decomp.), are described. Attempts to hydrolyse 2-anilinopyrimidine and 6-oxy-2-anilinopyrimidine with formation of 2-oxypyrimidine and uracil respectively were unsuccessful. Carbon disulphide does not react with these pyrimidines.

5:6-Diethoxy-2-ethylthiolpyrimidine,  $N \begin{smallmatrix} \diagup C(SET) \\ \diagdown C(OEt) \cdot C(OEt) \end{smallmatrix} > CH$ , was obtained as an oil by treating 6-chloro-5-ethoxy-2-ethylthiolpyrimidine (Johnson and McCollum, Abstr., 1906, i, 704) with sodium ethoxide; its *hydrochloride*, m. p. 129—131°, forms prismatic crystals.

6-Oxy-5-ethoxy-2-methylthiolpyrimidine is not changed by the action of alcoholic ammonia at 140—160° or at 210—235°. When 6-oxy-5-ethoxy-2-ethylthiolpyrimidine is heated with aniline at 185—216° for two hours, 6-oxy-2-anilino-5-ethoxypyrimidine,



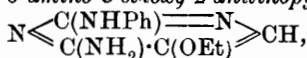
m. p. 231—232°, is produced, which crystallises in plates and, when warmed with phosphorus oxychloride, is converted into 6-chloro-2-anilino-5-ethoxypyrimidine,  $N \begin{smallmatrix} \diagup C(NHPh):N \\ \diagdown CCl-C(OEt) \end{smallmatrix} > CH$ , m. p. 111—112°, which forms stout prisms. On treating the last-mentioned compound with zinc dust and water, 2-anilino-5-ethoxypyrimidine,



m. p. 130—131°, is obtained, and crystallises in short prisms.



When 6-chloro-2-anilino-5-ethoxypyrimidine is heated with alcoholic ammonia at 180—188°, 6-amino-5-ethoxy-2-anilino-*pyrimidine*,



m. p. 133—134°, is formed, and crystallises in prisms.

E. G.

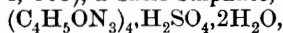
**Pyrimidines. XXII. Salts of Cytosine, *iso*Cytosine, 6-Aminopyrimidine, and 6-Oxypyrimidine.** HENRY L. WHEELER (*J. Biol.*

*Chem.*, 1907, 3, 285—297).—6-Oxypyrimidine,  $\text{CH} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{N} \end{array} \text{CH} \begin{array}{c} \text{=N} \\ \text{>CH} \end{array}$ , is

formed by the action of hydrogen peroxide on 2-thiouracil (Wheeler and Bristol, *Abstr.*, 1905, i, 483) or, better, by the action of hydriodic acid and red phosphorus on 2:6-dichloropyrimidine. It crystallises from benzene or ethyl acetate in colourless needles, m. p. 164—165°, and, unlike uracil (dioxypyrimidine), gives no coloration with bromine and barium hydroxide. The *acetyl* derivative,  $\text{C}_6\text{H}_8\text{O}_3\text{N}_2$ , forms colourless needles melting at 180° to a clear oil, which then solidifies and subsequently melts and decomposes at 215—220°, and is probably acetylformamide-acrylic acid. The *picrate*,  $\text{C}_{10}\text{H}_7\text{O}_8\text{N}_5$ , forms flat crystals, m. p. 190°, and is more readily soluble than the picrates of cytosine and *isocytosine*. The *hydrochloride*,  $\text{C}_4\text{H}_4\text{ON}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , is readily soluble, and crystallises in thick, transparent prisms which melt partially at 100° and completely at 205—210°. The *sulphate*,  $(\text{C}_4\text{H}_4\text{ON}_2)_2 \cdot \text{H}_2\text{SO}_4$ , m. p. 218° (decomp.), is also readily soluble.

6-Aminopyrimidine (Büttner, *Abstr.*, 1903, i, 658) is readily obtained by reducing 2-chloro-6-aminopyrimidine with hydriodic acid and red phosphorus. The *acetyl* derivative,  $\text{C}_6\text{H}_7\text{ON}_3$ , crystallises from water in slender needles, m. p. 202°. The *picrate*,  $\text{C}_{10}\text{H}_8\text{O}_7\text{N}_6$ , forms bright yellow, slender needles, m. p. 226°. The *hydrochloride*,  $\text{C}_4\text{H}_5\text{N}_3 \cdot \text{HCl}$ , forms transparent prisms or plates, m. p. 257°. *Cytosine hydrochloride*,  $\text{C}_4\text{H}_5\text{ON}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , is obtained when the normal chloride (Wheeler and Johnson, *Abstr.*, 1903, i, 526) is recrystallised from water. It loses its water at 50° and then melts at 275—279°.

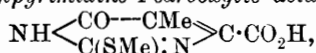
An *isocytosine hydrochloride*,  $\text{C}_4\text{H}_5\text{ON}_3 \cdot \text{HCl}$ , m. p. 270° (decomp.), and *sulphate*,  $(\text{C}_4\text{H}_5\text{ON}_3)_2 \cdot \text{H}_2\text{SO}_4$ , m. p. 276° (decomp.), have been prepared. Cytosine forms a normal sulphate,  $(\text{C}_4\text{H}_5\text{ON}_3)_2 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (Levene, *Abstr.*, 1903, i, 668), a basic sulphate,



and an acid sulphate,  $\text{C}_4\text{H}_5\text{ON}_3 \cdot \text{H}_2\text{SO}_4$ , m. p. 197° (Kossel and Steudel, *Abstr.*, 1903, i, 667).

J. J. S.

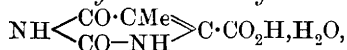
**Pyrimidines. Synthesis of Thymine-4-carboxylic Acid.** TREAT B. JOHNSON (*J. Biol. Chem.*, 1907, 3, 299—306).—6-Oxy-2-methylthiol-5-methylpyrimidine-4-carboxylic acid,



is formed by the condensation of  $\psi$ -methylthiocarbamide hydriodide and ethyl sodio-oxalylpropionate in the presence of potassium hydroxide solution (2 equiv.). It crystallises from hot water or alcohol, in both of which it is sparingly soluble, in prisms, m. p. 243—244° (decomp.).

When 1 equiv. of potassium hydroxide is used in the condensation, the product is the *ethyl* ester,  $C_9H_{12}O_3N_2S$ , of the above acid. It crystallises in slender needles, m. p. 201—202°. The *potassium* salt,  $C_7H_7O_3N_2SK \cdot 6H_2O$ , crystallises from hot water in needles, decomp. 230°. When heated in a sulphuric acid bath at 245° until effervescence is completed, it yields 6-oxy-2-methylthiol-5-methylpyrimidine.

A quantitative yield of *thymine-4-carboxylic acid*,



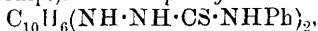
is obtained when the pyrimidine-carboxylic acid is digested with concentrated hydrochloric acid. It crystallises from water in an anhydrous state, and also with  $1H_2O$ , but both forms decompose at 328—330°. The acid is not affected by treatment at 160—170° with 20% sulphuric acid, and hence thymine cannot exist in nucleic acids as a 4-carboxylic derivative. *Potassium*, *barium*, and *lead* salts have been prepared. The *ethyl* ester,  $C_8H_{10}O_4N_2$ , crystallises from water in distorted prisms, m. p. 255°. Bromine and water convert the acid into 5-bromo-4-hydroxy-5-methyl-4:5-dihydrothymine-4-carboxylic acid,

$NH \begin{array}{c} \diagup CO \cdot CMeBr \\ \diagdown CO - NH \end{array} > C(OH) \cdot CO_2H$ , which crystallises in small prisms decomposing rapidly at 295—300°. J. J. S.

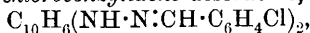
**2:3-Naphthylenedihydrazine.** HARTWIG FRANZEN (*J. pr. Chem.*, 1907, [ii], 76, 205—232).—If phenols are heated with ammonia, ammonio-zinc chloride, or ammonio-calcium chloride, the hydroxyl groups are replaced by amino-groups. The present work was undertaken to determine the conditions under which the hydroxyls of phenols can be displaced similarly by the hydrazino-group  $\cdot NH \cdot NH_2$ . Although, according to Hoffmann (Abstr., 1899, i, 221),  $\alpha$ - and  $\beta$ -naphthols form the corresponding hydrazines when heated with hydrazine hydrate at 160°, and small amounts of phenylhydrazine are obtained by heating phenol with hydrazine hydrate at 220°, attempts to prepare hydrazines in this manner from polyphenols of the benzene series were unsuccessful. Bucherer and his co-workers have shown that amino-compounds are formed when phenols are heated with ammonium sulphite and ammonia (Abstr., 1903, i, 627; 1904, i, 309, 395; 1905, i, 48, 585; this vol., i, 509); it is found now that 1:5- and 2:3-dihydroxynaphthalenes form the corresponding dihydrazines when heated with hydrazine sulphite and hydrazine hydrate, whilst in the same manner  $\alpha$ - and  $\beta$ -naphthols form  $\alpha$ - and  $\beta$ -naphthylhydrazines in yields greater than are obtained under Hoffmann's conditions.  $\alpha$ - and  $\beta$ -Naphthylhydrazines are formed also when hydrazine  $\alpha$ - and  $\beta$ -hydroxynaphthates are heated slightly above their m. p's.

2:3-Naphthylenedihydrazine,  $C_{10}H_6(NH \cdot NH_2)_2$ , prepared in a 57% yield by boiling 2:3-dihydroxynaphthalene with hydrazine sulphite and hydrazine hydrate in absolute alcoholic solution in a reflux apparatus, or in a 30% yield in the absence of the sulphite, crystallises from benzene in white needles or from alcohol in reddish-brown needles, m. p. 155—156° (decomp.), or from water in reddish-brown needles, m. p. 167—168° (decomp.), or from amyl alcohol in brownish-yellow needles, m. p. 175—176° (decomp.); the alcoholic mother-

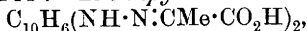
liquor has a strong blue fluorescence. The dihydrazine readily reduces Fehling's and ammoniacal silver solutions, gives a dark red coloration when treated with mercuric oxide in ethereal solution, or with concentrated sulphuric acid a dark red coloration becoming yellow on dilution, and on treatment with sodium nitrite in hydrochloric or sulphuric acid solution yields a yellow precipitate changing into a dark brown powder. The *hydrochloride*,  $C_{10}H_{12}N_4 \cdot 2HCl$ , *sulphate*,  $C_{10}H_{12}N_4 \cdot H_2SO_4$ , decomp.  $120^\circ$ , *picrate*,  $C_{10}H_{12}N_4 \cdot 2C_6H_3O_7N_3$ , bronze-yellow leaflets, and *acetate*,  $C_{10}H_{12}N_4 \cdot 2C_2H_3O_2$ , m. p.  $141-142^\circ$  (decomp.), are described. When boiled with 15% hydrochloric acid, the dihydrazine is converted into 2:3-naphthyleneazoimide and ammonia, and is reduced to naphthalene when boiled with copper sulphate in aqueous solution. 2:3-Dichloronaphthalene is formed when the dihydrazine is boiled with copper sulphate in hydrochloric acid solution. The *disemicarbazide*,  $C_{10}H_6(NH \cdot NH \cdot CO \cdot NH_2)_2$ , has m. p.  $234-235^\circ$  (decomp.). The *diphenylthiosemicarbazide*,



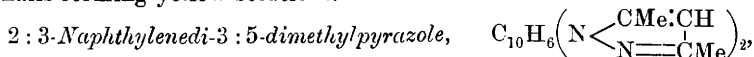
forms brown crystals, m. p.  $166^\circ$  (decomp.). The *diacetyl* derivative,  $C_{10}H_6(N_2H_2Ac)_2$ , crystallises in white needles, m. p.  $231^\circ$  (decomp.). *Dibenzylidene-2:3-naphthylenedihydrazone*,  $C_{10}H_6(NH \cdot N : CHPh)_2$ , crystallises in lemon-yellow needles, m. p.  $205^\circ$  (decomp.), which cannot be obtained quite free from 1:3-dibenzylideneamino-2-phenyl-2:3-dihydro- $\beta\beta$ -naphthiminazole; when treated with amyl nitrite, the hydrazone forms a red substance, soluble in alcohol, whilst the iminazole remains unchanged. On reduction with zinc dust and glacial acetic acid, the dibenzylidenehydrazone yields 2:3-naphthyleneazoimide. The *di-m-chlorobenzylidene* derivative,



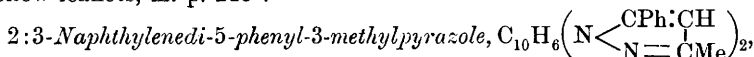
crystallises in yellow needles, m. p.  $192-193^\circ$ . The *dipropylidene* derivative,  $C_{10}H_6(NH \cdot N : CMe_2)_2$ , crystallises in white needles, m. p.  $145-146^\circ$ , and decomposes gradually when exposed to air. The *diacetophenone* derivative,  $C_{10}H_6(NH \cdot N : CPhMe)_2$ , forms browni-yellow leaflets, m. p.  $144^\circ$ . The *dipyrvic acid* derivative,



crystallises in yellow needles, m. p.  $180^\circ$  (decomp.), and dissolves in alkalis forming yellow solutions.



formed with development of heat by the action of acetylacetone on the dihydrazine in alcoholic solution, crystallises in yellow needles, m. p.  $126-127^\circ$ . The *picrate*,  $C_{32}H_{26}O_{14}N_{10}$ , crystallises in yellow needles, m. p.  $187-188^\circ$ ; the *hydrochloride*,  $C_{20}H_{20}N_4 \cdot 2HCl$ , is hydrolysed by water; the *dimethiodide*,  $C_{22}H_{26}N_4I_2$ , crystallises in yellow leaflets, m. p.  $225^\circ$ .



formed by boiling the dihydrazine with benzoylacetone in alcoholic solution, separates in white crystals, m. p.  $191^\circ$ . The *picrate*,  $C_{42}H_{30}O_{14}N_{10}$ , crystallises in yellow leaflets, m. p.  $200^\circ$ ; the *hydrochloride*,  $C_{30}H_{24}N_4 \cdot 2HCl$ , crystallises in white needles.

2:3-Naphthylenedi-3-phenylpyrazolone,  $C_{10}H_6(N \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{N} = \text{CPh} \end{smallmatrix})_2$ , prepared by heating 2:3-naphthylenedihydrazine with ethyl benzoyl-acetate, forms a yellowish-brown, crystalline powder, m. p.  $245^\circ$ , and yields a diisonitroso-derivative,  $C_{28}H_{18}O_4N_6$ , crystallising in reddish-brown needles, m. p.  $222^\circ$ .

1:3-Dibenzylideneamino-2-phenyl-2:3-dihydro- $\beta\beta$ -naphthiminazole,  $C_{10}H_6 \begin{smallmatrix} \text{N}(\text{N}:\text{CHPh}) \\ \text{N}(\text{N}:\text{CHPh}) \end{smallmatrix} > \text{CHPh}$ , prepared by boiling 2:3-naphthylene-dihydrazine with benzaldehyde in alcoholic solution in a reflux apparatus, crystallises from xylene in yellow needles, m. p.  $227-228^\circ$  (decomp.). The corresponding di-o-hydroxybenzylidene compound,  $C_{31}H_{24}O_3N_4$ , is obtained as a lemon-yellow, crystalline powder, m. p.  $242^\circ$  (decomp.). The di-m-chlorobenzylidene compound,  $C_{31}H_{21}N_4Cl_2$ , forms a yellow, crystalline powder, m. p.  $218^\circ$ . G. Y.

**Behaviour of Diazonium Compounds towards Keto-Enolic Desmotropic Compounds.** J. BISHOP TINGLE (*J. Amer. Chem. Soc.*, 1907, 29, 1242—1243).—The author points out that a number of additive compounds of the type discussed by Dimroth (this vol., i, 662) have been described by himself and his co-workers (compare Abstr., 1906, i, 902), and adds that if Dimroth's reasoning is correct, the problem under consideration may be regarded as having been solved years ago. E. G.

**Action of Diazo-salts on Vanillin.** ERNESTO PUXEDDU (*Gazzetta*, 1907, 37, i, 592—595).—The action of diazobenzene chloride on vanillin yields bisbenzeneazovanillin,  $C_{20}H_{16}O_3N_4$ , which crystallises from aqueous alcohol in dark chocolate-coloured, prismatic needles, m. p.  $122^\circ$ , dissolves in dilute alkali solutions giving a blood-red solution which subsequently deposits the unchanged compound, and is readily soluble in organic solvents. With phenylhydrazine, it gives a yellow compound, m. p.  $178^\circ$ , which is probably a reduction product. T. H. P.

**Oxidising Ferments. [IV.] Specific Nature of Tyrosinase and its Action on the Products of Protein Degradation.** ROBERT CHODAT and W. STAUB (*Arch. Sci. Phys. Nat.*, 1907, [iv], 24, 172—191. Compare this vol., i, 574, 575).—The oxidising action of tyrosinase on tyrosine is diminished by the presence of amino-acids, such as glycine, leucine, or alanine. Tyrosinase acts on dipeptides, such as tyrosine anhydride and glycytyrosine anhydride, giving rise to a yellow coloration which does not become subsequently red, violet, or black, as in the case of tyrosine. When, however, an amino-acid, such as glycine, leucine, or alanine, is added to the mixture, the red coloration characteristic of tyrosine is obtained. A mixture of glycytyrosine anhydride with glycine gives a rose colour changing to a bluish-green; it shows a deeper red with alanine and a deep brown with leucine. It is possible with tyrosinase to detect tyrosine in the products of peptolysis, and, with the addition of amino-acids, peptides containing tyrosine can be recognised.

Phenylalanine is not attacked by tyrosinase; the action of this ferment does not therefore depend on the presence of a benzene nucleus in an amino-acid. Tyrosinase acts markedly on *p*-cresol, less strongly on *m*-cresol, and only feebly on *o*-cresol, giving brownish-yellow or yellow solutions. The hydrogen peroxide-peroxydase system (the equivalent of laccase) behaves very differently, forming an insoluble, colourless compound with *p*-cresol, a flesh or dirty-red substance with *m*-cresol, and a deep brown compound with *o*-cresol. Tyrosinase is thus specifically different from laccase; it oxidises the homologues of phenol, in particular, those like tyrosine which have side-chains in the para-position. Millon's reagent is specific for benzene derivatives containing one hydroxyl group; unlike tyrosinase, it acts most vigorously on meta-derivatives.

The action of tyrosinase on *p*-cresol is well suited for its detection and differentiation from laccase. The addition of glycine or other amino-acids much increases the rapidity of the reaction, a violet and finally a blue solution with a red fluorescence being obtained.

E. F. A.

**Coagulation of the Proteins by the Action of Ultra-violet Light and of Radium.** GEORGES DREYER and OLAV HANSEN (*Compt. rend.*, 1907, 145, 234—236).—The action of the light from a Bang lamp on solutions of the natural proteins, serum- and egg-albumin, crystalline globulin, fibrinogen, horse-serum, syntonin, peptone, vegetable vitellin, and caseinogen, has been examined. Serum and egg-albumin and, most of all, globulin are coagulated by the intense and prolonged action of the light, both in alkaline, neutral, and acid solution, but most readily in the latter. A fibrinogen solution remains clear during illumination. Horse-serum is only slightly coagulated, but if previously acidified with acetic acid a very pronounced coagulation results. Syntonin is not coagulated either in acid or alkaline solution. Solutions of peptone and of caseinogen are not coagulated, but acquire a straw-yellow colour. Vitellin coagulates more readily than any other substance studied. Continuous illumination appears to produce a quantitative precipitation. A yellow solution of lecithin is decolorised, but remains clear.

That the phenomenon is a real coagulation and not mere precipitation is shown by the insolubility of the precipitates. It is produced by the ultra-violet rays retained by the glass. When a solution of protein thus acted on is exposed with a large free surface to the action of the light, the surface becomes covered with a protein membrane of thickness varying with the substance.

Vitellin, but not the other proteins, is coagulated by the radiation from radium.

E. H.

**Action of Neutral Salts on the Coagulation Temperature of One of the Muscular Proteins.** G. BONAMARTINI (*Gazzetta*, 1907, 37, ii, 190—200).—The author has isolated from ox-muscle a solution of a protein which coagulates at 41—42°, this temperature being influenced neither by the salts naturally accompanying the protein nor by a change in the concentration from 1 muscle : 5 water

to 1 muscle : 20 water. The influence of sodium chloride, ammonium chloride and sulphate, and magnesium sulphate in lowering the temperature of coagulation of the protein was studied, the results being given in the form of curves and tables. At definite concentrations, the various salts produce spontaneous coagulation of the protein at the ordinary temperature. The coagulation of the protein under the influence of larger or smaller proportions of salts probably yields a mixture of coagulated with precipitated protein in some cases, and precipitated protein only in others. Indeed, the coagulum obtained by means of ammonium chloride or sulphate at  $14.5^{\circ}$  re-dissolves completely in water, and all the coagulums obtained at temperatures lower than that of true coagulation are more or less soluble in water.

T. H. P.

**Fractionation of Agglutinins and Antitoxin.** ROBERT B. GIBSON and KATHARINE R. COLLINS (*J. Biol. Chem.*, 1907, 3, 233—251); EDWIN J. BANZHAF and ROBERT B. GIBSON (*ibid.*, 253—264).—Researches of others, and the present investigations, show the untrustworthiness of any differentiation of antitoxins, &c., as contained in the various protein fractions separable by salting-out (pseudoglobulin, euglobulin, &c.). The same is true for agglutinins.

The globulin obtained by saturation of serum with sodium chloride is more potent in antitoxin per gram of protein than the fractions precipitated by lower concentrations of ammonium sulphate, and it is practicable by such a method to prepare a solution of high antitoxic value from relatively weak plasma.

W. D. H.

**Hydrolysis of Nucleoproteins.** E. CARAPELLE (*Centr. Bakt. Par.*, 1907, i, 44, 440—441).—The nucleoprotein obtained from *Bacillus prodigiosus*, grown on large Petri dishes, by extraction with dilute sodium carbonate and precipitation with acetic acid, was hydrolysed with sulphuric acid, the solution neutralised, and evaporated to dryness. The alcoholic extract of the residue gave a syrup which, when dissolved in water, was dextrorotatory, reduced Fehling's solution and ammoniacal silver nitrate, and formed a yellow phenylosazone, m. p.  $185^{\circ}$ , after crystallisation from xylene.

E. F. A.

**Koilin.** K. B. HOFMANN and FRITZ PREGL (*Zeitsch. physiol. Chem.*, 1907, 52, 448—471).—The horny material constituting the cuticle of the birds' stomach is termed *koilin*. This substance does not belong to the keratins, as the cystin group is either entirely absent or present in only minute quantities. It cannot be grouped with the *membrana testacea* of the hen.

The *membrana testacea* does not consist of keratin, and the name ovokeratin should not be used for this material, and neither it nor koilin can be grouped with any of the ordinary sub-groups of the proteins.

J. J. S.

## Organic Chemistry.

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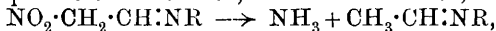
**Preparation of Tetranitromethane.** CONRAD CLAESSEN (D.R.-P. 184229).—The production of tetranitromethane from nitroform, which is itself obtained with difficulty from explosive substances such as mercury fulminate, is too dangerous to admit of this process being employed on a large scale. It is now found that the aromatic hydrocarbons and their nitro-derivatives when warmed with a mixture of nitric-sulphuric acid (40%  $\text{H}_2\text{SO}_4$ , 60%  $\text{HNO}_3$ ) and fuming sulphuric acid (50%  $\text{SO}_3$ ) furnish a large amount of tetranitromethane; a yield of 50% on the weight of the organic substance being sometimes obtained. Nitrobenzene when gradually heated with excess of the acid mixture to  $120^\circ$  is decomposed, giving rise to tetranitromethane and a large amount of nitrous fumes. G. T. M.

**Improved Method for the Preparation of Alkyl Chlorides.** WILLIAM M. DEHN and GRANT T. DAVIS (*J. Amer. Chem. Soc.*, 1907, 29, 1328—1334).—A method is described for the preparation of alkyl chlorides by the action of phosphorus trichloride on alcohols in presence of zinc chloride. Propyl chloride has been obtained in a yield amounting to 94% of the theoretical by the use of anhydrous zinc chloride. It has been found that, if a solution of zinc chloride (b. p.  $150$ — $160^\circ$ ) is used instead of the anhydrous salt, the yield of propyl chloride is decreased, but that in the case of *isobutyl* and *isoamyl* chlorides larger yields (85% and 88% respectively) are produced.

The reaction takes place in accordance with the equation:  $6\text{ROH} + 2\text{PCl}_3 + \text{ZnCl}_2 = \text{Zn}(\text{H}_2\text{PO}_3)_2 + 6\text{RCl} + 2\text{HCl}$ . Evidence has been obtained, however, of the formation of complex intermediate products.

By the action of stannic chloride on propyl alcohol, an additive compound, b. p.  $148^\circ$ , is obtained. E. G.

**Constitution of Methazonic Acid.** WILHELM MEISTER (*Ber.*, 1907, 40, 3435—3449. Compare Dunstan and Goulding, *Trans.*, 1900, 77, 1262; Scholl, *Abstr.*, 1901, i, 359).—Methazonic acid behaves as a primary nitro-compound, since it gives the nitrolic acid reaction and Konowaloff's reaction, and hence contains the grouping  $\cdot\text{CH}_2\cdot\text{NO}_2$ . It reacts with primary aromatic amines and hydrazines, yielding products which also contain the primary nitro-group. These products are formed by the replacement of  $\text{NHO}$  by  $\cdot\text{NR}$ , and hydroxylamine is also formed. The reactions are most readily explained by the presence of the oximino-group in methazonic acid, and the formula thus arrived at is  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}:\text{N}\cdot\text{OH}$ . When the condensation products are reduced, ammonia is formed,



and the residue, when distilled with acid, yields an amine and acet-

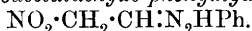
aldehyde,  $\text{CH}_3\cdot\text{CH}\cdot\text{NR} + \text{H}_2\text{O} \rightarrow \text{CH}_3\cdot\text{CHO} + \text{NH}_2\text{R}$ . They closely resemble Schiff's bases.

An isonitro-formula,  $\beta$ -isonitroacetaldoxime,  
 $\text{OH}\cdot\text{NO}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ ,

is also possible. The formation and reactions of methazonic acid are discussed from the point of view of the new formula.

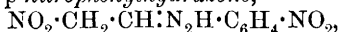
Attempts have been made to synthesise methazonic acid from  $\beta$ -chloro- or  $\beta$ -iodo-acetaldoxime and silver nitrite, but without success.

Methazonic acid and phenylhydrazine in the presence of hydrochloric acid yield  $\beta$ -nitroacetaldehyde-phenylhydrazone,



It may be crystallised in small amounts (0.1–0.2 gram) from light petroleum and forms glistening, white plates, m. p. 74–74.5°. When kept in closed vessels, it rapidly decomposes, but can be kept at 0° in open vessels if protected from sunlight. It dissolves in alkalis, gives the nitrolic acid reaction, and yields precipitates with the salts of the heavy metals.

Nitroacetaldehyde-p-nitrophenylhydrazone,



forms orange-brown flakes which decompose at 141–142°.

$\beta$ -Nitroethylidene-p-chloroanil,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ , obtained from the acid and p-chloroaniline, crystallises from light petroleum in minute, canary-yellow needles decomposing at about 165°. The corresponding p-nitroanil,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , crystallises from chloroform in shimmering, yellow needles which decompose at about 183°.

$\beta$ -Nitroethylideneanil,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}$ , forms golden-yellow needles, m. p. 94–95° after sintering at 90°.

When hydrolysed with alkali, the p-chloroanil yields p-chloroaniline, ammonia, hydrogen cyanide, formic acid, methazonic acid, and carbon dioxide. With acids, the same compound yields the same products with the exception of ammonia and methazonic acid, hydroxylamine being formed in place of ammonia.

J. J. S.

**The Series Resulting from the Methylation of Ethyl Alcohol, with Regard to the Aptitude for Isomeric Change of the Halide Ethers.** LOUIS HENRY (*Compt. rend.*, 1907, 145, 547–549).—A comparison is given of the facility with which the halide ethers derived from the ethyl halides,  $\text{CH}_3\cdot\text{CH}_2\text{X}$ , by replacement (1) in the  $\cdot\text{CH}_3$  group exclusively; (2) in the  $\cdot\text{CH}_2\text{X}$  group exclusively, and (3) in the  $\cdot\text{CH}_3$  and  $\cdot\text{CH}_2\text{X}$  group simultaneously of hydrogen by methyl, undergo isomeric change. (1) The normal propyl derivatives change into the isocompounds, the isobutyl more readily into the tertiary butyl, and the trimethylethyl halides still more readily into the tertiary amyl derivatives. (2) The isopropyl and tert.-butyl halides do not change isomerically. (3) The secondary butyl halides are stable, but the methylisopropyl carbinol and the methyl tert.-butyl carbinol halide ethers are easily transformed into tertiary halide derivatives. The tertiary halide compounds are stable. This review reveals the fact that isomeric change occurs the more



readily the less the number of hydrogen atoms combined with the carbon atom attached to the halide-ether chain. Thus the abundant presence of hydrogen confers stability on the polycarbon chains.

E. H.

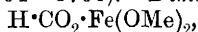
**Beeswax.** II. **Psyllostearyl Alcohol as a Constituent.** ERNST EDW. SUNDWIK (*Zeitsch. physiol. Chem.*, 1907, 53, 365—369. Compare Abstr., 1898, i, 617; 1901, i, 358).—By the use of improved methods, the surmise that psyllostearyl alcohol is present in beeswax was confirmed. The wax of *Bombus terrestris* was used in the present instance, acetone being used as the extracting agent. W. D. H.

**Propylene Oxide,**  $\begin{array}{c} \text{CHMe} \\ | \\ \text{CH}_2 \end{array} \text{---} \text{O}$ . LOUIS HENRY (*Compt. rend.*, 1907, 145, 453—456).—The action of magnesium ethyl bromide on propylene oxide has been studied in order to ascertain whether it gives rise to a product by simple addition as in the case of ethylene oxide (this vol., i, 745), or whether isomeric change initially occurs as with *s*-dimethylethylene oxide (this vol., i, 817) and *as*-dimethylethylene oxide (this vol., i, 744). The product actually obtained was methyl-*n*-propylcarbinol,  $\text{CHMePr} \cdot \text{OH}$ , which was identified by means of the semicarbazone (m. p. 100°) of the ketone,  $\text{COMePr}$ , formed on oxidation. The behaviour of propylene oxide is thus similar to that of ethylene oxide; the substitution of a single methyl group is not sufficient to bring about the possibility of undergoing isomeric change which exists in the dimethylated derivatives. It is to be observed that epichlorohydrin on combining with magnesium ethyl bromide gives  $\alpha$ -chloro- $\gamma$ -hydroxy- $\beta$ -ethylpropane,  
 $\text{CH}_2\text{Cl} \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{OH}$ . W. A. D.

**Bisecundary Butylene Monochlorohydrin,**  
 $\text{OH} \cdot \text{CHMe} \cdot \text{CHMeCl}$ .

LOUIS HENRY (*Compt. rend.*, 1907, 145, 498—499).—*Bisecundary butylene monochlorohydrin* ( $\gamma$ -chloro-*sec*-butyl alcohol) is prepared by the addition of hypochlorous acid to *s*-dimethylethylene obtained by the action of alcoholic potash on *sec*-butyl iodide,  $\text{CHMeEtI}$ ; it is a colourless, somewhat viscous liquid, soluble in about 15 vols. of water at 20°,  $D_{20}^{20}$  1.105,  $\mu$  1.44376, mol. refraction 26.05 (calc. 26.98), b. p. 138—139°/753 mm. It is very sensitive to alkalis and alkali carbonates, being converted into *s*-dimethylethylene oxide,  $\begin{array}{c} \text{CHMe} \\ | \\ \text{CHMe} \end{array} \text{---} \text{O}$  (b. p. 56°). W. A. D.

**Crystalline Iron Methoxides.** KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1907, 40, 3764—3766).—*Dimethoxyferric formate*,



and *dimethoxyferric acetate*,  $\text{Me} \cdot \text{CO}_2 \cdot \text{Fe}(\text{OMe})_2$ , are obtained by dissolving iron wire in formic or acetic acid, evaporating the solution, and treating the residue with methyl alcohol in an atmosphere of carbon dioxide; both form yellow, double-refracting crystals, yield formaldehyde in contact with a glowing copper spiral, and decompose

gradually in contact with water and immediately with hydrochloric acid, the solution showing the reactions of a ferric salt.

The formation of these compounds depends on the esterification of the basic ferric salts formed intermediately (compare Hofmann and Höchtlein, Abstr., 1905, i, 38).

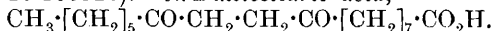
The substance,  $(\text{MeCO}_2)_2\text{Fe}\cdot\text{OEt}$ , is a red powder, which is obtained by the evaporation in a vacuum of an ethyl-alcoholic solution of ferrous acetate after rapid oxidation in air. C. S.

**Some Salts of Glucinum and Zirconium.** SEBASTIAN TANATAR and E. KURORSKI (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 936—943. Compare this vol., i, 261).—The salts obtained by the action of organic acids on glucinum carbonate mostly correspond with the formula  $\text{Gl}_4\text{OX}_6$ . They are non-volatile, but most are soluble in benzene, some also in other organic solvents and in water. In the liquid state they are non-conductors of electricity. The following salts are described. *Formate* [the compound  $\text{Gl}(\text{CHO}_2)_2$  was also obtained], *crotonate*, *isocrotonate*, *lævulate*, and *propionate*. Glucinum also forms compounds of the type  $\text{Gl}_4\text{OX}_2\text{X}'_4$  and  $\text{Gl}_4\text{OX}_3\text{X}'_3$ ; thus, by heating glucinum butyrate with acetyl chloride, the compound  $\text{Gl}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_4(\text{C}_2\text{H}_3\text{O}_2)_2$  is obtained as a viscous liquid solidifying at  $-15^\circ$ , b. p.  $351^\circ$ . Similarly, the compound  $\text{Gl}_4\text{O}(\text{C}_3\text{H}_5\text{O}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_3$  was obtained as a crystalline substance, m. p.  $127^\circ$ , b. p.  $330^\circ$ . The normal salts of glucinum with dibasic acids can be obtained quite readily; the following are described: *succinate*, *citraconate*, *maleate*, and *fumarate*. The salts of glucinum are very similar in constitution and solubility to the corresponding zirconium salts. Zirconium *propionate*, *isobutyrate*, *crotonate*, and *succinate* are described. The quadrivalency of glucinum is again insisted on; thus the compounds formed by the metals of the fourth group with acetylacetone are analogous in properties to the corresponding glucinum compound, whereas the compounds of the metals of the second group are quite different. Z. K.

**Preparation of Double Lactates containing Antimony.** CHEMISCHE FABRIK VON HEYDEN (AKTIEN-GESELLSCHAFT) (D.R.-P. 184202).—Antimonyl sulphate, obtained by the action of sulphuric acid on antimonious sulphide, is introduced into a neutral solution of sodium lactate, the solution is concentrated until the sodium sulphate has separated, and the filtrate then evaporated to dryness. The *sodium antimonyl lactate* thus obtained is a crystalline double salt which dissolves in water without decomposition. *Sodium calcium antimonyl lactate*, a soluble, crystalline, slightly hygroscopic salt, is obtained by partially replacing sodium lactate by the corresponding calcium salt in the foregoing double decomposition.

G. T. M.

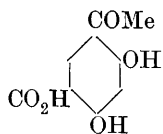
**Preparation of  $\theta\kappa$ -Diketostearic Acid.** ANDREAS G. GOLDSOBEL (D.R.-P. 180926).— $\theta\kappa$ -Diketostearic acid,



m. p.  $96.5^{\circ}$ , obtained by oxidising  $\theta$ -ketohydroxystearic acid with chromic and acetic acids, was crystallised from water and obtained in white, lustrous leaflets soluble in warm alcohol or benzene. With the exception of its sparingly soluble alkali and ammonium compounds, its salts are insoluble in water. This acid behaves as a  $\delta$ -diketone, and owing to this circumstance yields derivatives of technical importance. Its *dioxime*, m. p.  $113$ — $114^{\circ}$ , and its *pyrrole* derivative,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \overset{\text{CH}}{\underset{\text{||}}{\text{C}}} \cdot \text{NH} \cdot \overset{\text{CH}}{\underset{\text{||}}{\text{C}}} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$ , have been prepared.

G. T. M.

**Xanthophanic Acid. II.** CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1907, 40, 3570—3583. Compare Abstr., 1906, i, 556).—The products obtained from xanthophanic acid methyl and ethyl ethers have been further investigated. The acid, m. p.  $256^{\circ}$  ( $255^{\circ}$ : *loc. cit.*), obtained from the magnesium methoxide “transformation product” of xanthophanic acid methyl or ethyl ether, is shown to be a resacetophenonecarboxylic acid, having probably the annexed structure; the *bromophenylhydrazone* of this,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$ , crystallises in white needles, m. p.  $243^{\circ}$ . The acid cannot be esterified by means of alcohol and hydrogen chloride. The *methyl* ester,  $\text{C}_{10}\text{H}_{10}\text{O}_5$ , formed by the action of methyl iodide on the silver salt, crystallises in colourless needles, m. p.  $124$ — $125^{\circ}$ , is hydrolysed by boiling alkalis, and when treated with hydrazine hydrate in methyl-alcoholic solution yields a white *hydrazone*, m. p.  $174^{\circ}$ , solidifying to a yellow substance, m. p. above  $300^{\circ}$ .

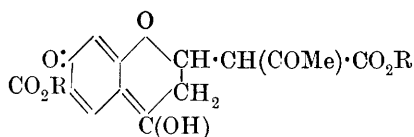


The *bromophenylhydrazone*,  $\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{Br}$ , m. p.  $224^{\circ}$  (*loc. cit.*), has the constitution  $\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$ , and is a hydrazone, not of the “transformation product” from which it is prepared, but of methyl resacetophenonecarboxylate; when heated with hydrogen chloride in glacial acetic acid at  $125$ — $130^{\circ}$ , it yields a mixture of resacetophenonecarboxylic acid and its methyl ester.

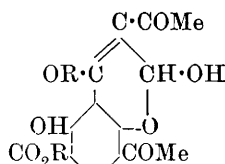
The “transformation products,” m. p.  $162^{\circ}$ , obtained by the action of magnesium methoxide on xanthophanic acid methyl and ethyl ethers respectively, are not identical, as they yield different bromides on treatment with hydrogen bromide in benzene solution. The *bromide*,  $\text{C}_{17}\text{H}_{17}\text{O}_7\text{Br}$ , derived from the ethyl ester, crystallises in lemon-yellow needles, m. p.  $208^{\circ}$  (decomp.), and when shaken with methyl or ethyl alcohol, acetone, or water is hydrolysed, yielding the “transformation product,”  $\text{C}_{17}\text{H}_{18}\text{O}_8$ . The *bromide*,  $\text{C}_{16}\text{H}_{15}\text{O}_7\text{Br}$ , derived from the methyl ester, crystallises in similar needles, m. p.  $188^{\circ}$  (decomp.), and on hydrolysis yields the “transformation product,”  $\text{C}_{16}\text{H}_{16}\text{O}_8$ .

The constitutions of these substances are discussed; it is concluded that the xanthophanic acid ethers have the structure I, and under the influence of magnesium methoxide are transformed into derivatives of the type II. In the transformation of the ethyl ether, a methyl is substituted for the carboxylic ethyl group. The hydroxyl substi-

tuted by bromine by the action of hydrogen bromide is that in the heterocyclic nucleus:



I.



II.

When boiled with hydrazine sulphate and sodium acetate in alcoholic



solution, xanthophanic acid ethyl ether forms a *hydrazone* crystallising in white needles, m. p. 193—195°, which is considered to have the annexed constitution, and is formed also by the action of semicarbazide on the ethyl ether.

The corresponding *hydrazone*,  $C_{11}H_{10}O_4N_2$ , derived from the methyl ether, crystallises in needles, m. p. 220°. When heated with fuming hydrochloric acid or hydrogen iodide in acetic anhydride or 10% alkali, these hydrazones yield the *acid*,  $C_{10}H_8O_4N_2$ , crystallising in yellowish-green needles, m. p. 331—333° (decomp.), and forming solutions with slight blue fluorescence.

G. Y.

**Glaucophanic Acid. III.** CARL LIEBERMANN and H. TRUCHSÄSS (*Ber.*, 1907, 40, 3584—3588. Compare Abstr., 1906, i, 556; and preceding abstract).—Glaucophanic acid methyl and ethyl ethers, which are formed as by-products in the preparation of xanthophanic acid methyl and ethyl ethers respectively, undergo reactions similar to those of the xanthophanic acid ethers, differing only in that the methyl and ethyl ethers yield identical magnesium methoxide “transformation products.” In the case of glaucophanic acid ethyl ether, therefore, the action of magnesium methoxide must lead to complete substitution of the ethoxy- by methoxy-groups, whereas only the carboxylic ethoxy-group of xanthophanic acid ethyl ether is substituted. The glaucophanic acid and xanthophanic acid ethers must have a  $C_{12}$  nucleus in common, as the action of hydrazine sulphate and sodium acetate on glaucophanic acid ethyl ether leads to the formation of the hydrazone, m. p. 193—195°, obtained from xanthophanic acid ethyl ether.

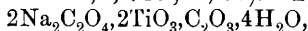
The magnesium methoxide “transformation product,”  $C_{20}H_{18}O_9$ , is formed from glaucophanic acid methyl ether in a 79% yield; it crystallises in yellow needles, m. p. 217°, and when heated with acetic anhydride and sodium acetate yields a *triacetate*,  $C_{20}H_{15}O_9Ac_3$ , which crystallises in needles, m. p. 130°, and is hydrolysed to the “transformation product” by cold concentrated sulphuric acid. In presence of a limited amount of acetic anhydride, a yellow *diacetate*,  $C_{20}H_{16}O_9Ac_2$ , m. p. 166°, is formed. The *bromide*,  $C_{20}H_{17}O_8Br$ , crystallises in orange-red needles, m. p. 245°, and is stable when dry, but is readily hydrolysed by moist solvents. A *dibromo-compound*,  $C_{20}H_{16}O_8Br_2$  or  $C_{20}H_{18}O_8Br_2$ , formed by the action of bromine on the

"transformation product" in carbon disulphide solution, separates from ethyl acetate in crystals, m. p.  $225^{\circ}$  (decomp.).

The "transformation product" forms a *hydrazone*,  $C_{20}H_{20}O_8N_2$ , crystallising in white needles, m. p.  $217^{\circ}$  (decomp.), but when heated with bromophenylhydrazine in boiling methyl-alcoholic solution forms the *bromophenylhydrazone* of a decomposition product,  $C_{17}H_{17}O_4N_2Br$ , which crystallises in needles, m. p.  $161-163^{\circ}$  (decomp.), and resembles, but is not identical with, the bromophenylhydrazone obtained from the "transformation product" of xanthophanic acid methyl ether.

The mol. formula of glaucophanic acid ethyl ether, which remains undecided, must lie between  $C_{23}$  and  $C_{27}$  (compare Claisen, *Abstr.*, 1897, i, 594).  
G. Y.

**Certain Complex Salts of Titanium Peroxide.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 265-273, 349-352; compare this vol., i, 748; ii, 54).—The compound,



prepared by adding excess of hydrogen peroxide to a solution of sodium titano-oxalate and precipitated from solution by the addition of alcohol, is a dense, dark orange, sandy powder, which dissolves readily in water and is extremely hygroscopic in presence of alcohol. It remains unaltered for some time in a dry atmosphere, but in ordinary air it deliquesces, swells, and begins to decompose. The corresponding *potassium* compound,  $2K_2C_2O_4, 2TiO_3, C_2O_3, 2H_2O$ , prepared by adding alcoholic potassium acetate solution to alcoholic titanium hydrogen oxalate solution containing hydrogen peroxide, resembles the sodium derivative.

By adding an insufficient amount of barium chloride, together with ammonium acetate, to a solution of sodium titano-oxalate containing the three constituents in the proportions  $TiO_2 : 2H_2C_2O_4 : 2Na$  and mixed with hydrogen peroxide, various fractions are precipitated which consist apparently of mixtures of  $2BaC_2O_4$ ,  $2TiO_3$ ,  $C_2O_3$ , and  $BaC_2O_4$ .

The complexity of the titano-oxalates is shown by the ease with which they can be recrystallised, almost unchanged, from their solutions and by their resistance to hydrolysis by the action of heat. That the degree of complexity is not high is seen from the fact that these salts are decomposed, not only by alkalis, but even by an excess of a barium or calcium salt (compare Rosenheim and Schütte, *Abstr.*, 1901, ii, 244). The alkali pertitano-oxalates, however, are more highly complex, since they are not completely precipitated by ammonia. The introduction of active oxygen into the molecule of titanium oxide is hence, in general, favourable to the formation of complex anions. The statement of Melikoff and Pissarjewsky (*Abstr.*, 1898, ii, 374) that, in the preparation of titanium peroxide, by Classen's method, the clear liquid at first contains an ammonium pertitanate, which decomposes with precipitation of  $TiO_3 \cdot Aq$ , is probably inaccurate; it is more likely that the  $TiO_3$  is present initially as a complex anion, which is gradually decomposed by the alkali.

The so-called acetate of titanium peroxide (Faber, this vol., ii, 557) is most probably a mixture of peroxide and basic acetate of titanium

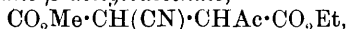
dioxide. The existence of the phosphate is in accord with the views of the author (*loc. cit.*). T. H. P.

**Velocity of the Decomposition of Malonic Acid into Carbon Dioxide and Acetic Acid.** JOSEF LINDNER (*Monatsh.*, 1907, 28, 1041—1047).—The decomposition of malonic acid into carbon dioxide and acetic acid takes place with measurable velocity in glacial acetic acid at 100°. The velocity constant when calculated with the aid of the equation for unimolecular reactions remains satisfactorily uniform throughout the course of the decomposition. The graph formed by plotting the velocity constants determined at 98.5° to 104° against the temperatures is approximately a straight line. G. Y.

**Action of  $\alpha$ -Chloroacetoacetic Esters on Sodiocyanoacetic Esters.** J. CHASSAGNE (*Bull. Soc. chim.*, 1907, [iv], 1, 914—916. Compare Haller and Barthe, *Abstr.*, 1888, 937).—*Ethyl  $\alpha$ -cyano- $\beta$ -acetylsuccinate*,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , prepared by the action of ethyl  $\alpha$ -chloroacetoacetate on ethyl sodiocyanoacetate, separates from alcohol in crystals, m. p. 83.5—84.5° (corr.), and has the normal molecular weight in freezing acetic acid.

*Methyl  $\alpha$ -cyano- $\beta$ -acetylsuccinate*,  $\text{CO}_2\text{Me}\cdot\text{CH}(\text{CN})\cdot\text{CHAc}\cdot\text{CO}_2\text{Me}$ , similarly prepared, separates in crystals, m. p. 89.5—90.5°.

*Methyl ethyl  $\alpha$ -cyano- $\beta$ -acetylsuccinate*,



obtained by the interaction of ethyl  $\alpha$ -chloroacetylacetate and methyl sodiocyanoacetate, forms crystals, m. p. 93.5—94.5°. The *isomeric ester*,  $\text{CO}_2\text{Me}\cdot\text{CHAc}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , prepared from methyl  $\alpha$ -chloroacetylacetate and ethyl sodiocyanoacetate, has m. p. 88.5—89.5°.

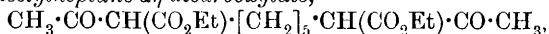
Since these compounds in alcoholic solution give no red coloration with ferric chloride, it is possible that they have an enolic structure.

T. H. P.

**Conversion of Methyl Alcohol into Formaldehyde. Preparation of Formalin.** E. J. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 855—868).—Experiment shows that the ordinarily accepted view of the conversion of methyl alcohol into formaldehyde as well as the ordinary method of preparation are essentially wrong. An elaborate apparatus has been devised which yields satisfactory results for technical purposes. The first stage in the reaction is the catalytic decomposition of methyl alcohol, thus:  $\text{MeOH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$ . The catalysts employed were freshly reduced copper and asbestos containing precipitated lower oxides of vanadium. The former is the most efficient catalyst, but not more than 60% of the alcohol is ever thus changed. In addition, the formaldehyde decomposes, forming carbon monoxide and hydrogen, which together with carbon dioxide are generally found in the gaseous products. The presence of impurities such as acetone makes no difference in the decomposition of the alcohol. Z. K.

**The Effect of Light and Temperature on the Preservation of Formaldehyde Solutions.** J. W. de WAAL (*Pharm. Weekblad*, 1907, **44**, 1207—1213).—At the ordinary temperature when exposed to light, formaldehyde solutions are not oxidised to formic acid, even in presence of traces of ferric chloride. Rise of temperature promotes the oxidation somewhat, although the effect produced by a temperature of 50° during 400 hours is only slight. A. J. W.

**Synthesis of Ketones by aid of Dibromopentane.** JULIUS VON BRAUN (*Ber.*, 1907, **40**, 3943—3948. Compare Perkin and Freer, *Trans.*, 1888, **53**, 202; Perkin and Kipping, *ibid.*, 1890, **57**, 320).— $\alpha$ -Dibromopentane, ethyl acetoacetate, and sodium react in warm alcoholic solution to form two compounds. *Ethyl 1-acetylcyclohexane carboxylate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_{10}\cdot\text{COMe}$ , b. p. 241—245° (decomp.), or 120—124°/11 mm., is a colourless liquid with a piercing aromatic odour, which forms a *semicarbazone*, m. p. 144°, and a *p-nitrophenylhydrazone*, m. p. 145°, and is hydrolysed by aqueous-alcoholic alkali, yielding *cyclohexanecarboxylic acid* and Darzens' and Bouveault's methyl *cyclohexanyl ketone*, which has  $D^{22}_D$  0.893 and forms a reddish-violet *p-nitrophenylhydrazone*, m. p. 154°. The second compound is *ethyl  $\alpha$ -diacetylheptane- $\alpha$ -dicarboxylate*,



which is very difficultly volatile with steam, and cannot be distilled without decomposing into the *diketone*,  $\text{COMe}\cdot[\text{CH}_2]_7\cdot\text{COMe}$ , the formation of which is completed by boiling with alkali. The diketone, m. p. 65°, crystallises in glistening leaflets, and forms a *semicarbazone*,  $\text{C}_{13}\text{H}_{26}\text{O}_2\text{N}_4$ , m. p. 184°, *p-nitrophenylhydrazone*,  $\text{C}_{23}\text{H}_{30}\text{O}_4\text{N}_6$ , m. p. 88°, softening at 85°, and an oxime which yields apparently a mixture of two benzoyl derivatives, of which one has been isolated and has m. p. 90°. C. S.

**Isolation of Carbohydrates and Glucosides by Precipitation with Metallic Salts.** G. MEILLÈRE (*J. Pharm. Chim.*, 1907, **26**, 300—304).—The method of precipitating carbohydrates and glucosides by means of the lead acetates under different conditions is discussed, and attention is drawn to various causes which tend to complicate the fractional precipitation. It is shown that copper acetate may be employed in place of lead acetate for precipitating glucosides, the only difference being that the precipitates are most readily formed in hot solutions. Fractional precipitation may be accomplished by working in acetic acid, neutral, and finally in ammoniacal solutions.

The copper method does not yield good results with many carbohydrates, especially lactose and maltose, as they reduce the copper salt, but may be employed for isolating inositol provided the liquid is neutralised with ammonia. J. J. S.

**Action of Cold Aqueous Sodium Hydroxide on Cellulose.** WALTHER VIEWEG (*Ber.*, 1907, **40**, 3876—3883).—Wichelhaus and the author (this vol., i, 186) have shown that natural and mercerised cellulose differ from one another in chemical properties. The author now shows the effect of the variation in strength of the sodium

hydroxide on cellulose. Experiments are quoted to show the amount of sodium hydroxide taken up by cellulose from alkaline solutions of varying concentration; the conclusion is drawn that a chemical action takes place. The compounds of sodium hydroxide and cellulose are completely decomposed by water, and a product remains which takes up more sodium hydroxide than the original cellulose. Specimens of cellulose were found to differ with respect to the amount of sodium hydroxide which they take up; the "degree of mercerisation" varies from 1 to 3%, and may be estimated by the Schotten-Baumann method.

A. McK.

#### Chemistry and Physiological Action of the Humic Acids.

R. A. ROBERTSON, JAMES C. IRVINE, and MILDRED E. DOBSON (*Bio-Chem. J.*, 1907, 2, 458—480).—The natural humic acids prepared from peat differ greatly in composition, and also from the artificial form prepared from sucrose. The acids themselves and their potassium salts serve as organic food for *Penicillium*, both as regards carbon and nitrogen.

W. D. H.

**Further Observations on the Behaviour of Alkyl Attached to Nitrogen towards Boiling Hydriodic Acid.** GUIDO GOLDSCHMIEDT (*Monatsh.*, 1907, 28, 1063—1068. Compare this vol., i, 30; Goldschmiedt and Hönigschmid, *Abstr.*, 1904, ii, 94).—Whilst many substances containing an alkyl group attached to nitrogen have been found when boiled with hydriodic acid to yield the alkyl iodide, with greater or less ease depending on the structure of the nucleus, only negative results have been obtained previously with aliphatic compounds, including tetramethylammonium iodide, benzyldimethylamine, and compounds such as betaine, sarcosine, and methylaminoacetophenone, containing the grouping  $\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{NMe}$ , which in the piperidine series yields methyl iodide with special ease. The behaviour towards boiling hydriodic acid of a number of compounds having the group  $\text{N}\cdot\text{Alkyl}$  attached to a tertiary aliphatic carbon has now been investigated, as such substances resemble aromatic compounds in certain respects.

When boiled with hydriodic acid, b. p.  $127^\circ$ , for six hours, and then for a further six hours with hydriodic acid, D 1.9, the following substances yield the percentages quoted of the *N*-alkyl group as the alkyl iodide: 1:2:4:4-tetramethyltrimethyleneimine, 5.4%; 2:4:4-trimethyl-1-ethyl-trimethyleneimine, 2.5%; methylldiacetonealkamine, 7.0%; methylpropyldiacetonealkamine, 20.5%;  $\beta$ -dimethylamino- $\beta$ -methyl- $\Delta^5$ -pentene, 4.4%. On the other hand,  $\alpha$ -methylamino- $\alpha$ -phenylbutan- $\gamma$ -ol, in which the methylamino-group is attached to a secondary carbon atom, does not yield methyl iodide. Since the propyl group must be less reactive than the ethyl group, the high result obtained with methylpropyldiacetonealkamine cannot be ascribed to the formation of propyl iodide.

Whilst the average stability of the methyl groups of a dimethylarylamine is greater than the stability of the methyl of a methylarylamine, the average stability of the methyls of a trimethylarylammonium iodide is much smaller, and the velocity of the formation

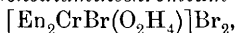


of methyl iodide correspondingly greater. Thus methylaniline in sixteen and a half hours yields 3·4%, dimethylaniline in eleven and a half hours, 3·9%, and phenyltrimethylammonium iodide in two hours, 6·5% of the total methyl as methyl iodide. Of interest as compared with the behaviour of dimethylaniline is that of tetramethylbenzidine, which in eleven and a half hours yields 7·02% of its methyl as methyl iodide.

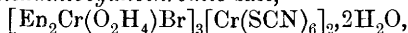
When boiled with hydriodic acid, *as*-phenylmethylhydrazine yields 2·93% of the methyl as methyl iodide; at the same time, free iodine is formed in consequence of the reduction of the hydrazine. Which of these is the primary reaction cannot be decided. G. Y.

**Bisaquochromium Salts.** PAUL PFEIFFER [and, in part, ARMIN TRIESCHMANN, STERN, and PRADE] (*Ber.*, 1907, 40, 3828—3839).—A number of salts of the diethylenediaminechromium series have been prepared corresponding with the recently described diaquotetraamminechromium salts (Pfeiffer, this vol., ii, 694). In each case, however, it is found that the diethylenediamine salt contains twice the quantity of water not removed in a desiccator which is present in the corresponding diethylenediamine compound; consequently it is necessary to assume that the single water molecules in the metal complex of the diamine salt are replaced by  $O_2H_4$  molecules in the diethylene-diamine compound. The author proposes to name such salts containing the  $O_2H_4$  complex, *bisaquo*-salts (compare Werner and Gubser, *Abstr.*, 1906, ii, 452).

*cis-Bromobisaquodiethylenediaminechromium bromide,*

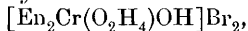


was originally wrongly described as a monoaquo-salt (*Abstr.*, 1905, i, 34). A concentrated solution of the salt yields with potassium iodide the *iodide*, a brilliant, crystalline, red powder; with potassium thiocyanate, the orange *cis-dithiocyanodiethylenediaminechromium thiocyanate*,  $[En_2Cr(SCN)_2]SCN$ ; with ammonium oxalate, the bordeaux-red *double salt*,  $[En_2CrC_2O_4][EnCr(C_2O_4)_2]$ ; with potassium chromithiocyanate, the *hexathiocyanochromic salt*,

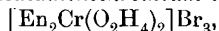


crystallising in brilliant, violet-red, transparent needles, which are decomposed by light. Concentrated nitric acid probably converts the bromide into the *nitrate*: obtained as an orange-red precipitate.

*cis-Hydroxybisaquodiethylenediaminechromium bromide,*



prepared by the action of pyridine on the bromobisaquo-bromide, forms compact, bordeaux-red crystals. A concentrated solution of the salt gives with silver nitrate a precipitate of silver bromide free from silver hydroxide; with potassium iodide, a red, crystalline precipitate of the *iodide*. Concentrated hydrobromic acid converts the salt into *cis-dibisaquodiethylenediaminechromium bromide*,



crystallising in small, orange-red, transparent plates. This salt is converted by pyridine into the hydroxybisaquo-bromide and slowly by hydrobromic acid at the ordinary temperature into the bromobisaquo-bromide. A concentrated aqueous solution of the salt yields with

solid potassium oxalate, small, brilliant, orange leaflets of the *oxalate*. The salt is converted when heated alone at 100—120°, also when evaporated with hydrobromic acid on a water-bath, into the *anhydrous* form of *cis-dibromodiethylenediaminechromium bromide*,  $[\text{En}_2\text{CrBr}_2]\text{Br}$ . This substance is also obtained, by evaporating a solution of the bromobisquo-bromide with a drop of hydrobromic acid on a water-bath, in the form of a violet powder. The anhydrous salt is converted by small quantities of water into a *monohydrate*: obtained as a fine crystalline, violet powder. The *iodide* forms glittering, violet leaflets; the *dithionate* forms brilliant bluish-violet needles; the *nitrate* is obtained as a violet powder. W. H. G.

**Complex Derivatives of Optically-Active *l*-Propylenediamine.** LEO TSCHUGAEFF and W. SOKOLOFF (*Ber.*, 1907, 40, 3461—3465).—The great increase in optical activity caused by the addition of certain salts to various optically-active compounds, containing hydroxy-groups, has been ascribed by Walden and others to the formation of cyclic complexes. The influence of ring formation on rotation has been investigated by the authors with certain metal derivatives of *l*-propylenediamine, the cyclic nature of metallic derivatives of *dl*-propylenediamine having already been demonstrated by Werner.

*l*-Propylenediamine, obtained by the resolution of the *dl*-base by *d*-tartaric acid, has b. p. 121°,  $D_4^{23}$  0.8633,  $[\alpha]_D - 28.04^\circ$ , whereas Baumann gives  $D_4^{24.3}$  0.91186 and  $[\alpha]_D - 20.96^\circ$ .

*l*-Propylenediamine hydrochloride,  $\text{C}_3\text{H}_6(\text{NH}_2)_2 \cdot 2\text{HCl}$ , has m. p. 240°,  $D_4^{25}$  1.0575, and  $[\alpha]_D^{25} - 4.04^\circ$  (in aqueous solution,  $p = 19.92$ ).

The platinum compounds studied were prepared by the interaction of platinum *cis*-dichloro-*l*-propylenediamine,  $[\text{PtPnCl}_2]$ , in aqueous solution at 100° and the calculated amount of the corresponding bases (*l*-propylenediamine, ammonia, ethylenediamine, or trimethylenediamine); the resulting solutions were concentrated and the compounds precipitated by the addition of alcohol or a mixture of ether and alcohol.

The compound,  $l\text{-}[\text{PtPn}_2]\text{Cl}_2$  (where  $\text{Pn} = \text{NH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{NH}_2$ ), has  $[\alpha]_D^{25} + 46.37^\circ$  for  $p$  16.61 and  $D_4^{25}$  1.0958. [Solvent not stated in this and other cases.—ABSTRACTOR.]

The compound,  $l\text{-}[\text{Pt}_{2\text{NH}_3}^{\text{Pn}}]\text{Cl}_2$ , has  $[\alpha]_D^{25} + 25.17^\circ$  for  $p$  17.47 and  $D_4^{25}$  1.1141.

The compound,  $l\text{-}[\text{Pt}_{\text{En}}^{\text{Pn}}]\text{Cl}_2$ , has  $[\alpha]_D^{25} + 24.07^\circ$  for  $p$  19.08 and  $D_4^{25}$  1.1195.

The compound,  $l\text{-}[\text{Pt}_{\text{Tr}}^{\text{Pn}}]\text{Cl}_2$ , has  $[\alpha]_{\text{Auer}}^{25} + 23.60$  for  $p$  13.09 and  $D^{23}$  1.0747.

The compound,  $l\text{-}[\text{PdPn}_2]\text{Cl}_2$ , obtained from  $\text{K}_2\text{PdCl}_4$  and *l*-propylenediamine, has  $[\alpha]_D^{25} + 79.25^\circ$  for  $p$  17.68 and  $D_4^{25}$  1.0772.

The compound,  $[\text{NiPn}_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , has  $[\alpha]_D^{25} + 14.13^\circ$  for  $p$  11.04 and  $D_4^{25}$  1.0253.

It will be observed that, although *l*-propylenediamine and its hydro-

chloride are lævorotatory, the metallic derivatives examined are dextrorotatory.

The influence of the number of propylenediamine molecules in the complex molecule of the platinum derivatives is clearly seen by a comparison of the molecular rotations of these compounds. A. McK.

**Isomeric  $\alpha\beta$ -Dialkylhydroxylamines.** I.  $\alpha$ -Methyl- $\beta$ -ethylhydroxylamine. II.  $\beta$ -Methyl- $\alpha$ -ethylhydroxylamine. LAUDER W. JONES (*Amer. Chem. J.*, 1907, **38**, 253—257).—It has been shown previously (Abstr., 1898, i, 174) that when the sodium salt of hydroxyurethane (carbethoxyhydroxamic acid) is treated with methyl iodide, the methyl ether,  $\text{OEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{OMe}$ , is produced together with  $\alpha\beta$ -dimethylcarbethoxyhydroxylamine (hydroxymethylurethane methyl ether),  $\text{CO}_2\text{Et}\cdot\text{NMe}\cdot\text{OMe}$ , which on hydrolysis yields  $\alpha\beta$ -dimethylhydroxylamine. The corresponding ethyl derivatives were obtained in a similar manner.

When hydroxyurethane methyl ether is treated with ethyl iodide in presence of sodium ethoxide, *carbethoxy- $\alpha$ -methyl- $\beta$ -ethylhydroxylamine* (*hydroxyethylurethane methyl ether*),  $\text{CO}_2\text{Et}\cdot\text{NEt}\cdot\text{OMe}$ , b. p.  $165\text{--}166^\circ$ , is produced as a colourless oil which has a peculiar, rather unpleasant odour. If this compound is heated with strong hydrochloric acid, it is converted into  *$\alpha$ -methyl- $\beta$ -ethylhydroxylamine*,  $\text{NHEt}\cdot\text{OMe}$ , b. p.  $60\text{--}61^\circ$ , which is a colourless, alkaline liquid, readily soluble in water, and does not reduce silver nitrate; the *hydrochloride*, m. p.  $46\text{--}47^\circ$  (approx.), and the *platinichloride*, m. p.  $174\text{--}175^\circ$  (decomp.), are described.

Similarly, methyl iodide reacts with hydroxyurethane ethyl ether to form *carbethoxy- $\beta$ -methyl- $\alpha$ -ethylhydroxylamine* (*hydroxymethylurethane ethyl ether*),  $\text{CO}_2\text{Et}\cdot\text{NMe}\cdot\text{OEt}$ , b. p.  $166\text{--}167^\circ$ , which on hydrolysis yields  *$\beta$ -methyl- $\alpha$ -ethylhydroxylamine*,  $\text{NHMe}\cdot\text{OEt}$ , b. p.  $65\text{--}65.5^\circ$ , which furnishes a *hydrochloride*, m. p.  $74\text{--}75^\circ$ , and a *platinichloride*, m. p.  $170\text{--}171^\circ$  (decomp.). E. G.

**Preparation of Acylated Aminoalkyl Esters.** J. D. RIEDEL (D.R.-P. 181175. Compare Abstr., 1906, i, 631).—This patent deals with the preparation of substances having the general formula  $\text{NR}^{\text{III}}\text{R}^{\text{IV}}\cdot\text{CH}_2\cdot\text{CR}^{\text{I}}\text{R}^{\text{II}}\cdot\text{OR}$ , where R and  $\text{R}^{\text{IV}}$  are acyl groups and  $\text{R}^{\text{I}}$ ,  $\text{R}^{\text{II}}$ , and  $\text{R}^{\text{III}}$  are alkyl, aryl, or mixed arylalkyl groups. These compounds have useful antipyretic and hypnotic properties.

*Methylaminodimethylethylcarbinol*,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$ , an oil, b. p.  $80^\circ/52\text{ mm.}$ , was obtained by heating chlorodimethylethylcarbinol with methylamine in 25% alcoholic solution.

*Valerylmethylaminodimethylethylcarbinyl valerate*,

$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}_2$ , b. p.  $162^\circ/26\text{ mm.}$ , was prepared by the action of valeryl chloride and aqueous sodium hydroxide on the preceding compound.

*Methylaminophenylldimethylcarbinol*,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$ , b. p.  $136\text{--}138^\circ/31\text{ mm.}$ , obtained from chlorophenylldimethylcarbinol and methylamine on treatment with benzoyl chloride at  $150^\circ$ , yielded *benzoylmethylaminophenylldimethylcarbinyl benzoate*,

$\text{NMeBz}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OBz}$ ,

m. p.  $122^\circ$ .

G. T. M.

**Hydroxy- and Ethoxy-Derivatives of Normal Primary Butylamine.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 384—397).— $\delta$ -Ethoxybutylamine,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , b. p. 153—154°/746 mm.,  $D^{20}_D$  0.8640,  $n_D$  1.42751, obtained by reducing  $\gamma$ -ethoxybutyronitrile by Ladenburg's method, is a colourless, mobile liquid of disagreeable odour and piquant taste, and dissolves in water with development of heat, probably forming a hydrate.

Aminoethyl ether,  $\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{OEt}$ , boils at 73° higher than ethyl ether and 89° higher than ethylamine, whilst  $\delta$ -ethoxybutylamine boils only 62° higher than ethyl butyl ether and 78° higher than normal primary butylamine, so that the influence on volatility of the two components,  $-\text{CH}_2\cdot\text{NH}_2$  and  $-\text{CH}_2\cdot\text{OEt}$ , is less marked when they are separated by the system  $-\text{CH}_2\cdot\text{CH}_2-$  than when they are close together.

The fall in boiling point due to the conversion of normal primary butyl alcohol into the corresponding ethyl ether is 25°, and that resulting from the change of  $\delta$ -hydroxybutylamine into its ethyl ether is 53°. Similarly, the increase in boiling point due to the introduction of the  $\text{NH}_2$  group into normal butane is 74°, whilst that due to the introduction of the same group in the  $\delta$ -position in normal butyl alcohol is 90°. These differences are probably due to mutual action between the  $-\text{CH}_2\cdot\text{OH}$  and  $-\text{CH}_2\cdot\text{NH}_2$  groups being greater than that between the groups  $-\text{CH}_2\cdot\text{OEt}$  and  $-\text{CH}_2\cdot\text{NH}_2$ .

The increase of boiling point resulting from the conversion of the normal paraffins into the corresponding primary alcohols is greater than that due to their conversion into the corresponding primary amines, probably because the alcohols are associated. Similarly, the increase in boiling point on passing from alcohols to the corresponding glycols is greater than that observed in changing from monoamines to the corresponding diamines.

The transformation of an amine into the corresponding amino-alcohol is accompanied by a rise of boiling point almost as great as that observed on passing from the hydrocarbon to the corresponding alcohol, and greater than that due to the conversion of the alcohol into the corresponding amino-alcohol, as the following example shows:  $\text{CH}_3\cdot\text{CH}_2\cdot\text{NH}_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2 = +152^\circ$ ,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} = +93^\circ$ . This difference is probably due, in part, to association in the case of the hydroxy-compounds, and, in part, to mutual action between the  $-\text{CH}_2\cdot\text{NH}_2$  and  $-\text{CH}_2\cdot\text{OH}$  groups.

The increase in boiling point resulting from the change from the simple alcohol to the glycol or from the monoamine to the diamine is less than that due to the conversion of the hydrocarbon into the simple alcohol or monoamine respectively, and as the difference between the increases due to the two changes, hydrocarbon  $\rightarrow$  alcohol  $\rightarrow$  glycol, is greater than that exhibited in the case of the two changes, hydrocarbon  $\rightarrow$  monoamine  $\rightarrow$  diamine, it may be assumed that the mutual action between two  $-\text{CH}_2\cdot\text{OH}$  groups is greater than that between two  $-\text{CH}_2\cdot\text{NH}_2$  groups. This also explains the fact that a greater difference in volatility is shown between successive members in a homologous series of diamines than between successive members of a homologous series of glycols. The differences observed in the

latter series are of the same order as those which obtain in a homologous series of amino-alcohols. The replacement of a  $-OH$  group in a glycol by a  $-NH_2$  group gives rise at the stages  $C_2$ ,  $C_3$ , and  $C_4$  to the same lowering ( $24-26^\circ$ ) of the boiling point, and this value is less than that ( $41-59^\circ$ ) due to the replacement of  $-OH$  in a simple alcohol by  $-NH_2$ . The former case affords a further example of the mutual influence exerted by the groupings  $-CH_2 \cdot NH_2$  and  $-CH_2 \cdot OH$ .  
T. A. H.

**Diacetoneamine.** MORITZ KOHN (*Monatsh.*, 1907, 28, 1049—1053).—It has been shown previously that the action of magnesium methyl iodide on diacetone alcohol leads to the formation of  $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol (Franke and Kohn, *Abstr.*, 1905, i, 111; this vol., i, 171). The action of magnesium methyl iodide on diacetoneamine is found now to lead in the same manner to the formation of  $\beta$ -amino- $\beta\delta$ -dimethylpentane- $\delta$ -ol, only a small amount of the diacetoneamine undergoing decomposition into ammonia and mesityl oxide.

$\beta$ -Amino- $\beta\delta$ -dimethylpentane- $\delta$ -ol,  $NH_2 \cdot CMe_2 \cdot CH_2 \cdot CMe_2 \cdot OH$ , is obtained as a mobile oil, b. p.  $82^\circ/19-20$  mm., has a slight ammoniacal odour, and absorbs carbon dioxide rapidly on exposure to air. The *platinichloride*,  $(C_7H_{17}ON)_2 \cdot H_2PtCl_6$ , crystallises in scarlet, rhombohedral plates; the *picrate*,  $C_{13}H_{20}O_8N_4$ , forms monoclinic crystals, m. p.  $153-155.5^\circ$ ; the *oxalate*, m. p.  $212^\circ$  (decomp.). The action of methyl iodide on  $\beta$ -amino- $\beta\delta$ -dimethylpentane- $\delta$ -ol leads to the formation of a base which yields an *aurichloride*,  $C_{10}H_{23}ON \cdot HAuCl_4$ , crystallising in golden leaflets, m. p.  $142-143^\circ$ .  $\beta$ -Phenylthiocarbamino- $\beta\delta$ -dimethylpentane- $\delta$ -ol,  $C_{14}H_{22}ON_2S$ , formed by the action of phenylthiocarbimide on  $\beta$ -amino- $\beta\delta$ -dimethylpentane- $\delta$ -ol, crystallises in white leaflets, m. p.  $115-117^\circ$ .  
G. Y.

**Cyanogen Bromide as a Means of Testing the Stability of Groups attached to Nitrogen.** JULIUS VON BRAUN (*Ber.*, 1907, 40, 3933—3943).—Previous investigations (*Abstr.*, 1900, i, 430, 641, 687; 1902, i, 365; 1903, i, 464) have shown that the reaction between tertiary bases and cyanogen bromide is represented by  $NR'R''R''' + Br \cdot CN = NR'R'' \cdot CN + R'''Br$ , and that the series allyl, benzyl, methyl, ethyl, propyl, isopropyl, and phenyl denotes the increasing order of difficulty with which the group  $R'''$  is eliminated. Tertiary bases containing the group  $\cdot CH_2 \cdot CN$  or  $\cdot CH_2 \cdot CO_2Et$  ( $=X$ ) react thus:  $NR_2X + BrCN \rightarrow$  (I)  $NR_2 \cdot CN + BrX$  or (II)  $NRX \cdot CN + RBr$ . Reaction (I) increases and (II) diminishes as R increases from methyl to butyl.

*Biscyanomethylpiperidinium bromide*,  $C_5NH_{10}(CH_2 \cdot CN)_2Br$ , obtained from piperidinoacetonitrile and bromoacetonitrile, has m. p.  $173^\circ$  (decomp.); the *platinichloride*, m. p.  $192^\circ$  (decomp.), forms reddish-yellow needles.

Dimethylaminoacetonitrile and cyanogen bromide react energetically to form *cyanomethylaminoacetonitrile*,  $CN \cdot NMe \cdot CH_2 \cdot CN$ , b. p.  $150-151^\circ/12$  mm., and methyl bromide; the latter reacts with the unchanged dimethylaminoacetonitrile to form *trimethylcyanomethylammonium bromide*,  $CN \cdot CH_2 \cdot NMe_3Br$ , which is readily converted into

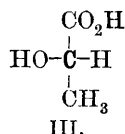
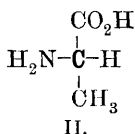
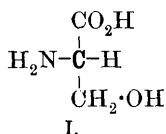
betaine. The odour of bromoacetonitrile is perceptible only when large quantities of dimethylaminoacetonitrile and cyanogen bromide are reacting.

Diethylaminoacetonitrile and cyanogen bromide react to form diethylcyanamide, bromoacetonitrile, *cianoethylaminoacetonitrile*,  $\text{CN}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CN}$ , b. p.  $150^\circ/9$  mm., and *ethylaminoacetonitrile hydrobromide*,  $\text{NHEt}\cdot\text{CH}_2\cdot\text{CN}\cdot\text{HBr}$ . Ethyl diethylglycine and cyanogen bromide yield diethylcyanamide, ethyl bromoacetate, and *ethyl ethylcyanoglycine*,  $\text{CN}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $139^\circ$ .

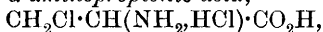
*Dipropylaminoacetonitrile*,  $\text{NPr}_2\cdot\text{CH}_2\cdot\text{CN}$ , b. p.  $89-90^\circ/12$  mm., is obtained from dipropylamine by Knoevenagel's method (Abstr., 1904, i, 981); the *methiodide* sinters at  $130^\circ$  and has m. p.  $150^\circ$  (decomp.). It reacts with cyanogen bromide at  $100^\circ$ , and yields dipropylcyanamide, bromoacetonitrile, and 20—25% of *cyanopropylaminoacetonitrile*,  $\text{CN}\cdot\text{NPr}\cdot\text{CH}_2\cdot\text{CN}$ , b. p.  $155-156^\circ/12$  mm.

*Ethyl dipropylglycine*,  $\text{NPr}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained from dipropylamine and ethyl bromoacetate, has b. p.  $204^\circ$  (decomp.) or  $104^\circ/15$  mm., and reacts with cyanogen bromide to form probably ethyl bromoacetate, dipropylcyanamide, and ethyl propylcyanoglycine. *Diisobutylaminoacetonitrile*,  $\text{N}(\text{C}_4\text{H}_9)_2\cdot\text{CH}_2\cdot\text{CN}$ , b. p.  $95-96^\circ/11$  mm., requires heating for thirty hours with cyanogen bromide; the products have not been definitely isolated.  *$\alpha$ -Diisobutylaminopropionitrile*,  $\text{N}(\text{C}_4\text{H}_9)_2\cdot\text{CHMe}\cdot\text{CN}$ , b. p.  $101-102^\circ/10$  mm., and  *$\alpha$ -diisomethylpropionitrile*,  $\text{N}(\text{C}_3\text{H}_7)_2\cdot\text{CHMe}\cdot\text{CN}$ , b. p.  $129^\circ/12$  mm., react even less favourably with cyanogen bromide. C. S.

**Conversion of *l*-Serine into *d*-Alanine.** EMIL FISCHER and KARL RASKE (*Ber.*, 1907, 40, 3717—3724).—The conversion of *l*-serine into *d*-alanine is effected by treating the hydrochloride of *l*-serine methyl ester with acetyl chloride and phosphorus pentachloride at  $0^\circ$ , whereby the *hydrochloride* of *methyl l*- $\beta$ -chloro- $\alpha$ -aminopropionate, m. p.  $157^\circ$  (decomp.), is obtained (Fisher and Jacobs, this vol., i, 393), which by hydrolysis with 20% hydrochloric acid at  $100^\circ$  yields the hydrochloride of *l*- $\beta$ -chloro- $\alpha$ -aminopropionic acid; the free acid, liberated by lithium or ammonium hydroxide, is reduced to *d*-alanine by sodium amalgam in faintly acid solution. It is highly probable that these reactions are optically normal, and therefore the known configuration of *l*-serine (I) determines that of *d*-alanine (II) and also of *d*-lactic acid (III) obtained from the latter by the action of nitrous acid:



The following constants are given. In aqueous solution, the *hydrochloride* of *l*- $\beta$ -chloro- $\alpha$ -aminopropionic acid,



has  $[\alpha]_{\text{D}}^{20} + 0.7^\circ$ , and the *acid* itself,  $[\alpha]_{\text{D}}^{20} - 15.46^\circ$ . *r*- $\beta$ -Chloro- $\alpha$ -aminopropionic acid, m. p.  $160^\circ$  (decomp.), is reduced to *r*-alanine by sodium

amalgamin acid solution; the *hydrochloride*,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{NH}_2, \text{HCl})\cdot\text{CO}_2\text{H}$ , m. p.  $172^\circ$  (decomp.), crystallises in slender needles, and is converted by ammonium hydroxide at  $100^\circ$  into Kleb's hydrochloride of  $\gamma$ -diaminopropionic acid. The *hydrochloride* of *methyl r- $\beta$ -chloro- $\alpha$ -amino-propionate* has m. p.  $134^\circ$  (decomp.). C. S.

**Aminotrimethylacetic [ $\beta$ -Amino- $\alpha\alpha$ -dimethylpropionic] Acid.** MORITZ KOHN and AUGUST SCHMIDT (*Monatsh.*, 1907, 28, 1055—1062).—Four of the twelve possible aminovaleric acids have been prepared by Slimmer (*Abstr.*, 1902, i, 206). A fifth isomeride is described in the present paper.

$\beta$ -Bromo- $\alpha\alpha$ -dimethylpropionic acid, m. p.  $47^\circ$  ( $40.5$ — $41^\circ$ : Blaise and Marcilly, *Abstr.*, 1904, i, 283), is obtained in a 65—70% yield by treating hydroxypivalic acid at  $80^\circ$  and then at  $100^\circ$  with aqueous hydrogen bromide saturated at  $0^\circ$ .  $\beta$ -Iodo- $\alpha\alpha$ -dimethylpropionic acid,  $\text{CH}_2\text{I}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , prepared by boiling hydroxypivalic acid with hydriodic acid, D 1.7, and amorphous phosphorus in a reflux apparatus, crystallises in glistening prisms, m. p.  $54^\circ$ .

$\beta$ -Amino- $\alpha\alpha$ -dimethylpropionic acid,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , obtained in a 60% yield by the action of alcoholic ammonia, saturated at  $0^\circ$ , on  $\beta$ -bromo- $\alpha\alpha$ -dimethylpropionic acid at the ordinary temperature, crystallises in leaflets, decomp. about  $220^\circ$ , and forms a copper salt crystallising in microscopic, hexagonal plates. The *benzoyl* derivative,  $\text{C}_5\text{H}_{10}\text{O}_2\text{NBz}$ , crystallises in thin needles, m. p.  $149$ — $151^\circ$ . The *phenylcarbamyl* derivative,  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$ , crystallises in needles, m. p.  $173$ — $175^\circ$ . The *methylated base* forms a *hydrochloride* as a white, crystalline mass; the *aurichloride*,  $\text{C}_8\text{H}_{16}\text{O}_2\text{N}\cdot\text{HAuCl}_4$ , crystallises in needles, m. p.  $195$ — $201^\circ$  (decomp.); the *picrate* crystallises in plates, m. p.  $223$ — $225^\circ$  (decomp.). G. Y.

**Polypeptides. XXI. Derivatives of Tyrosine and of Glutamic Acid.** EMIL FISCHER (*Ber.*, 1907, 40, 3704—3717. Compare this vol., i, 652, 684, 737).—*d*-Alanylglycyl-*l*-tyrosine and *l*-leucyltriglycyl-*l*-tyrosine have been examined in anticipation of the study of the complex derivatives of tyrosine obtained, among other products, by the partial hydrolysis of silk-fibroin. *d*- $\alpha$ -Bromopropionylglycyl-*l*-tyrosine,

$\text{CHMeBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , m. p.  $157^\circ$  (corr.), obtained by the interaction of glycyl-*l*-tyrosine and *d*- $\alpha$ -bromopropionyl chloride in cold alkaline solution, separates from water in elongated leaflets, and has in aqueous solution  $[\alpha]_D^{20} + 50.6^\circ$ . By treatment with 25% ammonium hydroxide for three and a half days at  $25^\circ$ , it is converted into *d*-alanylglycyl-*l*-tyrosine,

$\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , which froths at  $140^\circ$  and darkens at  $180^\circ$ , responds to Millon's and the biuret reactions, and has  $[\alpha]_D^{20} + 41.9^\circ$  in aqueous solution. *d*- $\alpha$ -Bromoisohexoyltriglycyl-*l*-tyrosine,

$\text{C}_4\text{H}_9\cdot\text{CHBr}\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_3\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , is prepared from *l*-tyrosine and *d*- $\alpha$ -bromoisohexoyldiglycylglycyl chloride in cold alkaline solution; it crystallises in needles, and has  $[\alpha]_D^{20} + 28.7^\circ$  in aqueous solution. The air-dried substance softens at

100°, and has m. p. 115° (decomp.), whilst the anhydrous compound softens at 100°, gradually darkens, and has m. p. 220°. 1-*Leucyl-triglycyl-l-tyrosine*,  $C_{21}H_{31}O_7N_5$ , obtained from the preceding compound and 25% ammonium hydroxide at 25°, is a colourless, amorphous substance, which begins to decompose at 160°, and has  $[\alpha]_D^{20} + 36.5^\circ$  in aqueous solution. It has a bitter taste and an acid reaction, responds to Millon's and the biuret tests, and forms an amorphous *nitrate*, oily *picrate*, and *picrolonate*, and a dark blue *copper* salt. Characteristic of this pentapeptide and of the preceding tripeptide is the property of being precipitated from aqueous solution by ammonium sulphate, a behaviour which recalls that of the albumoses and also of the tetrapeptide obtained by Fischer and Abderhalden (this vol., i, 737) by the partial hydrolysis of silk fibroin.

Glutamic acid is contained in many proteins, but the study of its polypeptides has hitherto been retarded by the difficulty of obtaining crystalline derivatives of the acid. 1-*Leucyl-d-glutamic acid*,

$CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , m. p. 232° (decomp. corr.), obtained by the action of 25% ammonium hydroxide on *d*- $\alpha$ -bromoisohexoyl-*d*-glutamic acid, separates from water in long needles, has  $[\alpha]_D^{20} + 10.5^\circ$  in *N*-hydrochloric acid, is not precipitated from a solution in dilute sulphuric acid by phosphotungstic acid, and forms easily soluble *sodium* and *barium* salts. On the other hand, the *silver* salt is sparingly soluble in water; in virtue of this property, many derivatives of glutamic and also of aspartic acid may be separated from other polypeptides.

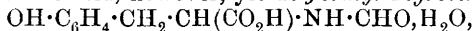
The *d*- $\alpha$ -bromoisohexoyl-*d*-glutamic acid, m. p. 108—109° (corr.), required in the preceding preparation, is prepared from *d*-glutamic acid and *d*- $\alpha$ -bromoisohexoyl chloride in cold alkaline solution.

*Triglycylglycinamide*,

$NH_2 \cdot CH_2 \cdot CO \cdot [NH \cdot CH_2 \cdot CO]_2 \cdot NH \cdot CH_2 \cdot CO \cdot NH_2$ , is prepared by heating methyl triglycylglycine for two hours at 80—100° with methyl alcoholic ammonia saturated at 0°. It crystallises in slender needles, sinters and darkens at 225°, and by solution in the dilute acid yields the *nitrate* and the *hydrochloride*; the *picrate* forms orange-red leaflets, and has m. p. 240° (decomp.). Methyl pentaglycylglycine is converted only partially into the amide by liquid ammonia at the ordinary temperature, or by methyl or ethyl alcoholic ammonia at 100°.

The molecular weights of glycyl-*l*-tyrosine, diglycylglycine, triglycylglycine, leucyldiglycylglycine, *l*-alanyldiglycyl-*l*-alanylglycylglycine, and glycyl-*d*-valine anhydride, determined in aqueous solution by the cryoscopic method, are approximately normal.

The acylation of tyrosine leads, as a rule, to the formation of diacyl derivatives; formic acid, however, yields *formyl-l-tyrosine*,



which has m. p. 171—174° (decomp. corr.) in the anhydrous state and  $[\alpha]_D^{20} + 84.9^\circ$  in alcoholic solution.

C. S.

**Preparation of Alkyl Dialkylmalonamates.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 182045).—The alkyl dialkylmalonamates are employed in the production of the dialkyl-

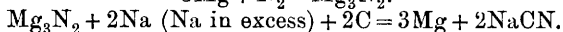
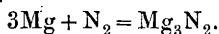


barbituric acids. *Ethyl diethylmalonamate*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{C}(\text{Et})_2 \cdot \text{CO}_2\text{Et}$ , needles, m. p.  $79^\circ$ , is preferably produced by alkylating ethyl malonamate in two stages by the repeated action of ethyl iodide in alcoholic sodium ethoxide.

*Ethyl dipropylmalonamate*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{C}(\text{Pr})_2 \cdot \text{CO}_2\text{Et}$ , white needles, m. p.  $92^\circ$ , is prepared by the action of sodium (2 atoms) and propyl iodide (2 mols.) on ethyl malonamate in alcoholic solution.

The alkyl sulphates may also be employed in producing the alkyl dialkylmalonamates. G. T. M.

**Production of Alkali Cyanides.** OTTO SCHMIDT (D.R.-P. 180118. Compare this vol., i, 299).—By passing nitrogen over a mixture of magnesium, carbon, and an alkali carbonate, an amount of alkali cyanide is obtained equivalent to the quantity of the magnesium present. If, however, the carbonate is replaced by the alkali metal itself, it becomes possible to convert a much larger proportion of alkali metal into cyanide.



One molecule of magnesium will bring about the transformation of 4 molecules of sodium into sodium cyanide. The magnesium has undoubtedly a specific action on the absorption of nitrogen, and the formation of sodium cyanide occurs far more rapidly and completely than in the absence of this metal. G. T. M.

**Glutamine.** ERNST SCHULZE and CH. GODET (*Landw. Versuchs-Stat.*, 1907, 67, 313—319. Compare this vol., i, 114).—Fresh preparations of glutamine from (1) sugar-beet and (2 and 3) mangolds gave  $[\alpha]_D + 6.45^\circ$ ,  $+ 8.2^\circ$ , and  $+ 9.5^\circ$  respectively. At  $16^\circ$ , it dissolves in 25.7 parts of water; the copper derivative,  $\text{Cu}(\text{C}_5\text{H}_9\text{O}_3\text{N}_2)_2$ , can be obtained in small, bluish-violet crystals by heating a solution of glutamine with copper acetate. The cadmium derivative,  $\text{Cd}(\text{C}_5\text{H}_9\text{O}_3\text{N}_2)_2$ , obtained by adding freshly precipitated cadmium hydroxide to a heated solution of glutamine until no longer dissolved, separates in fine prisms; when boiled with water, the compound is slowly hydrolysed.

Glutamine (1 mol.) forms a compound with tartaric acid (1 mol.) which separates in rather large, transparent crystals. N. H. J. M.

**Calcium Cyanamide. II.** GEORG BREDIG, W. FRAENKEL, and E. WILKE (*Zeitsch. Elektrochem.*, 1907, 13, 605—612. Compare this vol., i, 369).—The influence exerted by various substances on the absorption of nitrogen by calcium carbide has been further studied. Experiments with glucinum, magnesium, and strontium chlorides confirm the view that for metals in the same periodic group the acceleration of the reaction is greater the lower the atomic weight of the metal. This relationship holds for 10% admixture. The formation of cyanide increases, on the other hand, with the atomic weight of the metal, but the quantity is always small. Metallic calcium, magnesium and sodium do not appreciably accelerate the absorption of nitrogen when mixed with the carbide. The view that the nitrogen absorption is directly due to calcium produced from the carbide is not supported

by these experiments. Water vapour and calcium oxide, either alone or mixed with other substances, have no influence on the rate of the reaction. The authors suppose that the acceleration phenomena are connected with the fusibility of the added substance and the solubility of the carbide in the flux. For each flux, however, there may be a specific reaction constant. Determination of the velocity of the nitrogen absorption in nitrogen at different pressures shows that this is proportional to the pressure of the gas. Whether diffusion, absorption, or chemical reaction is the determining factor in the velocity of the reaction has not yet been ascertained. H. M. D.

**Compounds of Ethylcarbylamine with Cobaltous, Ferrous, and Ferric Chlorides.** KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1907, 40, 3759—3764. Compare this vol., i, 419; Ramberg, *ibid.*, 604).—Guillemard, in another way (this vol., i, 300), has arrived at the authors' conclusion that metallic cyanides are of the carbylamine type.

*Cobaltous chloride bisethylcarbylamine*,  $\text{CoCl}_2 \cdot 2\text{EtNC}$ , obtained from its constituents in methyl-alcoholic solution, forms green crystals; the chlorine is precipitated completely by silver nitrate. *Ferric chloride bisethylcarbylamine*,  $\text{FeCl}_3 \cdot 2\text{EtNC}$ , similarly obtained in ethereal solution, forms stout, yellow prisms. *Ferric chloride triphenylcarbylamine*,  $\text{FeCl}_3 \cdot 3\text{PhNC}$ , crystallises in greenish-yellow plates. *Ferric oxychloride tetra-ethylcarbylamine*,  $\text{Fe}_2\text{OCl}_4 \cdot 4\text{EtNC}$ , obtained from ferrous chloride and ethylcarbylamine in ether, forms yellow plates. *Ferric oxychloride penta-ethylcarbylamine*,  $\text{Fe}_2\text{OCl}_4 \cdot 5\text{EtNC}$ ,

is obtained in golden-yellow crystals from a 6% methyl-alcoholic solution of ferrous chloride and ethylcarbylamine (3 mols.).

All these compounds are decomposed by alkalis, but the last-mentioned exhibits its greater stability in giving a precipitate with silver nitrate only in the presence of dilute nitric acid, and in forming Prussian-blue only in the presence of hydrochloric acid. C. S.

**Cobalt Dioximines. II.** LEO TSCHUGAEFF (*Ber.*, 1907, 40, 3498—3504. Compare Abstr., 1906, i, 814).—Since metal-ammonia derivatives, which contain all the components of the complex molecules in the non-ionisable form, are of especial interest, the author describes two general reactions for preparing compounds of this type.

The compounds  $[\text{CoNH}_3\text{ClD}_2\text{H}_2]$  and  $[\text{CoD}_2\text{H}_3\text{NH}_3\text{NO}_2]$  (where  $\text{DH}_2 = \text{R}^1 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{R}^2$ ), obtained by the interaction of dimethylglyoxime with derivatives of the pentamine series,  $[\text{Co}5\text{NH}_3\text{Cl}]\text{X}_2$  and  $[\text{Co}5\text{NH}_3\text{NO}_2]\text{X}_2$ , in the presence of an excess of ammonium acetate have already been described.

It is found that the presence of an excess of acid is important for the success of this reaction in order to prevent the formation of a derivative of the diammine series, thus:  $[\text{CoNH}_3\text{XD}_2\text{H}_2] + \text{NH}_3 = [\text{Co}2\text{NH}_3\text{D}_2\text{H}_2]\text{X}$ .

Bromopentamine bromide reacts with dimethylglyoxime, thus:  $[\text{Co}5\text{NH}_3\text{Br}]\text{Br}_2 + 2\text{DH}_2 = [\text{CONH}_3\text{BrD}_2\text{H}_2] + 2\text{NH}_4\text{Br} + 2\text{NH}_3$ . The

resulting *compound* is a typical non-electrolyte and reacts very slowly with silver nitrate in the cold; it separates from dilute acetic acid in glistening, reddish-brown needles; its solution in concentrated sulphuric acid is red.

The *compound*  $[\text{CoNH}_3(\text{NO}_2)_2\text{D}_2\text{H}_2]$ , obtained by the interaction of the xantho- or isoxantho-salts,  $[\text{Co}_5\text{NH}_3\text{NO}_2]\text{X}_2$ , and methylethylglyoxime, separates from alcohol in yellowish-brown crystals and is also a non-conductor. The *compound*  $[\text{CoNH}_3\text{D}_2\text{H}_2\text{Cl}]$  was also obtained from methylglyoxime and purpureo-cobalt chloride,  $[\text{Co}_5\text{NH}_3\text{Cl}]\text{Cl}_2$ . The reaction failed when an attempt was made to prepare the compound  $[\text{CoD}_2\text{H}_2\text{NH}_3\text{NO}_3]$ . The compound  $[\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2]\text{NO}_3$  was the only product of the action of dimethylglyoxime on the pentammine nitrate,  $[\text{Co}_5\text{NH}_3\text{NO}_3](\text{NO}_3)_2$ .

The *compound*  $[\text{CoNH}_3\text{ID}_2\text{H}_2]$ , obtained from dimethylglyoxime and roseopentammine iodide,  $[\text{Co}_5\text{NH}_3\text{H}_2\text{O}]\text{I}_3$ , crystallises in dark brown needles. The iodine atom in this compound is not so firmly bound as in the corresponding chloro- and bromo-compounds. When heated with dilute ammonia at  $100^\circ$ , it forms the *compound*  $[\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2]\text{I}$ , an iodide of the diammine series, which contains an ionisable iodine atom.

The behaviour of the roseo-iodide in comparison with the corresponding chloro- and bromo-salts is remarkable, since the bromide gives with dimethylglyoxime only traces of the compound  $[\text{CoNH}_3\text{BrD}_2\text{H}_2]$ , whilst the roseo-chloride does not give the compound  $[\text{CoClNH}_3\text{D}_2\text{H}_2]$ .

The praseo-halogen salts of the tetrammine series,  $[\text{Co}_4\text{NH}_3\text{Cl}_2]\text{Cl}$  and  $[\text{Co}_4\text{NH}_3\text{Br}_2]\text{Br}$ , behave towards dimethylglyoxime like the corresponding pentammine compounds, giving the *compounds*  $[\text{CoClNH}_3\text{D}_2\text{H}_2]$  and  $[\text{CoBrNH}_3\text{D}_2\text{H}_2]$ . The isomeric croceo- and flaveo-salts appear to behave similarly, and are at present under investigation.

Another method for preparing the compounds in question is described. A process of autoxidation takes place between 1 mol. of cobalt salt and 1 mol. of dimethylglyoxime in alcoholic solution and in the presence of pyridine, or a similar base in the presence of air. The formation of the *compound*  $[\text{CoClPyD}_2\text{H}_2]$  is expressed by the equation:  $2\text{CoCl}_2 + 4\text{DH}_2 + 4\text{Py} + \text{O} = 2[\text{CoClPyD}_2\text{H}_2] + 2\text{PyHCl} + \text{H}_2\text{O}$ . The reaction was also conducted with  $\alpha$ -picoline, isoquinoline, and acridine. In addition to the chlorine atom, there may be substituted bromine or iodine atoms or the electronegative groups,  $\text{NO}_2$ ,  $\text{SCN}$ ,  $\text{NCO}$ , and  $\text{N}_3$ . For dimethylglyoxime, other 1:2-dioximes, for example, methylethylglyoxime, may be substituted. The compounds obtained are crystalline and brown to reddish-brown in colour; they are soluble in water with difficulty and exhibit properties typical of non-electrolytes. The *compound*  $[\text{CoPyClD}_2\text{H}_2]$  forms yellowish-brown crystals. The *compounds*  $[\text{CoPyNCOD}_2\text{H}_2]$  and  $[\text{CoPyN}_3\text{D}_2\text{H}_2]$  are the first metal ammine derivatives of cyanic acid and hydrazoic acid respectively known which are non-conductors. The compound  $[\text{CoPyN}_3\text{D}_2\text{H}_2]$  forms reddish-brown crystals and is very stable. The following derivatives of dimethylglyoxime have been prepared:  $[\text{CoNH}_3\text{ClD}_2\text{H}_2]$ ,  $[\text{CoNH}_3\text{BrD}_2\text{H}_2]$ ,  $[\text{CoNH}_3\text{ID}_2\text{H}_2]$ ,  $[\text{CoNH}_3\text{NO}_2\text{D}_2\text{H}_2]$ ,  $[\text{CoPyClD}_2\text{H}_2]$ ,

[CoPyID<sub>2</sub>H<sub>2</sub>], [CoPyNO<sub>2</sub>D<sub>2</sub>H<sub>2</sub>], [CoPySCND<sub>2</sub>H<sub>2</sub>], [CoPyNCOD<sub>2</sub>H<sub>2</sub>], [CoPyN<sub>3</sub>D<sub>2</sub>H<sub>2</sub>], [Co *isoquinoline* ClD<sub>2</sub>H<sub>2</sub>], [Co *acridine* ClD<sub>2</sub>H<sub>2</sub>].

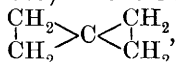
The following derivatives of methylethylglyoxime have been prepared: [CoNH<sub>3</sub>NO<sub>2</sub>D<sub>2</sub>H<sub>2</sub>] and [CoPySCND<sub>2</sub>H<sub>2</sub>]. The following derivative of methylglyoxime has been prepared: [CoClNH<sub>3</sub>D<sub>2</sub>H<sub>2</sub>].

A. McK.

**Action of Nitrous Oxygen Compounds with Organo-zinc and -magnesium Compounds.** IWAN J. BEWAD (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 947—973. Compare Abstr., 1900, i, 629; this vol., i, 671).—The group -N:O in organic nitrites behaves towards zinc alkyls similarly to the >C:O group in aldehydes, consequently nitrosyl chloride and zinc ethyl react thus: O:NCl + Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> → ZnEt·O·N Et<sub>2</sub> → OH·N Et<sub>2</sub> from analogy to O:CCl<sub>2</sub>, which also forms OH·CEt<sub>3</sub>. The β-diethylhydroxylamine thus produced is identical with the product obtained by the action of zinc ethyl on organic nitrites. An abstract of the rest of this paper has already appeared (this vol., i, 671).

Z. K.

**Spirocyclanes.** HERMANN FECHT (*Ber.*, 1907, 40, 3883—3891. Compare Baeyer, Abstr., 1901, i, 135, for nomenclature).—Vinyltrimethylene (Abstr., 1896, i, 669) is in reality *spiropentane*,

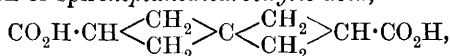


for the nitrile, obtained from its dibromide, yields on hydrolysis

*aa-ethyleneglutaric acid*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 > \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$ , m. p. 162°,

identical with the acid prepared from ethyl glutaconate, ethylene dibromide, and sodium ethoxide in alcoholic solution.

The reaction between pentaerythritol tetrabromohydrin, sodium, and methyl malonate in boiling amyl-alcoholic solution leads ultimately to the formation of *spiroheptanedicarboxylic acid*,



m. p. 210°, which is stable to potassium permanganate, bromine, hydrobromic acid at 150°, and fused potassium hydroxide.

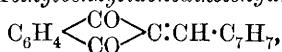
Pentaerythritol tetrabromohydrin, benzene, and aluminium chloride react on the water-bath to give, in very bad yield, a deep yellow *hydrocarbon*, m. p. 148°, and a pale yellow, fluorescent *hydrocarbon*,

m. p. 161°. The formula C<sub>6</sub>H<sub>4</sub> <  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$  > C <  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$  > C<sub>6</sub>H<sub>4</sub> is not ascribed

to either of these substances, because their properties are not analogous to those of *xylylenefluorene*,  $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 > \text{C} < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C} < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C}_6\text{H}_4 \end{array}$ , m. p. 220°, which is prepared from fluorene, *o*-xylylene dibromide, and potassium hydroxide at 230°, crystallises in colourless, refractive needles, and is stable to acids or alkalis.

*Xylylenediketohydrindene*, C<sub>6</sub>H<sub>4</sub> <  $\begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array}$  > C <  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$  > C<sub>6</sub>H<sub>4</sub>, m. p. 150°, is obtained by the addition of an alcoholic solution of sodium ethoxide

to *o*-xylylene dibromide and diketohydrindene dissolved in ethyl acetate; it crystallises in yellow needles, decomposes by warming with alkalis, develops a violet colour with concentrated sulphuric acid, and in hot alcoholic solution changes to a yellow *polymeride*, m. p. 245° (decomp.). The *dioxime* has m. p. 215°; the yellow *phenylhydrazone* has m. p. 177°, and the brown *diphenylhydrazone*,  $C_{29}H_{24}N_4$ , has m. p. 225°. 2-*o*-Methylbenzylidenediketohydrindene,



m. p. 156°, forms pale yellow needles, gives a yellow colour with concentrated sulphuric acid, and does not show any tendency to polymerise. C. S.

**Preparation of *tert*-Butyltoluene and *tert*-Butylxylene.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 184230).—*tert*-Butyl-*m*-xylene, employed in the production of artificial musk, is obtained in almost theoretical amount by passing *isobutylene* gas through a mixture of *m*-xylene and aluminium chloride to which some *isobutyl* chloride has been added, or into which hydrogen chloride has been introduced. *iso*Butyl bromide or hydrogen bromide may also be employed to start the reaction, and *tert*-butyltoluene may be produced in a similar manner. The aluminium chloride may be replaced by other condensing agents, such as the chlorides of magnesium, zinc, or iron; the corresponding bromides may also be employed. G. T. M.

**Reductions with Amorphous Phosphorus. III. Action of Amorphous Phosphorus and Hydrochloric Acid, D 1·19, on Nitrobenzene.** THEODOR WEYL (*Ber.*, 1907, 40, 3608—3612. Compare this vol., i, 118, 305).—Nitrobenzene is reduced to only a very small extent when heated with red phosphorus and hydrochloric acid, D 1·19, at temperatures not above 140°, but at 140—160° considerable amounts of aniline and *p*-chloroaniline are formed. In one experiment, 75% of the nitrobenzene entering into the reaction formed *p*-chloroaniline.

As aniline and *p*-chloronitrobenzene do not form chloroaniline when heated with phosphorus and hydrochloric acid, D 1·19, at temperatures up to 220°, but according to Bamberger, Büsdorf, and Szolayski (*Abstr.*, 1899, i, 341) *p*-chloroaniline is formed by the action of hydrochloric acid on phenylhydroxylamine or on nitrosobenzene, one or both of these substances must be formed intermediately in the reduction of nitrobenzene by phosphorus and hydrochloric acid.

Whilst aniline gives the well-known violet-purple coloration with calcium hypochlorite in aqueous, but a yellow coloration in acetone, solution, *o*- and *m*-chloroaniline give no coloration in aqueous, but a yellow becoming brown in acetone, solution, and *p*-chloroaniline gives a reddish-brown in both solvents.

*p*-Chloroacetanilide has m. p. 182° (172·5°; Beilstein and Kurbatoff, this Journ., 1877, i, 473). G. Y.

**Mercury Derivatives of *o*-Nitrotoluene.** ARNOLD REISSERT (D.R.-P. 182217, 182218).—An aqueous suspension of *o*-nitrotoluene when heated for eight hours with freshly precipitated mercuric oxide and 30% sodium hydroxide solution, or an equivalent amount of some other alkali hydroxide or carbonate, furnishes a *mercury* derivative soluble in aqueous alkali hydroxides and precipitated as a very voluminous, yellow mass on addition of dilute acids, including carbonic acid. The *hydrochloride* of this product is obtained in a crystalline form in colourless needles, m. p. 145—158°, by precipitating an ammoniacal solution with hydrochloric acid. The compound contains mercury and *o*-nitrotoluene in the proportion of one atom of the former to two molecules of the latter.

A sparingly soluble *dimercury* derivative is obtained by prolonging the boiling with mercuric oxide until a product insoluble in hydrochloric acid is obtained. The new compound contains one *o*-nitrotoluene residue combined with two atomic proportions of mercury. The sparingly soluble pale yellow chloride is decomposed by dilute aqueous sodium hydroxide, the free dimercury derivative is dissolved in dilute acetic acid, and reprecipitated by alkali as a heavy, microcrystalline, yellow mass, which explodes on heating, and when gradually warmed decomposes above 220° without melting. It also dissolves in dilute nitric or sulphuric acid, but is insoluble in ammonia.

G. T. M.

**Salts and Esters of Benzenesulphonitroanilide.** ST. OPOLSKI (*Ber.*, 1907, 40, 3528—3536).—Benzenesulpho-*o*-nitroanilide, m. p. 102—103·5°, forms pale yellow or almost colourless, microscopic crystals, and dissolves in alcohol or benzene with a yellow coloration. The *ammonium* salt is yellow; the *sodium* salt orange, m. p. 230°, to a red liquid: when freshly made and cooled to -70° it becomes yellow. The same yellow salt is formed on the addition of sodium ethoxide to a cooled ethereal solution of the *o*-nitroanilide; it becomes orange when rubbed with a glass-rod, but is obtained in silky, glistening, yellow needles when slowly crystallised, or in the orange modification when crystallised quickly.

The *thallium* salt is likewise orange when prepared warm, and yellow when made at lower temperatures; it melts to a red liquid at 150°, which becomes orange again when it solidifies.

The *lithium*, *potassium*, *rubidium*, and *mercury* salts were obtained in one, the yellow, form only; the *silver sodium* double salt is also yellow.

*Benzenesulphomethyl-o-nitroanilide*,  $C_6H_5 \cdot SO_2 \cdot NMe \cdot C_6H_4 \cdot NO_2$ , forms colourless crystals, m. p. 116—117°, and gives colourless solutions.

Benzenesulpho-*m*-nitroanilide forms colourless crystals, m. p. 136—137° (Lellmann, *Abstr.*, 1883, 807, describes it as yellow crystals, m. p. 131—132°). The *ammonium* salt is yellow, likewise the *sodium* and *potassium* salts, which retain this colour on heating and show no tendency to form the red modification. *Benzenesulphomethyl-m-nitroanilide* is colourless, m. p. 82—83°. *Benzenesulpho-*

*p*-nitroanilide, m. p. 139—140°, is colourless and forms yellow salts only; the *methyl* ester, m. p. 120—121°, is also colourless.

Both the *o*- and *p*-benzenesulphonitroanilides are converted by nitric acid into the same *trinitro*-derivative,  $C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_2(NO_3)_3$ , m. p. 210—211°, crystallising in almost colourless needles which give yellow solutions in acetone. E. F. A.

**Action of Phosphorus Oxychloride on 1-Naphthylamine-8-sulphonic Acid.** FREDERIC DANNERTII (*J. Amer. Chem. Soc.*, 1907, 29, 1319—1328).—On heating 1-naphthylamine-8-sulphonic acid with concentrated sulphuric acid, Dressel and Kothe (Abstr., 1894, i, 608) obtained the sulphonic acid of an inner anhydride which they termed naphthasultam. They were unable to obtain the naphthasultam itself, since the anhydride formation was always accompanied by sulphonation in the nucleus. This has now been effected, however, by the action of phosphorus oxychloride on potassium 1-naphthylamine-8-sulphonate, a yield of 60% of the theoretical being obtained.

1 : 8-Naphthasultam,  $C_{10}H_6 \begin{smallmatrix} SO_2 \\ | \\ NH \end{smallmatrix}$ , m. p. 177—178°, crystallises from hot water in needles and dissolves in many organic liquids to form solutions with an apple-green fluorescence. The *methyl* derivative, m. p. 125°, and the *ethyl* derivative, m. p. 85°, are crystalline, and yield fluorescent solutions; the former, when heated with potassium hydroxide, is converted into 1-methylnaphthylamine-8-sulphonic acid, thus proving that the methyl group is attached to the nitrogen atom. Naphthasultam forms yellow salts of the alkali earth metals, gives dark blue precipitates with potassium dichromate and ferric chloride, and when treated with nitrous acid is converted into a red, crystalline substance. The *sodium* salt condenses with diazo-compounds to form dyes. Dibromonaphthasultam, m. p. 239°, is a white compound which turns blue when boiled with alcohol. Nitronaphthasultam, m. p. 253°, forms white crystals which gradually become yellow. The 2 : 4-dinitro-derivative, m. p. 259°, forms six-sided prisms; this compound can also be prepared by the nitration of 1 : 8-naphthasultam-2 : 4-disulphonic acid (Dressel and Kothe, *loc. cit.*). 2 : 4-Diamino-1 : 8-naphthasultam is unstable; its dihydrochloride forms slender, pale yellow needles, and its diacetyl derivative, m. p. 290°, greenish-yellow needles.

When 1 : 8-naphthasultam is boiled with acetic anhydride, 1 : 8-isonaphthasultam,  $C_{10}H_6 \begin{smallmatrix} SO_2H \\ | \\ N \end{smallmatrix}$ , is produced, which forms rhombic crystals and yields a yellow *sodium* salt. When a solution of this compound in methyl alcohol is treated with hydrogen chloride, a *chloro*-derivative, m. p. 200—201°, is produced; the same substance can be obtained by the action of chlorine on isonaphthasultam. The *bromo*-derivative, m. p. 162°, is a white, crystalline substance. The *nitro*-derivative, m. p. 212°, forms pale yellow crystals. 2 : 4-Dinitro-1 : 8-isonaphthasultam, m. p. 256°, forms yellow crystals; if this compound is heated with sodium hydroxide and the product acidified, the "normal" dinitrosultam is produced.

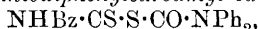
By the action of fuming nitric acid on either naphthasultam or iso-

naphthasultam, 1:3-dinitronaphthalene-5-sulphonic acid is produced, which does not melt but explodes at about 300°. 1:3-Naphthylene-diamine-5-sulphonic acid forms black needles, and does not melt when heated.

E. G.

**Thiocyanates and isoThiocyanates [Thiocarbimides]. VII. Diphenylcarbamyl Thiocyanate.** TREAT B. JOHNSON and L. H. LEVY (*Amer. Chem. J.*, 1907, **38**, 456—461).—When an alkyl halide is treated with ammonium or potassium thiocyanate, an alkyl thiocyanate is first produced, although it sometimes undergoes rearrangement into the corresponding thiocarbimide. In the case of the acyl halides, however, the products of the reaction have always been regarded as thiocarbimides. It has now been found that diphenylcarbamyl chloride reacts smoothly with potassium thiocyanate with formation of diphenylcarbamyl thiocyanate, and it is considered probable that the carbamyl chlorides examined by Dixon (*Trans.*, 1895, **67**, 1040; 1896, **69**, 855, 1593; 1904, **85**, 807) would also yield thiocyanates if treated with potassium thiocyanate under suitable conditions.

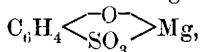
*Diphenylcarbamyl thiocyanate*,  $\text{NPh}_2 \cdot \text{CO} \cdot \text{SCN}$ , m. p. 138°, forms prismatic crystals, is not affected by hot concentrated hydrochloric acid, and does not react with ammonia or aniline at the ordinary temperature. When heated with thiobenzoic acid, carbon oxysulphide is evolved and *benzoyldithiodiphenylcarbamyl carbamate*,



m. p. 128—129°, is produced, which crystallises in prisms. *Benzoyldiphenylamine*, m. p. 177°, is also formed in this reaction and separates from alcohol in prismatic crystals. The thiocyanate does not show any tendency to undergo rearrangement at the ordinary temperature, but when heated at 150—160°, a thiocarbimide is produced which reacts with ammonia to form diphenylthiobiuret.

E. G.

**Action of Sulphuric Acid on Phenol.** JULIUS OBERMILLER (*Ber.*, 1907, **40**, 3623—3647).—Kekulé (*Ber.*, 1869, **2**, 330) found that the action of concentrated sulphuric acid on phenol at the ordinary temperature leads to the formation of the ortho-, together with traces of the para-, sulphonic acid, whilst at 100—110° the para-acid only is formed. Later authors (Engelhard and Latschinow, *Zeitsch. Chem.*, 1868, **4**, 77; Post, this Journ., 1876, **i**, 388) have been unable to separate the two sulphonic acids completely by Kekulé's method. The present author has found that the two isomerides may be separated readily by means of the barium or magnesium salts. On evaporation of the aqueous solution of the monobarium salts,  $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2\text{Ba}$ , the *o*-sulphonate crystallises out, and the para-acid may be obtained from the mother-liquor by conversion by means of magnesium sulphate into the monomagnesium salt,  $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2\text{Mg}$ , which crystallises on further evaporation. The monomagnesium *o*-sulphonate crystallises only with great difficulty, whilst the dimagnesium salt,



is only sparingly soluble; the magnesium salts of the para-acid have the converse solubilities.



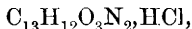
Contrary to Kekulé's statements, the *o*-sulphonic acid is not converted into the para-isomeride on prolonged boiling with water, and is only partially transformed on prolonged treatment with concentrated sulphuric acid at the ordinary temperature. The two isomerides form an equilibrium dependent on the temperature and concentration, the formation of the ortho-acid being favoured by low temperatures and dilution of the sulphuric acid. It is probable that even at 100—110° the ortho-acid is not transformed completely. The alkali, alkaline earth, lead, and zinc salts of the pure *o*- and *p*-sulphonic acids, and of phenol-2 : 4-disulphonic acid, are described.

The reaction solution after removal of the *o*- and *p*-sulphonic acids and of the 2 : 4-disulphonic acid, which is formed readily in presence of an excess of sulphuric acid, contains small amounts of an acid, probably phenol-*m*-sulphonic acid (Solomanoff, *Zeitsch. Chem.*, 1869, 5, 299). This has been isolated in the form of its *monoaluminium*, *monobarium*, and *monomagnesium*,  $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Mg}\cdot 8\text{H}_2\text{O}$ , salts, which are described. These three salts give a violet coloration with ferric chloride.

Merck's "aseptol," which is stated to be a 33½% aqueous solution of phenol-*o*-sulphonic acid, is found to be a solution of the *p*-sulphonic acid and an amount of the ortho-acid equal to about 6% of the para-acid. G. Y.

**Action of *p*-Nitrobenzyl Chloride on *p*-Aminophenol.** MARUSSIA BAKUNIN and C. PROFILO (*Gazzetta*, 1907, 37, ii, 240—250. Compare Abstr., 1906, i, 496).—As already stated (*loc. cit.*), the condensation of *o*- or *p*-aminophenol with benzyl chloride yields mono- or di-substituted derivatives in which the benzyl groups must be regarded as united directly with the amino-nitrogen. By the interaction of *m*-aminophenol (1 mol.) and *o*-nitrobenzyl chloride (2 mols.) in alcoholic solution and in presence of sodium acetate, Lellmann and Mayer (Abstr., 1893, i, 198) obtained a compound to which they ascribed the structure  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ; from the authors' results, it must be held that substitution occurs in the amino- and not in the hydroxyl-group of the *m*-aminophenol.

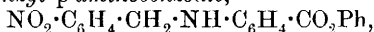
*p*-Nitrobenzyl-*p*-aminophenol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , obtained by the interaction of *p*-nitrobenzyl chloride and *p*-aminophenol in alcoholic solution, crystallises from water in silky, yellow, hydrated (+  $\text{H}_2\text{O}$ ) needles; from alcohol in yellow, micaceous, hydrated (+  $\text{H}_2\text{O}$ ) scales, m. p. 86—87°, and from anhydrous benzene or chloroform in brownish-red crystals, m. p. 114—115°. The *hydrochloride*,



has m. p. 191°.

*Di-p-nitrobenzyl-p-aminophenol*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , also obtained in the reaction between *p*-nitrobenzyl chloride and *p*-aminophenol in alcohol, separates from alcohol in red, acicular crystals, m. p. 179—180°. The *hydrochloride*,  $\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}_3\cdot\text{HCl}$ , m. p. 204°, is readily hydrolysed by water.

*Phenyl p-nitrobenzyl-p-aminobenzoate*,



prepared by the interaction of *p*-nitrobenzyl chloride and *p*-aminoc-

phenyl benzoate, separates from benzene in crystals, m. p. 218—220°. The *hydrochloride*,  $C_{20}H_{16}O_4N_2 \cdot HCl$ , m. p. 110—112°, readily undergoes change.

*Benzoyl-p-nitrobenzyl-p-aminophenol*,  $OH \cdot C_6H_4 \cdot NBz \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , prepared by the action of benzoyl chloride on *p*-nitrobenzyl-*p*-aminophenol in benzene solution, crystallises from alcohol in yellow needles, m. p. 208—210°.

*p*-Nitrobenzyl-*p*-aminophenol gives a violet coloration with ferric chloride and water and a red coloration with Liebermann's reagent and acetic acid. Di-*p*-nitrobenzyl-*p*-aminophenol, being insoluble in water, gives no colour with ferric chloride and water, but its hydrochloride gives a violet coloration; both the base and its hydrochloride give a red colour with Liebermann's reagent and acetic acid. Neither phenyl *p*-nitrobenzyl-*p*-aminobenzoate nor its hydrochloride gives a coloration with ferric chloride, but both yield red colorations with Liebermann's reagent. Benzoyl-*p*-nitrobenzyl-*p*-aminophenol gives no coloration with ferric chloride, possibly owing to its insolubility, but it yields the characteristic red coloration with Liebermann's reagent.

T. H. P.

**Binary Solution Equilibrium between Carbamide and the Three Isomeric Cresols.** ROBERT KREMANN (*Monatsh.*, 1907, 28, 1125—1136. Compare Abstr., 1906, ii, 268).—The melting-point curve for mixtures of carbamide and *p*-cresol falls from the m. p. of carbamide to a break at 25.5°, and then to a eutectic point at 20°, representing mixtures containing 21.5 mol. % and 15 mol. % of carbamide respectively; within these limits of temperature and concentration, carbamide and *p*-cresol form a molecular compound. Mixtures of *p*-cresol-carbamide and carbamide and of *p*-cresol-carbamide and *p*-cresol exist in the solid phase below 25.5° and 20° respectively; above these temperatures, but below the m. p.'s of carbamide and *p*-cresol, the liquid phase is in contact with the one solid component.

Carbamide forms molecular compounds in the same manner, but within wider limits of temperature and concentration, with *o*- and *m*-cresols. The melting-point curve for mixtures of carbamide and *o*-cresol falls from the m. p. of carbamide to a break at about 60°, and then to a eutectic point at about 26°, representing mixtures containing approximately 27.8 mol. % and 10 mol. % of carbamide respectively. The melting-point curve for mixtures of carbamide with *m*-cresol falls to a break at about 65°, and then to a eutectic point at about 2.5°, representing mixtures containing approximately 30 mol. % and 2 mol. % of carbamide.

G. Y.

**Derivatives of 6-Nitro-1:3:4-xylenol.** RAFFAELE MALTESE (*Gazzetta*, 1907, 37, ii, 284—288).—6-Nitro-4-methoxysophthalic acid,  $C_9H_7O_7N$ , prepared by oxidising the methyl ether of 6-nitro-1:3:4-xylenol with potassium permanganate, crystallises from water in slender, silky needles, m. p. 230°. The *dimethyl* ester,  $C_{11}H_{11}O_7N$ , separates from methyl or ethyl alcohol in minute, hard crystals, m. p. 118°. The *monomethyl* ester,  $C_{10}H_9O_7N$ , crystallises from methyl or ethyl alcohol in minute, white needles, m. p. 190°; the other *mono*-

*methyl ester* (?) has m. p.  $222^{\circ}$ . The *monoethyl ester*,  $C_{11}H_{11}O_7N$ , is deposited from alcohol as a white, crystalline powder, m. p.  $108^{\circ}$ . The *sodium salt*,  $C_9H_5O_7Na_2$ , is obtained as a yellow, anhydrous, crystalline powder.

The two *nitromethoxy-m-toluic acids* ( $NO_2 : OMe = 6 : 4$  and  $4 : 6$ ) have been prepared, but not distinguished. One of them,  $C_9H_9O_5N$ , separates from water or aqueous alcohol as a yellowish-white powder, m. p.  $174^{\circ}$ , which is gradually turned red by the action of light; the other isomeride, m. p.  $170^{\circ}$  (decomp.), is white, and does not redden under the action of light.

T. H. P.

**Isomerism with Schiff's Bases.** OTTO ANSELMINO (*Ber.*, 1907, 40, 3465—3474).—The author has shown previously (*Abstr.*, 1906, i, 13) that *p*-homosalicylaldehydeanil occurs in two forms, a yellow and a red, which by crystallisation at definite temperatures can be converted one into the other; when dry, the yellow form can be converted by heat into the red, but the reverse change cannot be effected with the dry substance. The effect of pressure is the same as that of heat.

Evidence is submitted to show that these forms are isomeric and not polymorphous. Density determinations gave different values for the two forms; thus, for the yellow form,  $D^{17}_4$  was 1.243, and for the red form 1.262. Solubility determinations in 95% alcohol were carried out at temperatures from  $11.8^{\circ}$  to  $50^{\circ}$ . Measurements of the heat of solution in benzene were also made, and the absorption spectra studied. The conclusion is drawn that solutions below  $33^{\circ}$  contain the yellow form, and above  $34^{\circ}$  the red.

The behaviour of the anil towards acetyl chloride, acetic anhydride, benzoyl chloride, methyl sulphate, and phenylcarbimide is indicated. When the Grignard action is applied, unchanged anil is obtained at temperatures below  $30^{\circ}$ ; above  $40^{\circ}$ , the red variety is transformed by the Grignard reagent, but the yellow variety is not. The same relationships with regard to Grignard's reagent hold with salicylaldehydeanil; it is known only in the yellow form, and does not interact, whereas its methyl ether does.

The picrate obtained from the yellow form differs in tint from that obtained from the red form.

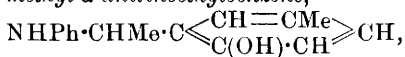
The conclusion is drawn that all yellow anils have a similar structure, whereas the red anil in question has the configuration of its ether. Crystallographic measurements also confirmed this view.

The crystalline form of salicylaldehydeanil differs from that of anisaldehyde.

The *acetyl derivatives of o-hydroxy-m-methylbenzylideneaniline*,  
 $C_{18}H_{19}O_4N$ ,  
 separates from light petroleum in needles, m. p.  $101^{\circ}$ .

*o-Hydroxy-m-methylbenzylideneaniline*,  $C_{15}H_{15}ON$ , prepared by the action of methyl sulphate at  $40^{\circ}$  on the anil, separates from light petroleum in yellow needles, m. p.  $70^{\circ}$ .

*o-Hydroxy-m-methyl- $\alpha$ -anilinoethylbenzene*,



obtained by the action of magnesium methyl iodide on the anil, separates from light petroleum in colourless, rectangular leaflets, m. p.  $98^{\circ}$ .

*o*-Methoxy-*m*-methyl-*a*-anilinoethylbenzene,  $C_{16}H_{19}ON$ , obtained from magnesium methyl iodide and the methylated anil, separates from light petroleum in glistening crystals, m. p.  $78^{\circ}$ .

*o*-Hydroxy-*m*-methyl-*a*-acetylanilinoethylbenzene,  $C_{17}H_{19}O_2N$ , separates from light petroleum in nodular crystals, m. p.  $123^{\circ}$ .

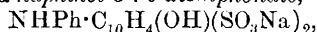
*o*-Methoxy-*m*-methyl-*a*-acetylanilinoethylbenzene,  $C_{18}H_{21}O_2N$ , is a syrup.

*a*-Anilino-*o*-ethylanisole,  $C_{15}H_{17}ON$ , separates from light petroleum in pyramids, m. p.  $46^{\circ}$ .  
A. McK.

**Preparation of Aminonaphthols.** FRANZ SACHS (D. R. P. 181333).—The aminonaphthols can be obtained by heating the naphthols or their alkali derivatives with sodamide at  $200$ – $210^{\circ}$ . The use of the latter compounds reduces the proportion of sodamide required. Naphthalene, quinoline, paraffin, and other heavy hydrocarbons are employed as diluents. Under these conditions,  $\beta$ -naphthol furnishes 5-amino- $\beta$ -naphthol, whilst  $\alpha$ -naphthol yields 5-amino- $\alpha$ -naphthol (compare Abstr., 1906, i, 829 and 949).  
G. T. M.

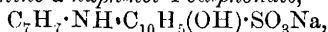
**Preparation of 8-Arylamino- $\alpha$ -naphtholsulphonic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D. R. P. 181929).—The 8-amino- $\alpha$ -naphtholsulphonic acids when heated with aromatic amines and their dry hydrochlorides give rise only to tarry products, but when these acids or their alkali salts are heated with aromatic amines in the presence of water, the hitherto unknown 8-arylamino- $\alpha$ -naphtholsulphonic acids are obtained.

*Sodium 8-anilino- $\alpha$ -naphthol-3 : 6-disulphonate,*



produced by heating sodium 8-amino- $\alpha$ -naphthol-3 : 6-disulphonate with aniline and water at  $120^{\circ}$  for forty-eight hours, crystallises from water in spherical aggregates of white needles; the *sodium hydrogen* salt separates in felted, white needles.

*Sodium 8-p-tolylamino- $\alpha$ -naphthol-4-sulphonate,*



prepared in a similar manner from sodium 8-amino- $\alpha$ -naphthol-4-sulphonate, *p*-toluidine, and water, crystallises in needles; the free acid separates in felted, white needles. The patent contains a tabulated description of ten 8-arylamino- $\alpha$ -naphtholsulphonic acids and other sodium salts.  
G. T. M.

**1 : 2-Methylnaphtha- $\psi$ -quinol.** GUIDO BARGELLINI and S. SILVESTRI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 255–261. Compare this vol., i, 862).—1-Methyl- $\beta$ -naphthol, when oxidised in acetic acid solution with chromic acid, yields 1 : 2-methylnaphtha- $\psi$ -quinol (compare Fries and Hübner, Abstr., 1906, i, 190).

6-Bromo-2-methoxy-1-methylnaphthalene,  $C_{10}H_5BrMe \cdot OMe$ , crystallises from acetic acid in white needles, m. p.  $65$ – $66^{\circ}$  (Fries and Hübner, *loc. cit.*).

**2-Benzeneazo-1-methylnaphthalene**,  $C_6H_4 \begin{smallmatrix} \text{CMe}:\text{C}(\text{N}_2\text{Ph}) \\ \text{CH}=\text{CH} \end{smallmatrix}$ , prepared by the action of phenylhydrazine on 1:2-methylnaphtha- $\psi$ -quinol, crystallises from alcohol in orange-red scales, m. p. 79—80° (decomp.), is soluble in ether, ethyl acetate, chloroform, or acetone, and dissolves in concentrated hydrochloric or sulphuric acid to a red solution.

**Methylnaphthylazocarbonamide**,  $C_6H_4 \begin{smallmatrix} \text{CMe}:\text{C}\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2 \\ \text{CH}=\text{CH} \end{smallmatrix}$ , prepared by the action of semicarbazide on 1:2-methylnaphtha- $\psi$ -quinol, crystallises from water in orange needles, m. p. 143—144° (decomp.), is readily soluble in ether, acetic acid, or chloroform, and dissolves in concentrated hydrochloric or sulphuric acid giving a green coloration which rapidly turns red.

**1:2-Methylnaphtha- $\psi$ -quinoloxime**,  $C_{10}H_6\text{Me}(\text{OH})\cdot\text{NOH}$ , separates from ethyl acetate in crystals, m. p. 140° (decomp.), and dissolves readily in chloroform, benzene, carbon disulphide, or alcohol, and sparingly in light petroleum. By acetic acid, it is decomposed probably in similar manner to the oxime of dimethylnaphtha- $\psi$ -quinol (compare Cannizzaro and Andreocci, Abstr., 1896, i, 488), yielding 2-nitroso-1-methylnaphthalene. Reduction of the oxime by means of zinc dust and acetic acid yields 1-methyl-2-naphthylamine and its acetyl derivative (compare Fries and Hübner, *loc. cit.*). **1-Methyl-2-naphthylamine hydrochloride** separates in shining scales, m. p. 245° (decomp.). T. H. P.

**Condensation Products of Formaldehyde.** J. BRESLAUER and AMÉ PICTET (*Ber.*, 1907, 40, 3784—3786).—Methylphthalimide is formed on heating phthalimide with a 40% solution of formaldehyde in a sealed tube at 150—160°; similarly, methylenedisuccinimide (Bechert, Abstr., 1894, i, 488) is obtained from formaldehyde and succinimide.

**Methylene phenyl methyl ether**,  $\text{OPh}\cdot\text{CH}_2\cdot\text{OMe}$ , is produced by the interaction of phenol and formaldehyde in the presence of sulphuric acid, and by the action of monochloromethyl ether on potassium phenoxide. It is a colourless liquid, b. p. 197—200°,  $D_{15}^{20}$  1.0814, and yields with bromine water a *dibromo*-derivative,  $C_8H_8O_2Br_2$ , which crystallises in colourless, silky needles, m. p. 112—113°.

The action of formaldehyde on  $\alpha$ -naphthol in the presence of potassium carbonate results in the formation of a *substance*,  $C_{23}H_{16}O_3$ , obtained as a dark brown, amorphous, infusible powder. This on distillation yields a *substance*,  $C_{22}H_{16}O$ , which forms small, pale yellow crystals, m. p. 79—80°, and gives a deep blue coloration with ferric chloride. W. H. G.

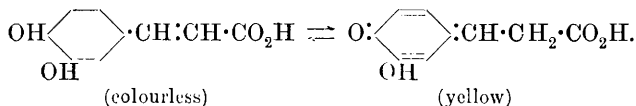
**Action of Benzyl Chloride on Resorcinol and Catechol.** MARUSSIA BAKUNIN and P. ALFANO (*Gazzetta*, 1907, 37, ii, 250—252).—The interaction of benzyl chloride and resorcinol in benzene solution in presence of zinc yields: (1) a *compound*,  $C_{13}H_{12}O_2$ , crystallising from carbon tetrachloride in slender, white needles, m. p. 74—76°; (2) a hydrocarbon crystallising in nacreous laminae, m. p. 203—206°, and containing 96% of carbon; (3) an *oily compound*,  $C_6H_4O_2(\text{CH}_2\text{Ph})_2$ .

Similarly, benzyl chloride and catechol yield a crystalline compound, m. p. 100°, the nature of which has not yet been determined.

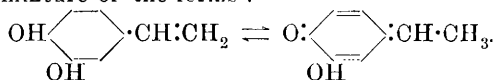
T. H. P.

**Cyclic Carbonic Esters of Vinylcatechol.** HERMANN PAULY and KARL NEUKAM (*Ber.*, 1907, 40, 3488—3498).—Pauly has lately shown (this vol., i, 709) that the cyclic esters of catechols are suitable for the isolation of the latter and that protocatechualdehyde carbonate,  $\text{CHO} \cdot \text{C}_6\text{H}_3 \langle \text{O} \rangle \text{CO}$ , is suitable for the carrying out of syntheses in the catechol group.

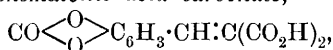
Vinylcatechol carbonate,  $\text{CO} \langle \text{O} \rangle \text{C}_6\text{H}_3 \cdot \text{CH} : \text{CH}_2$ , is now described, it being obtained from protocatechualdehyde carbonate by means of the corresponding benzylidenemalonic acid. The latter compound (colourless) is converted by aqueous pyridine into caffeic acid (yellow), thus:  $\text{CO} \langle \text{O} \rangle \text{C}_6\text{H}_3 \cdot \text{CH} : \text{C}(\text{CO}_2\text{H})_2 + \text{H}_2\text{O} = \text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H} + 2\text{CO}_2$ . The yellow tint of the latter acid is attributed to its partly undergoing the transformation:



Evidence is submitted to show that the free vinylcatechol is an equilibrium mixture of the forms:



3 : 4-Dioxybenzylidenemalonic acid carbonate,



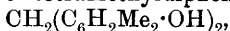
obtained by heating protocatechualdehyde carbonate, malonic acid, and anhydrous formic acid for nine to ten hours at about 65° in the absence of moisture, separates from glacial acetic acid in colourless needles, m. p. 197° (corr., decomp.), and is sparingly soluble in cold water; its aqueous solution exhibits a violet fluorescence; its solution in concentrated sulphuric acid is lemon-yellow. When boiled with acetic anhydride, it evolves carbon dioxide vigorously and gives a compound, m. p. about 245°. On account of the sensitiveness of the  $\text{CO}_3$  group, the acid could not be further characterised by means of its salts.

*Vinylcatechol carbonate*, prepared by the dry distillation of the preceding acid in an apparatus which is described in detail, separates from a mixture of light petroleum and ether in colourless, glistening prisms, m. p. 65—66°; it has a very intense odour. Although it decolorises a solution of bromine in carbon disulphide almost immediately, a dibromide could not be obtained on account of the ease with which hydrogen bromide is eliminated after the addition. It gives a brownish-yellow coloration with ferric chloride and a violet-brown

coloration with sodium carbonate; its solution in concentrated sulphuric acid is reddish-orange. Its solution in alkalis is dark yellow.  
A. McK.

**Reduction of Safrole and isoSafrole.** J. TH. HENRARD (*Chem. Weekblad*, 1907, 4, 630—632. Compare Klages, *Abstr.*, 1899, i, 585; Ciamician and Silber, *Abstr.*, 1890, 965, 966, 1294; Eykman, *Abstr.*, 1890, 244; and Jacobsen, *Abstr.*, 1878, 732).—The author has reduced safrole and isosafrole with nickel and hydrogen by Sabatier and Senderens's method. The reduction was never quantitative, the product always containing unchanged safrole or isosafrole. The reaction product was agitated with dilute sodium hydroxide, and the residual oil, containing unchanged safrole and isosafrole along with the dihydro-product, fractionated, the bulk distilling at 228°. The alkaline liquid contained *m*-propylphenol, formed by reduction of the dihydrosafrole with elimination of the para-hydrogen atom. The *m*-propylphenol could not be obtained crystalline, although Jacobsen gives its m. p. as 26°.  
A. J. W.

**Formation of *s*-Dihydroxydiphenylmethanes.** KARL AUWERS [and, in part, FR. JESCHECK and C. KIPKE] (*Annalen*, 1907, 356, 124—151).—It has been shown previously that hydroxybenzyl bromides and their transformation products readily undergo reactions leading to the formation of substances formulated at first as derivatives of stilbene, but later considered to be derivatives of diphenylmethane (*Abstr.*, 1903, i, 631; 1904, i, 487). The constitution of only one of these derivatives, 3:5:3':5'-tetrabromo-4:4'-dihydroxydiphenylmethane formed from 3:5-dibromo-4-hydroxybenzyl bromide, has been definitely established. As some of these derivatives decompose into compounds containing a single benzene nucleus, and that with an ease not to be expected of derivatives of diphenylmethane, it was necessary to establish the constitution also of one of these comparatively unstable products. This has been achieved now in the case of the product obtained from 3-bromo-4-hydroxy-2:5-dimethylbenzyl bromide, already shown (*loc. cit.*) not to be identical with 4:4'-dihydroxytetramethylstilbene. It is now found identical with 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane,



prepared by diazotisation of 4:4'-diamino-2:5:2':5'-tetramethyldiphenylmethane,  $\text{CH}_2(\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NH}_2)_2$ , which is obtained by transformation of methylenedi-*p*-xylylamine,  $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2)_2$ .

*Methylenedi-p-xylylamine*,  $\text{C}_{17}\text{H}_{22}\text{N}_2$ , prepared by shaking *p*-xylidine with formaldehyde in aqueous solution, crystallises in glistening needles, m. p. 67—68°, and when heated with 2 mols. of *p*-xylidine hydrochloride and  $\frac{1}{2}$  mol. of *p*-xylidine in a reflux apparatus on the water-bath, is transformed into 4:4'-diamino-2:5:2':5'-tetramethyldiphenylmethane,  $\text{C}_{17}\text{H}_{22}\text{N}_2$ , which separates from benzene as a colourless, crystalline powder, m. p. 138—139°. When diazotised with sodium nitrite and boiled in hydrochloric acid solution, this yields 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane, m. p. 181°.

The following substances were prepared in the course of endeavours

to synthesise dihydroxytetramethyldiphenylmethane by other reactions.

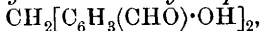
3 : 5-Dibromo-4-methoxybenzyl bromide,  $C_8H_7OBr_3$ , prepared by the action of hydrogen bromide on 3 : 5-dibromo-4-methoxybenzyl methyl ether in glacial acetic acid solution, crystallises in yellow needles, m. p. 66—67°. 4 : 4'-Dimethoxybenzophenone, m. p. 143—144°, is readily obtained by the action of carbonyl chloride on anisole in carbon tetrachloride solution in presence of aluminium chloride. The action of methylal on *p*-xylene in glacial acetic-sulphuric acid solution leads to the formation of a substance,  $C_{17}H_{20}$ , m. p. 149°; the comparatively high temperature at which this melts makes it probable that it is not dixylylmethane. On treatment with cold fuming nitric acid, it yields a yellow, crystalline derivative, m. p. 183°.

The product from 3-bromo-4-hydroxy-2 : 5-dimethylbenzyl bromide having been shown to be 4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane, analogous constitutions must be ascribed to the products obtained similarly from other benzyl bromides. Thus the substance, m. p. 234°, described previously as tetrabromodihydroxy-tetramethylstilbene (Abstr., 1896, i, 150), must be 2 : 5 : 2' : 5'-tetrabromo-4 : 4'-dihydroxy-3 : 6 : 3' : 6'-tetramethyldiphenylmethane; the diacetate,  $C_{21}H_{20}O_4Br_4$ , crystallises in needles, m. p. 224—225°. The constitution of this tetrabromo-compound is confirmed by its reduction by means of sodium and boiling amyl alcohol to dihydroxytetramethyldiphenylmethane. The supposed bromide, m. p. 179° (Abstr., 1896, i, 422), is now found to be tribromo-*p*-xenol.

Similarly, the substance, m. p. 232°, described previously as tetrabromodihydroxytetramethylstilbene (Abstr., 1899, i, 33), must be 2 : 6 : 2' : 6'-tetrabromo-4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenylmethane.

The conditions under which derivatives of dihydroxydiphenylmethane are formed from hydroxybenzyl bromides and their transformation products, and the mechanism of the reactions concerned, are discussed. The following new details are given.

Whilst the action of water or alkalis on 4-hydroxy-3-aldehydobenzyl bromide leads to the formation of hydroxymethylsalicylaldehyde, 4 : 4'-dihydroxy-3 : 3'-dialdehydodiphenylmethane,



m. p. 140°, was obtained on one occasion by long exposure to moist air of the residues from the preparation of the bromide.

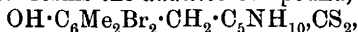
2 : 2'-Dihydroxy-3 : 5 : 6 : 3' : 5' : 6'-hexamethyldiphenylmethane, m. p. 170° (Zincke and Honorst, this vol., i, 614), is formed when trimethylsaligenin is boiled with slightly acidified water.

The product, m. p. 183—184°, obtained on treating dibromo-*p*-hydroxy-*ψ*-cumenol with sodium amalgam in alkaline solution (Auwers and Baum, Abstr., 1897, i, 34), is found to be 4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane.

Whilst readily decomposed by acids or water, dipiperidylmethane and its compounds remain unchanged when boiled with anhydrous solvents such as toluene. When heated with carbon disulphide at 100°, the piperidine derivative of 3 : 6-dibromo-4-hydroxy-2 : 5-di-



methylbenzyl alcohol forms the *additive* compound,



which crystallises in strongly refracting prisms, m. p. 180—181°, but if heated with ether at 100° and then shaken with carbon disulphide the piperidine derivative yields 3:6:3':6'-tetrabromo-4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane and the *additive* compound of carbon disulphide and dipiperidylmethane, m. p. 58°. G. Y.

**Fission of Dihydroxydiphenylmethanes on Bromination:** KARL AUWERS and ERICH RIETZ (*Annalen*, 1907, 356, 152—177).—Whilst hydroxybenzyl bromides readily form the corresponding dihydroxydiphenylmethanes, these tend to decompose into simple benzene derivatives. The two reactions in question differ in that, whereas the first is general, the second has been found to take place markedly only in the case of certain derivatives of dihydroxydiphenylmethane. This paper is a study of the relation of the constitution of dihydroxydiphenylmethanes to their stability on bromination. It is found that, other things being equal, the stability diminishes as the number of methyl groups in the benzene nuclei increases. Thus, on careful bromination (avoidance of an excess of bromine and dilution with a solvent), the carbon chain of 4:4'-dihydroxydiphenylmethane and its monomethyl derivative remains unbroken, whilst that of the dimethyl derivative is ruptured to the extent of 2%, and that of the tetramethyl derivative to the extent of 16%. Energetic bromination of the more highly methylated derivatives leads to almost complete rupture of the carbon chain. On the other hand, no decomposition takes place when 3:3'-dihydroxydiphenylmethane and its dimethyl derivative are brominated.

It is shown that the rupture of the carbon chain results from the action of the nascent hydrogen bromide; the chain remains intact on bromination in presence of sodium acetate or on treatment of the dihydroxydiphenylmethane with a solution of hydrogen bromide. The following details are new.

4:4'-Dihydroxy-3-methyldiphenylmethane,  $\text{C}_{14}\text{H}_{14}\text{O}_2$ , prepared by Claus' method (*Diss.*, Marburg, 1901), has m. p. 133°.

The action of boiling aqueous sodium hydroxide on the condensation product of 3:5-dibromo-4-hydroxy-2:6-dimethylbenzyl bromide with pyridine or diethylamine leads to the formation of a small amount of a yellowish-brown powder,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_4$ , m. p. 173—175°. Attempts to prepare 4:4'-dihydroxy-2:6:2':6'-tetramethyldiphenylmethane from the corresponding 4:4'-diamino-compound,  $\text{C}_{17}\text{H}_{22}\text{N}_2$ , m. p. 205—208°, were unsuccessful.

3:3'-Dihydroxydiphenylmethane,  $\text{C}_{13}\text{H}_{12}\text{O}_2$ , prepared from the 3:3'-diamino-compound, crystallises in needles, m. p. 103°; the *diacetate*,  $\text{C}_{17}\text{H}_{16}\text{O}_4$ , crystallises in white leaflets, m. p. 57·5—58·5°.

5:5'-Dihydroxy-2:2'-dimethyldiphenylmethane, prepared from the 5:5'-diamino-compound, forms white crystals, m. p. 159—160°.

5:5'-Dinitro-2:3:2':3'-tetramethyl- and 5:5'-dinitro-2:4:2':4'-tetramethyl-diphenylmethanes,  $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_2$ , are obtained as light brown powders, m. p. 164—167° and 173—176° respectively.

The following products are obtained on bromination of the corresponding dihydroxydiphenylmethanes.

3 : 5 : 3' : 5'-Tetrabromo-4 : 4'-dihydroxydiphenylmethane, m. p. 226—227°, from 4 : 4'-dihydroxydiphenylmethane. 5 : 3' : 5'-Tribromo-4 : 4'-dihydroxy-3-methyldiphenylmethane, m. p. 185—195°, together with traces of a substance, m. p. 42—92°, which may be a mixture of dibromo-*o*-cresol and tribromophenol, from 4 : 4'-dihydroxy-3-methyldiphenylmethane. 5 : 5'-Dibromo-4 : 4'-dihydroxydi-*m*-tolylmethane, m. p. 173°, and dibromo-*o*-cresol from 4 : 4'-dihydroxydi-*m*-tolylmethane. 3 : 3'-Dibromo-4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane, m. p. 172°, and dibromo-*p*-xylenol, m. p. 79—80°, from 4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane. Dibromo-*v-m*-xylenol, m. p. 83—85°, from 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenylmethane. A mixture of tetra- and hexa-bromo-derivatives from 3 : 3'-dihydroxydiphenylmethane. The pure *hexabromo*-derivative,  $C_{13}H_6O_2Br_6$ , m. p. 241—244°, is formed by the action of an excess of undiluted bromine; the *diacetate*,  $C_{17}H_{19}O_4Br_6$ , crystallises in needles, m. p. 224°. 4 : 6 : 4' : 6'-Tetrabromo-5 : 5'-dihydroxy-2 : 2'-dimethyldiphenylmethane,  $C_{15}H_{12}O_2Br_4$ , m. p. 227—228°, from 5 : 5'-dihydroxydi-*o*-tolylmethane. G. Y.

**Preparation of 1 : 3-Dimethylpyrogallol Carbamate.** BASLER CHEMISCHE FABRIK (D.R.-P. 181593).—1 : 3-Dimethylpyrogallol carbamate,  $C_6H_3(OMe)_2 \cdot O \cdot CO \cdot NH_2$ , white needles, m. p. 148—152°, has a beneficent action in tuberculosis which is greater than that of 1 : 3-dimethylpyrogallol. This is probably owing to the fact that the latter ether is too rapidly oxidised and eliminated in the form of cœrulignone, whereas the carbamate is only gradually hydrolysed, so that a sustained reaction is rendered possible. The carbamate is prepared by the interaction of 1 : 3-dimethylpyrogallol and carbamic acid chloride in anhydrous ether. G. T. M.

**Preparation of Substituted Chlorohydrins.** J. D. RIEDEL, AKTIEN-GESELLSCHAFT (D.R.-P. 183361).—When epichlorohydrin is subjected to the action of the magnesium derivatives of the aromatic halides, the condensation takes the normal course, and substituted chlorohydrins,  $CH_2Cl \cdot CHR \cdot CH_2 \cdot OH$ , are obtained, where R is an aryl or arylalkyl group.

$\gamma$ -Chloro- $\beta$ -phenylpropyl alcohol,  $CH_2Cl \cdot CHPh \cdot CH_2 \cdot OH$ , b. p. 153—154°/28 mm., results from the interaction of epichlorohydrin and magnesium phenyl bromide; it is, however, accompanied by chlorobromopropyl alcohol and phenylchloropropylene.

$\gamma$ -Chloro- $\beta$ -*p*-methoxyphenylpropyl alcohol,  
 $CH_2Cl \cdot CH(C_6H_4 \cdot OMe) \cdot CH_2 \cdot OH$ ,

b. p. 188—189°/25 mm., is the chief product of the interaction of magnesium *p*-methoxyphenyl bromide and epichlorohydrin.  $\gamma$ -Chloro- $\beta$ -benzylpropyl alcohol,  $C_6H_5 \cdot CH_2 \cdot CH(CH_2Cl) \cdot CH_2 \cdot OH$ , b. p. 165—166°/22 mm., is obtained when magnesium benzyl chloride is employed.

G. T. M.

**Cholesterol. III. Transformation of Cholestene.** JULIUS MAUTHNER (*Monatsh.*, 1907, 28, 1113—1124. Compare *Abstr.*, 1906, i, 579—663).—In view of the near relation of the cholesterol group to the terpenes, it appeared probable that, on addition of hydrogen chloride to cholesterol, cholesteryl chloride, and cholestene, a change might take place similar to that of pinene into camphene. This is now found to be the case with cholestene; on loss of hydrogen chloride, cholestene hydrochloride (chlorocholestane) yields a hydrocarbon different from cholestene and termed by the author  $\psi$ -cholestene.

Chlorocholestane, formed by the action of hydrogen chloride on cholestene, is obtained in two isomeric modifications, one of which crystallises in rhombic prisms, m. p. 96—97°,  $[\alpha]_D^{25} + 4.7^\circ$ , and is the chief product of the reaction. The other crystallises in flat needles, sinters at 70°, and is melted above 80°. Both isomerides yield the same  $\psi$ -cholestene.

$\psi$ -Cholestene,  $C_{27}H_{44}$ , formed by boiling chlorocholestane with sodium methoxide and potassium acetate, or by treatment of the chloro-compound with zinc dust and glacial acetic acid or alcoholic silver nitrate, crystallises in flat needles, m. p. 78—79°,  $[\alpha]_D + 64.86^\circ$ , and gives the colour reactions of cholestene. The *dibromide*,  $C_{27}H_{44}Br_2$ , prepared by adding bromine dissolved in glacial acetic acid to the hydrocarbon in ethereal solution, crystallises in colourless, flat needles, m. p. 116—117°, and has  $[\alpha]_D^{20} + 38.7^\circ$  immediately after solution in chloroform,  $[\alpha]_D^{20} + 36.0^\circ$  after three hours, and  $[\alpha]_D^{20} + 83.4^\circ$  after four days, the solution becoming gradually reddish-yellow or dark green with slight red fluorescence, or in benzene immediately after solution  $[\alpha]_D + 48.0^\circ$ , after twenty-four hours  $[\alpha]_D + 47.0^\circ$ , and after forty-seven days  $[\alpha]_D + 46.9^\circ$ , the solution remaining colourless. The mutarotation is probably connected with a *cis-trans* transformation; the initial fall in the rotatory power may result from the dissociation of molecular aggregates. G. Y.

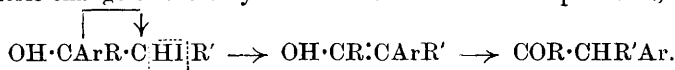
**Phytosterol.** ADOLF WINDAUS and A. HAUTH (*Ber.*, 1907, 40, 3681—3686).—A convenient method of separating stigmasterol from phytosterol is described, and a direct comparison of sitosterol and the phytosterol so obtained confirms completely the statement that they are identical (compare this vol., i, 129).

A comparison of the behaviour of cholesterol and phytosterol towards several reagents has been made. *Dihydrophytosterol*,  $C_{27}H_{48}O$ , prepared by reducing phytosterol with sodium and amyl alcohol, crystallises from acetone in stout needles or rectangular plates, m. p. 175°. This substance does not give the Salkowski colour reaction. Although the substance behaves towards bromine as an unsaturated compound, repeated reduction with sodium and amyl alcohol does not alter the melting point, and therefore the substance must be regarded as a chemical entity. A molecular weight determination of the acetyl derivative shows it to correspond with  $C_{29}H_{50}O_2$ . *Dihydrophytosteryl chloride*,  $C_{27}H_{47}Cl$ , forms long, glistening prisms, m. p. 114—115°; on reduction with sodium and amyl alcohol, it yields *dihydrophytostene*,  $C_{27}H_{48}$ , which crystallises in rectangular leaflets, m. p. 80—81°. Both

these compounds behave as unsaturated towards bromine. This state of unsaturation must either be due to the phytosterol not being reduced but only undergoing isomeric change through the intermediary of sodium amyl oxide, or, if reduction has taken place, then phytosterol must contain at least two ethylene linkings. However, on testing phytosterol with sodium amyloxyde, there was obtained, not the dihydrophytosterol, but a  $\psi$ -phytosterol,  $C_{27}H_{46}O$ , which crystallises in aggregates of needles, m. p. 146—147°. It is indifferent to sodium and amyl alcohol, but it is unsaturated towards bromine, the addition taking place more slowly than with phytosterol. The conclusion is drawn that dihydrophytosterol is a reduction product, and that phytosterol must contain two ethylene linkings, notwithstanding that only 1 mol. of bromine is absorbed.

Whereas cholesterol yields the same saturated substance with sodium amyloxyde, or sodium and amyl alcohol, it is probable that it is not a reduction product, but one due to isomeric change; phytosterol, however, gives rise to two different products with these different reagents (compare this vol., i, 610). W. R.

**Migration of the Phenyl Group of Aromatic Iodohydrins by Elimination of Hydrogen and Iodine from the Same Carbon Atom.** MARC. TIFFENEAU (*Compt. rend.*, 1907, 145, 593—596. Compare this vol., i, 39).—The author has previously proposed to explain the transformation of aromatic iodohydrins of the type  $OH \cdot CArR \cdot CHIR'$  into aldehydes or ketones, when deprived of hydrogen iodide, by (1) loss of hydrogen and iodine from the same carbon atom and migration of the aromatic group, followed by (2) isomeric change of the vinyl alcohol derivative at first produced, thus:



Study of the ethers of these iodohydrins affords experimental proof of the correctness of this view. Whilst the ethers of the aromatic iodohydrins react with silver nitrate, giving the aldehyde or ketone directly (owing to hydrolysis of the vinyl derivative by the liberated nitric acid), by using mercuric oxide the reaction can be stopped at the end of the first stage. When an ethereal solution of anethole ethyliodohydrin,  $OMe \cdot C_6H_4 \cdot CH(OEt) \cdot CHMeI$ , is shaken with mercuric oxide, the *vinyl ether*,  $OMe \cdot C_6H_4 \cdot CMe : CH \cdot OEt$ , is formed. This has b. p. 269—271°,  $D_4^{20}$  1.044, and combines directly with bromine. Its lower homologue,  $OMe \cdot C_6H_4 \cdot CMe : CH \cdot OMe$ , has b. p. 262—263°, and  $D_4^{20}$  1.065. Both are easily converted by acids into *p*-methoxyhydratropaldehyde.

The author considers that the iodohydrins of the type

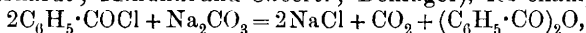


belong rather to the glycols than to the iodohydrins of the general type, since elimination of hydrogen iodide from the latter leaves a less resistant hydroxyl group, whilst elimination of HI or water from the two former types leaves a more resistant hydroxyl. E. H.

**A Product obtained in the Technical Preparation of Benzoic Acid from Coal Tar.** GUIDO GOLDSCHMIEDT (*Monatsh.*, 1907, 28, 1091—1097).—A method of preparing benzoic acid from

coal tar has been based (D.R.-P. 109122) on the observation by Krämer and Spilker (Abstr., 1890, 496) of benzonitrile in coal tar freed from phenol and bases. The present paper is an account of the examination of a product obtained together with the benzoic acid. It is found to consist of benzoic esters, chiefly 1:3:4-xylenyl benzoate, together with small amounts of free phenols and benzoic acid, and traces of coumarone. The crude material for the preparation of the benzoic acid, in spite of having been treated with alkalis, must contain 1:3:4-xylene together with not more than traces of phenol and cresol, which on hydrolysis of the benzonitrile esterify part of the benzoic acid. G. Y.

**Hyposulphites.** IV. ARTHUR BINZ and THEODOR MARX (*Ber.*, 1907, 40, 3855—3860. Compare Abstr., 1904, i, 964; 1905, ii, 521; 1906, ii, 23).—Where benzoyl chloride acts on potassium oxalate, sodium nitrite, or sodium carbonate, it forms benzoic anhydride (Gerhardt; Minunni and Caberti; Deninger), for example:



the reactions in question taking place with great ease in the presence of pyridine. The action of benzoyl chloride on sodium hyposulphite is similar, benzoic anhydride resulting either in the presence or absence of pyridine. Three additional products are, however, obtained; from benzoyl chloride alone, benzoyl disulphide is produced; from benzoyl chloride and pyridine, in addition to benzoyl disulphide, a red base of the probable formula  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}$ , and a yellow compound of a high molecular weight are formed.

The behaviour of benzoyl chloride towards sodium sulphite, both in the absence and presence of pyridine, has also been studied. Benzoyl disulphide is not formed in this case. The change  $2\text{C}_6\text{H}_5\cdot\text{COCl} + \text{Na}_2\text{SO}_3 = 2\text{NaCl} + (\text{C}_6\text{H}_5\cdot\text{CO})_2\text{O} + \text{SO}_2$  is accompanied by the formation of the red and yellow compounds already mentioned. The latter compounds are also formed by the action of sulphur dioxide on a mixture of benzoyl chloride and pyridine.

The yellow compound, to which the formula  $\text{C}_{23}\text{H}_{16}\text{O}_6\text{N}_4\text{S}_4$  is provisionally assigned, is either not dissolved by the ordinary solvents or is transformed into the red base,  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}$ , which forms ruby-red needles, m. p.  $259^\circ$ . The molecular weight of the latter compound was determined by the cryoscopic method. A. McK.

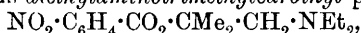
**Preparation of the Alkylamino-esters of *p*-Aminobenzoic Acid.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 179627, 180291, 180292).—The esters of aromatic acids are known to possess anæsthetic properties, but only in a few cases is this action of any practical importance, owing to the circumstance that it is somewhat transient and is accompanied by irritant after-effects. It has now been found that the soluble hydrochlorides of the alkylamino-esters of *p*-aminobenzoic acid produce a well-sustained anæsthesia without any disagreeable irritation.

*Chloroethyl p-nitrobenzoate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , white needles, m. p.  $56^\circ$ , is produced by heating equal quantities of chlorohydrin and *p*-nitrobenzoyl chloride at  $120$ — $125^\circ$ ; when heated with

piperidine it furnishes *piperidinoethyl p-nitrobenzoate*, m. p. 61—62°. *Piperidinoethyl p-aminobenzoate*, m. p. 90°, results from the reduction of the preceding ester; its *hydrochloride*, m. p. 213°, crystallises in white needles.

*Diethylaminoethyl p-nitrobenzoate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$ , a viscid oil, is produced by the interaction of chloroethyl *p*-nitrobenzoate and diethylamine. *Diethylaminoethyl p-aminonitrobenzoate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$ , m. p. 51°, crystallises from dilute alcohol with  $2\text{H}_2\text{O}$ ; *hydrochloride*, needles, m. p. 156°.

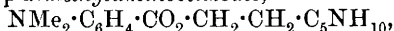
*Diethylaminotrimethylcarbinol*,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$ , b. p. 55°/11 mm., obtained by the action of magnesium methyl iodide on diethylaminoacetone, yields *diethylaminotrimethylcarbinyl p-nitrobenzoate*,



m. p. 47—48°, on treatment with *p*-nitrobenzoyl chloride. *Diethylaminotrimethylcarbinyl p-aminobenzoate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$ , a viscid oil, gives a crystalline *hydrochloride*, m. p. 183—184°. The patent contains a list of eighteen of these alkylamino-esters of *p*-nitrobenzoic acid with the corresponding esters of *p*-aminobenzoic acid and their *hydrochlorides*.

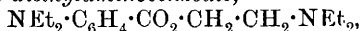
*Piperidylethyl p-aminobenzoate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_{10}$ , was obtained by dissolving hydroxyethylpiperidine and *p*-aminobenzoic acid in cold concentrated sulphuric acid. The solution was subsequently heated to 90—100°, poured into ice-water, and rendered ammoniacal; the base, m. p. 90°, which is obtained from its crystalline *hydrochloride*, m. p. 213°, crystallises from light petroleum in needles.

*Piperidylethyl p-dimethylaminobenzoate*,



m. p. 45°, was obtained from hydroxyethylpiperidine and *p*-dimethylaminobenzoyl chloride in benzene solution; its *hydrochloride*, m. p. 205°, is readily soluble in water to a neutral solution. The ester may also be prepared by heating hydroxyethylpiperidine with *p*-dimethylaminobenzoic acid and concentrated hydrochloric acid or by warming this base with *p*-dimethylaminobenzoic anhydride.

The following esters and their *hydrochlorides* were also prepared: *diethylaminoethyl p-diethylaminobenzoate*,



oily; *hydrochloride*, white needles, m. p. 162—163°: *diethylaminoethyl p-aminobenzoate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$ , m. p. 51°; *hydrochloride*, m. p. 156°: *diethylaminoethyl p-methylaminobenzoate*, oily; *hydrochloride*, m. p. 106—109°: *piperidylethyl p-methylaminobenzoate*, oily; *hydrochloride*, m. p. 145—147°: *diethylaminoethyl p-ethylaminobenzoate*, oily; *hydrochloride*, m. p. 119—121°.

These esters, which have important anæsthetic properties, can also be prepared by alkylating *p*-azobenzoic acid or its chloride with the amino-alcohols and then reducing the products.

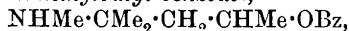
*Piperidylethyl p-azobenzoate*, m. p. 118—119°, separates in brick-red needles; *diethylaminoethyl p-azobenzoate*, m. p. 82°, forms yellowish-red leaflets.

G. T. M.

**Preparation of Alkylaminohexyl Benzoates.** CHEMISCHE FABRIK AUF AKTIEN, VORM. E. SCHERING (D.R.-P. 181287).—The

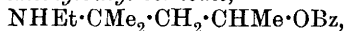
alkylaminoethyl alcohols on benzoylation furnish a series of complex esters having the general formula  $\text{NRR}'\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OBz}$ , where R is an alkyl group and R' either a hydrogen atom or another alkyl group. These compounds are less toxic than the anæsthetics of the stovaine series, and as their hydrochlorides react as neutral substances, even in concentrated solutions, they are devoid of any irritating action.

*γ-Methylamino-α-dimethylbutyl benzoate,*



is an oily substance produced by treating *γ*-methylamino-*α*-dimethylbutyl alcohol with benzoic anhydride in the presence of water on the water-bath; hydrochloride, needles, m. p. 161—162°.

*γ-Ethylamino-α-dimethylbutyl benzoate,*



oil, prepared from *γ*-methylamino-*α*-dimethylbutyl alcohol hydrochloride and benzoyl chloride, yields a hydrochloride forming small needles, m. p. 172—173°.

*γ-Dimethylamino-α-dimethylbutyl benzoate,*

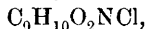


and *γ-diethylamino-α-dimethylbutyl benzoate* are oils; their hydrochlorides melt at 153—154° and 164—167° respectively.

G. T. M.

**Methyl *m*-Amino-*p*-dimethylaminobenzoate.** FRÉDÉRIC REVERDIN (*Ber.*, 1907, 40, 3686—3691; *Arch. sci. phys. nat.*, 1907, 24, 248—256; *Bull. Soc. Chim.*, [iv], 1, 995—1001).—It has been discovered that during the reduction of methyl nitrodimethylaminobenzoate, the ester is very easily hydrolysed, and accordingly the following compounds must be deleted from the literature. Methylaminodimethylaminobenzoate hydrochloride, m. p. 228°, the acetate, m. p. 232°, the condensation product with chlorodinitrobenzene, m. p. 253—254°, and the methyl hydroxy-*p*-dimethylaminobenzoate of m. p. 176°, and its barium salt (*Abstr.*, 1906, i, 273).

The re-investigation has resulted in the preparation of 3-acetylamino-4-dimethylaminobenzoic acid,  $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}_2$ , which forms glistening leaflets, m. p. 246—247°; the diacetyl compound, lamellæ, m. p. 194°; the picrate, m. p. 199—200°.



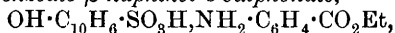
forms long prisms, m. p. 178—179°; the corresponding iodo-compound has m. p. 190—191°, and crystallises in white needles. The methyl ester was obtained from the acid, and by reduction of the nitro-derivative with sodium hyposulphite in the cold; it forms prisms, m. p. 56°; the monacetyl compound,  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$ , has m. p. 103—104°, and the picrate, m. p. 187°.

W. R.

**Naphtholmonosulphonates of Ethyl *p*-Aminobenzoate.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 181324).—The naphtholmonosulphonates of ethyl *p*-aminobenzoate possess the powerful anæsthetic properties of the amino-ester, and are distinguished from the salts of this substance with the mineral acids by their greater stability and solubility, and also by their neutral character. They are prepared either by the direct interaction of their

components or by double decomposition between a metallic naphthol-monosulphonate and ethyl *p*-aminobenzoate hydrochloride.

*Ethyl p-aminobenzoate β-naphthol-6-sulphonate,*



is moderately soluble in hot water, less so in the cold solvent.

G. T. M.

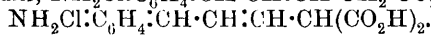
***p*-Aminocinnamylideneacetic Acid.** HERMANN FECHT (*Ber.*, 1907, 40, 3891—3893. Compare following abstract).—*p*-Aminocinnamylideneacetic acid is obtained by the reduction of the nitro-compound by a ferrous salt in ammoniacal solution. In addition to the acid, there is produced an amorphous, dark red substance, insoluble in water, which may be an abnormal ammonium salt. From *o*-aminocinnamylidenemalonic acid, the reddish-yellow hydrogen ammonium salt ( $2\text{H}_2\text{O}$ ) can be prepared, the aqueous solution of which is decolorised by a few drops of acetic acid or of ammonium hydroxide.

*p*-Aminocinnamylideneacetic acid, and also methyl *p*-dimethylaminocinnamylideneacetate, form dark red solutions in acetic acid or alcoholic hydrogen chloride, whereas in hydrochloric acid a yellow solution is obtained, from which red crystals of a hydrochloride are isolated; the aqueous solution is decolorised by the addition of hydroxylamine hydrochloride, with the separation of the colourless hydrochloride of an isomeric acid containing  $2\text{H}_2\text{O}$ . When the solution of this hydrochloride is boiled in the absence of excess of hydrochloric acid, the yellow, isomeric amino-acid is obtained, which is called the  $\beta$ -acid, in contradistinction to the original *p*-aminocinnamylideneacetic acid, which is called the  $\alpha$ -acid. The  $\beta$ -acid forms yellow solutions in alkalis or acetic acid, and colourless solutions in mineral acids. A hydrochloric acid solution in the cold deposits anhydrous colourless crystals of a hydrochloride, but by boiling the solution the red hydrochloride of the  $\alpha$ -acid is obtained.

The conversion of the  $\alpha$ - into the  $\beta$ -acid is promoted by phenylhydrazine, aminoguanidine, or semicarbazide, as well as by hydroxylamine.

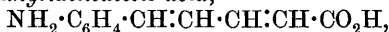
Both the  $\alpha$ - and  $\beta$ -acid give the same colourless *acetyl* derivative, m. p.  $265^\circ$  (decomp.). C. S.

**Quinone Formation. Constitution of Triphenylmethane Dyes.** HERMANN FECHT (*Ber.*, 1907, 40, 3893—3903. Compare preceding abstract).—To the coloured salts of the *p*-aminocinnamylidene derivatives of acetic and malonic acids, the author ascribes quinonoid formulæ,  $\text{NH}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  and

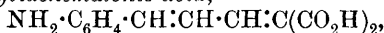


The carboxyl group in these acids has very little auxochromic influence. The pronounced difference in colour which exists between the salts of the two acids in alkaline solution disappears on acidification, because the group  $\text{C} \begin{smallmatrix} \text{CO} \cdot \\ \text{CO} \cdot \end{smallmatrix}$ , which endows the dicarboxylic acid with its deeper colour, no longer exists in the quinonoid salts which are formed in



*$\alpha$ -p-Aminocinnamylideneacetic acid,*

m. p.  $200^\circ$  (decomp.), separates from water or alcohol in brownish-yellow needles. The  $\beta$ -acid, m. p.  $200^\circ$  (decomp.), forms yellow crystals. They are regarded as stereoisomerides. The red *hydrochloride* of the  $\alpha$ -acid has m. p.  $260^\circ$  (decomp.), and the colourless hydrochloride of the  $\beta$ -acid decomposes at  $250$ – $260^\circ$ . The *methyl* esters of the  $\alpha$ - and  $\beta$ -acids, obtained by the action of diazomethane, both have m. p.  $145$ – $146^\circ$ . The  $\alpha$ -ester in benzene solution yields with alcoholic hydrogen chloride bluish-red needles of the *hydrochloride*, while the  $\beta$ -ester, which is turned red by cold hydrochloric acid, only yields a colourless *hydrochloride* in the presence of hydroxylamine. The tertiary base,  $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}$ , m. p.  $142^\circ$ , obtained from the  $\alpha$ -ester and methyl iodide, has the same colour as the non-methylated amino-acid.

*o-Aminocinnamylidenemalonic acid,*

m. p.  $175^\circ$ , forms orange-yellow needles, and does not yield coloured salts in acid solution; the *para-isomeride*, m. p.  $190^\circ$ , crystallises in brown needles.

as-*Dimethylaminodiphenylethylene*,  $\text{CH}_2 : \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m. p.  $56^\circ$ , is obtained from *p*-dimethylaminobenzophenone and magnesium methyl iodide, the intermediately-formed *carbinol*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPhMe} \cdot \text{OH}$ , has b. p.  $202^\circ/14$  mm., and loses water at  $130^\circ$ , yielding the preceding compound. Michler's ketone and magnesium methyl iodide yield the *carbinol*,  $\text{OH} \cdot \text{CMe}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , m. p.  $152^\circ$ , which crystallises in colourless needles and loses water on heating, forming as-*tetramethyldiaminodiphenylethylene*,  $\text{CH}_2 : \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , m. p.  $124^\circ$ , b. p.  $250^\circ/12$  mm., which, like the carbinol, gives a blue solution in acetic acid and yellow solutions in mineral acids.

*Benzylidene-p-dimethylaminoacetophenone*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} : \text{CH} : \text{CHPh}$ , m. p.  $165^\circ$ , prepared from cinnamanilide, dimethylaniline, and phosphorus oxychloride, crystallises in yellow needles, dissolves in acetic or mineral acids with a yellow colour, and forms a red solution with alcoholic hydrogen chloride. C. S.

**Sodium Salicylate.** WILHELM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1907, 651–652).—When water is added, drop by drop, to a weighed quantity of sodium salicylate until this just dissolves, it is found that 1 part of the salt dissolves in 1.55 parts of water or 6.45 parts in 10 c.c. In two out of eight experiments made in the reverse way, 6.57 and 6.60 parts of the salt dissolved in 10 c.c. of water, whence it is concluded that this salt shows some tendency to form supersaturated solutions. The specific gravities of a series of solutions of sodium salicylate are given in the original. T. A. H.

**Behaviour of Very Weak Acids and Pseudo-acids towards Ammonia.** ARTHUR HANTZSCH [and, in part, Miss EDITH MORGAN and HERBERT GORKE] (*Ber.*, 1907, 40, 3798–3805).—Although simple phenols and naphthols, such as thymol,  $\psi$ -cuminol, mesitol,  $\alpha$ -naphthol, and  $\beta$ -naphthol, are almost completely converted into ammonium salts when exposed in an atmosphere of ammonia, those

phenols and naphthols which contain the "negative" group  $-\text{CO}_2\text{R}$ , ortho to the hydroxyl group, such as ethyl salicylate, ethyl  $\alpha$ -naphthol-2-carboxylate, and ethyl  $\beta$ -naphthol-1-carboxylate, are practically indifferent towards ammonia at the ordinary temperature. The same retarding effect is produced by an acetyl or benzoyl group in the position ortho to the hydroxyl group. These phenols consequently belong to the group of "cryptophenols" (Auwers, Abstr., 1906, i, 838). Salol (phenyl salicylate) differs somewhat from ethyl salicylate, since it slowly absorbs ammonia to form an ammonium salt. The ammonium salt of ethyl salicylate is formed, however, when ammonia is passed into a solution of the ester in light petroleum or toluene at  $-40^\circ$ . Salicylaldehyde, ethyl *m*-hydroxybenzoate, and ethyl *p*-hydroxybenzoate absorb ammonia to form salts. Salicylic acid absorbs only 1 mol. of ammonia.

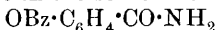
A new method for ascertaining whether a compound combines with ammonia in an indifferent solvent to form a salt is described. A known weight of the substance to be examined is dissolved in benzene and the depression of the freezing point observed; the calculated quantity of ammonia in the form of a *N*/10 solution in benzene is then added and the depression again noted. If an ammonium salt is formed, the mol. wt. obtained from the total depression of the freezing point of the benzene will correspond with the mol. wt. of the salt. If no combination has taken place, the value obtained will be the mean of the mol. wts. of ammonia and the substance. When the observed value lies between this mean value and the mol. wt. of the ammonium salt, it denotes the partial formation of an ammonium salt.

It is stated, in conclusion, that the apparent slow precipitation of the ammonium salts of various compounds recorded by Hantzsch and Dollfus (Abstr., 1902, i, 223) on passing ammonia into solutions of these compounds in benzene is due in some cases to supersaturation, whilst, in others, the crystals of the ammonium salt which separate out at first are so small that they can only be detected by illuminating the solution with a beam of light. The slow precipitation of an ammonium salt in benzene does not therefore indicate the presence of a pseudo-acid.

W. H. G.

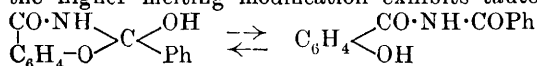
#### Acyl Derivatives of Salicylamide and Allied Compounds.

KARL AUWERS (*Ber.*, 1907, 40, 3506—3514).—The author has pointed out previously (Abstr., 1905, i, 894) that the isomeric benzoates of salicylamide described by Titherley and Hicks (Trans., 1905, 87, 1207) are not desmotropic in the sense of the formulæ:



(m. p.  $144^\circ$ , labile) and  $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{NH}$  (m. p.  $208^\circ$ , stable), and that the compound with the higher melting point is the *N*-benzoate,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHBz}$ .

The present paper is a discussion of the more recent work of McConnan and Titherley (Trans., 1906, 89, 1318); the latter authors are not in agreement with the author's conclusions, and suggest that the higher melting modification exhibits tautomerism in the sense:



*p*-Hydroxybenzamide *O*-benzoate,  $C_{14}H_{11}O_3N$ , separates from glacial acetic acid in colourless needles, m. p. 218—220°.

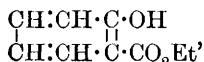
Determinations of the molecular weights of acetyl benzamide, *N*-acetylsalicylamide, and *O*-benzoylsalicylamide respectively in *p*-dibromobenzene solutions are submitted in support of the views advocated.

*o*-Benzoyloxyphenylacetamide,  $OBz \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH_2$ , obtained by benzoylating *o*-hydroxyphenylacetamide, separates from alcohol in glistening leaflets, m. p. 162—164°. It is insoluble in alkali and is converted by cold concentrated sulphuric acid into the original substance; it is accordingly an *O*-ester. The constitution was proved still further by conversion of the compound into *o*-benzoyloxybenzyl cyanide,  $C_{15}H_{11}O_2N$ , by means of phosphoric oxide; the latter compound separates from light petroleum in needles, m. p. 50°, and, when hydrolysed, forms *o*-hydroxybenzyl cyanide, which separates from a mixture of light petroleum and benzene in colourless needles, m. p. 117—119°.

A. MCK.

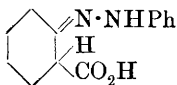
**Phenylhydrazone of Salicylic Acid.** HUGO SCHRÖTTER AND JOSEF FLOOH (*Monatsh.*, 1907, 28, 1099—1106. Compare Madsen, this vol., i, 423).—The resemblance of the enolic formula of ethyl

acetoacetate,  $\begin{array}{c} CMe \cdot OH \\ | \\ CH \cdot CO_2Et \end{array}$ , to the formula of ethyl salicylate,



suggested that the latter or its ketonic form should undergo condensations similar to those of ethyl acetoacetate. This view has led the authors to investigate the action of phenylhydrazine on methyl salicylate.

When heated with 2 mols. of freshly distilled phenylhydrazine and a few drops of piperidine in a reflux apparatus on a water-bath, methyl salicylate forms *salicylic acid-phenylhydrazone*,  $C_{13}H_{12}O_2N_2$ , in a 10% yield. This crystallises in white leaflets, m. p. 130°, gives a violet coloration when heated with aqueous, or in the cold with aqueous-alcoholic, ferric chloride, reduces ammoniacal silver, platinum chloride, and Fehling's solutions, dissolves in aqueous alkali carbonates, and can be recrystallised from concentrated sulphuric acid. It must have the annexed constitution. The *ammonium* salt exists



only in solution; the *potassium*, *sodium*, *calcium*, and *barium* salts readily decompose on recrystallisation or on evaporation of their aqueous solutions. The *piperidine* salt,  $C_{13}H_{12}O_2N_2 \cdot C_5H_{11}N$ , is obtained in a 55—60% yield by heating methyl salicylate and phenylhydrazine with an excess of piperidine; it crystallises in nacreous leaflets, m. p. 162°, is neutral in cold, but alkaline in hot, aqueous solution, and is decomposed slowly at 100° or by prolonged action of steam, or more quickly by aqueous alkalis.

G. Y.

**Synthesis of Iodogorgonic Acid.** HENRY L. WHEELER (*Amer. Chem. J.*, 1907, 38, 356—358).—Henze (this vol., i, 370) has referred to the iodogorgonic acid prepared by Wheeler and Jamieson (*Abstr.*,

1905, i, 350) as *l*-di-iodotyrosine. It has now been found that the supposed *l*-tyrosine, which, on treatment with iodine, yielded iodo-gorgonic acid, was really the inactive variety, and that the iodogorgonic acid (di-iodotyrosine) produced was also inactive and identical in every respect with the natural acid. E. G.

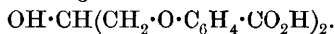
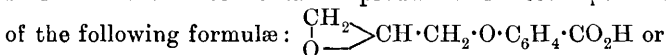
***m*-Hydroxytritanolactone.** HANS VON LIEBIG and PAUL KEIM (*J. pr. Chem.*, 1907, [ii], 76, 275—277. Compare Abstr., 1905, i, 781; this vol., i, 45).—The condensation of benzil with phenol in presence of zinc chloride leads to the formation of a substance, crystallising in colourless needles, m. p. 239°, and *m*-hydroxytritanolactone,  $C_{20}H_{14}O_3$ , which crystallises in rhombic leaflets, m. p. 120°. The sodium,  $C_{20}H_{15}O_3Na$ , disodium,  $C_{20}H_{14}O_3Na_2$ , potassium, and dipotassium salts have been analysed. Whilst *m*-hydroxytritanolactone remains unchanged on evaporation of its solutions, the alkali salts decompose forming diphenylmethane. Bromo-*m*-hydroxytritanolactone,  $C_{20}H_{13}O_2Br$ , forms colourless, rhombic leaflets, m. p. 129°.

***m*-Methoxytritanic acid**,  $C_{21}H_{18}O_3$ , prepared by hydrolysis of the methyl ester, crystallises in rhombic leaflets, m. p. 235°, and loses carbon dioxide at about 280°. The potassium salt,  $C_{21}H_{17}O_3K \cdot 2H_2O$ , crystallises in needles. The methyl ester,  $C_{22}H_{20}O_3$ , forms stout prisms, m. p. 134°.

***m*-Ethoxytritanic acid**,  $C_{22}H_{20}O_3$ , crystallises in needles, m. p. 264°, boils slightly above its m. p. in a vacuum, and loses carbon dioxide when heated under atmospheric pressure. The potassium salt,  $C_{22}H_{19}O_3K$ , was analysed. The ethyl ester,  $C_{24}H_{24}O_3$ , forms rhombohedra, m. p. 84°.

***m*-Methoxytritanol**,  $C_{20}H_{18}O_2$ , prepared by the action of concentrated sulphuric acid or of lead dioxide and glacial acetic acid on *m*-methoxytritanic acid, remains unchanged when heated at 360° or when boiled with ethereal or alcoholic hydrogen chloride. ***m*-Methoxytritane**,  $C_{20}H_{18}O$ , formed by heating *m*-methoxytritanic acid, separates from alcohol in small, rhombic crystals, m. p. 116°. ***m*-Ethoxytritane** crystallises in large prisms, m. p. 68°. ***m*-Hydroxytritane**,  $C_{19}H_{16}O$ , formed by heating the methyl ether or methoxytritanol or ethoxytritane with hydrogen iodide and glacial acetic acid, crystallises in hexagonal leaflets, m. p. 124°. These tritanic acids and tritanol derivatives give a violet coloration with concentrated sulphuric acid; the tritane derivatives give a yellow coloration. Only *m*-hydroxytritanolactone does not give a coloration. G. Y.

**The Condensation of Salicylic Acid with Epichlorohydrin or the Dichlorohydrins.** MARTIN LANGE (D.R.-P. 184382).—Salicylic acid, when condensed in sodium hydroxide solution with epichlorohydrin or  $\alpha$ - or  $\beta$ -dichlorohydrin, gives rise to the soluble sodium salt of a condensation product which corresponds with either of the following formulæ:



The free acid, m. p. 167°, crystallises from dilute alcohol in aggregates

of white needles. It is not decomposed by boiling with aqueous acids or alkalis. G. T. M.

**Polymerisation of Ethyl Phenylpropiolate.** PAUL PFEIFFER and W. MÖLLER (*Ber.*, 1907, 40, 3839—3844. Compare Stobbe, this vol., i, 769).—Ethyl phenylpropiolate is converted when heated in a sealed tube at 210° for ten to twelve hours into *diethyl 1-phenyl-naphthalene-2:3-dicarboxylate*, m. p. 127—128°, identical with the compound described wrongly by Lanser as triethyl triphenyltrimesate (*Abstr.*, 1899, i, 916). Only one of the carbethoxy-groups is hydrolysed by an aqueous or alcoholic solution of potassium hydroxide; the *ester acid*, m. p. 202—203°, so formed, probably has the formula

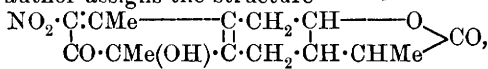
$$\text{C}_6\text{H}_4 \begin{cases} \text{CPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CH} = \text{C} \cdot \text{CO}_2\text{H} \end{cases}$$
, and is identical with the compound wrongly

described by Lanser and Halversen (*Abstr.*, 1902, i, 458) as monoethyl diphenyltetrenecarboxylate. It crystallises with 4H<sub>2</sub>O, which are driven off on heating the substance; the *sodium* salt, C<sub>20</sub>H<sub>15</sub>O<sub>4</sub>Na·6H<sub>2</sub>O, crystallises in small, silvery leaflets; the *calcium* salt, (C<sub>20</sub>H<sub>15</sub>O<sub>4</sub>)<sub>2</sub>Ca, forms small, slender needles; the *pyridinium* salt, C<sub>20</sub>H<sub>15</sub>O<sub>4</sub>·C<sub>5</sub>H<sub>5</sub>NH, forms brilliant, quadratic plates, m. p. 150—152°. A mixture of the calcium salt and calcium hydroxide yields, on distillation at 325°, a substance which crystallises in brilliant, brownish-yellow needles, m. p. 157°, and is probably *allochrysoketone* (compare Stobbe, this vol., i, 765).

W. H. G.

**ψ-Quinol Derivatives of the Santonin Group.** GUIDO BARGELINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 262—265).—Since the desmotroposantonins and the santonous acids contain the same ring,  $\begin{matrix} \cdot \text{C} \cdot \text{CMe} \cdot \text{C} \cdot \text{OH} \\ \cdot \text{C} \cdot \text{CMe} \cdot \text{CH} \end{matrix}$ , as is present in 1:4-dimethyl-β-naphthol, the author

has investigated the oxidation of these compounds to ascertain if they also yield derivatives of the ψ-quinol type (compare this vol., i, 914). Desmotroposantonous acid gives a ψ-quinol which is apparently isomeric with santoninic acid and yields an azo-compound when treated with phenylhydrazine. From desmotroposantonin has been prepared, not the corresponding ψ-quinol or hydroxysantonin, but its nitro-derivative which was obtained by Andreocci (*Abstr.*, 1898, i, 266), and to which the author assigns the structure



as it forms an acetyl compound. The corresponding quinitrole,  $\begin{matrix} \text{NO}_2 \cdot \text{C} \cdot \text{CMe} & \text{---} & \text{C} \cdot \text{CH}_2 \cdot \text{CH} & \text{---} & \text{O} \\ & & | & & \\ & & \text{CO} \cdot \text{CMe}(\text{NO}_2) \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CHMe} & > & \text{CO}, \end{matrix}$  has also been prepared.

This capacity of the aromatic ring of desmotroposantonin and desmotroposantonous acid of becoming alicyclic in the transformation of these compounds into ψ-quinols would indicate that the type changes from that of desmotroposantonin to that of santonin, and that the

latter should have the formula:  $\begin{matrix} \text{CH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH} & \text{---} & \text{O} \\ | & & \\ \text{CO} \cdot \text{CHMe} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CHMe} & > & \text{CO}. \end{matrix}$

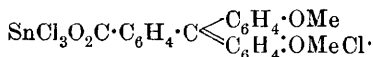
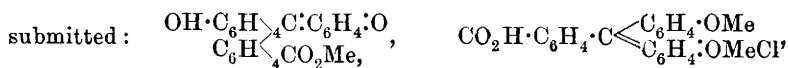
T. H. P.

**Constitution of Phthalein Salts.** RICHARD MEYER and KARL MARX (*Ber.*, 1907, 40, 3603—3605).—An intensely yellow *diethyl* quinonoid derivative of phenolphthalein, m. p. 98—104°, similar to the quinonoid derivative of tetrabromophenolphthalein (this vol., i, 421), has been prepared by the action of ethyl iodide on the solid potassium salt; on recrystallisation, it is transformed into the stable lactone ether, m. p. 118—120°.

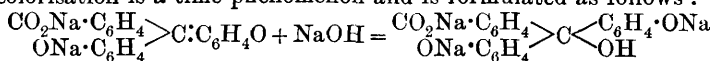
The absorption spectra of the alkali salts of phenolphthalein, quinolphthalein, and fluorescein are compared. If the wave-lengths of the absorbed light are taken as a function of the concentration of the solutions, the three spectra give similar curves. That the curve for fluorescein, although differing in position, is similar in shape to those for phenolphthalein and quinolphthalein, which lie close together, shows that the difference between these three substances is one of degree and not fundamental. G. Y.

**Halochromism of Phenolphthalein and its Esters.** KURT H. MEYER and ARTHUR HANTZSCH (*Ber.*, 1907, 40, 3479—3488).—Whilst the behaviour of phenolphthalein towards alkalis and the constitution of its alkali salts have been frequently investigated, its basic properties and its power of forming salts with acids have been comparatively little studied. The authors have accordingly found that phenolphthalein forms a red salt with hydrogen chloride at -30°, but the salt could not be isolated; on the other hand, brilliant red compounds were obtained with aluminium chloride and stannic chloride respectively. The lactoid dimethyl ether of phenolphthalein exhibits a similar behaviour towards these chlorides.

The authors confirm the results of Green and King (*Abstr.*, 1906, i, 670) with regard to the quinonoid methyl ester of phenolphthalein and agree with their theoretical conclusions. This compound also forms double salts. Since the alkali salts of phenolphthalein have the same colour as those of the quinonoid ester, the quinonoid formula is assigned to the former. The following formulæ are accordingly



The fact that the red colour of phenolphthalein in alkaline solution is discharged by excess of alkali is not due to the formation of the colourless sodium salt of phenolphthalein, as is often supposed; the decolorisation is a time phenomenon and is formulated as follows:

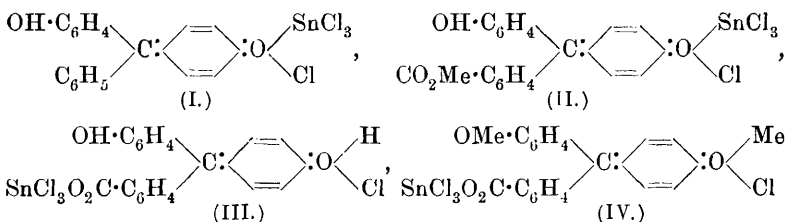


The quinonoid monomethyl ester of phenolphthalein also forms red double salts with stannic chloride and aluminium chloride; these salts are undoubtedly of quinonoid structure.

The double salts of phenolphthalein and its lactoid dimethyl ether have, not only the same colour when solid, namely, cinnabar-red, but in solution have almost the same absorption spectra as the salts of the

quinonoid ester, exhibiting a characteristic green band. The conclusion is drawn that the salts of the lactoid ether are quinonoid, in fact, *all salts of phenolphthalein with acids are quinonoid*.

The tin double salts of benzaurin (I), the quinonoid ester (II), phenolphthalein (III), and the lactoid dimethyl ether (IV) are respectively represented as follows:



When hydrogen chloride is passed over dry phenolphthalein at the ordinary temperature, there is no change, but at  $-30^{\circ}$  addition of from 1—2 mols. of the acid takes place, the salt being red; on rise of temperature, however, all the hydrogen chloride is eliminated.

The *salt*,  $\text{C}_{20}\text{H}_{14}\text{O}_4\cdot\text{AlCl}_3$ , obtained by adding the calculated amount of a solution of aluminium chloride in nitrobenzene to a solution of phenolphthalein in nitrobenzene and then pouring the mixture into carbon disulphide, is a cinnabar-red powder, which chars on being heated. The *salt*,  $\text{C}_{20}\text{H}_{14}\text{O}_4\cdot\text{C}_6\text{H}_5\cdot\text{NO}_2\cdot\text{SnCl}_4$ , obtained from stannic chloride in a similar manner, is a red, hygroscopic powder. The *salt*,  $\text{C}_{22}\text{H}_{18}\text{O}_4\cdot\text{AlCl}_3$ , obtained from the lactoid dimethyl ether, is a cinnabar-red powder. The *salt*,  $\text{C}_{22}\text{H}_{18}\text{O}_4\cdot\text{SnCl}_4$ , forms red crystals, m. p.  $128-129^\circ$ ; its solution in chloroform is red; its alcoholic solution orange-yellow.

Quinonoid phenolphthalein methyl ester (methyl benzaurincarboxylate), obtained by the action of methyl sulphate on phenolphthalein (compare Green and King, *loc. cit.*), is a red, amorphous powder melting indefinitely between 127° and 130°. Its concentrated solutions are red, but become yellow on dilution; its solution in liquid ammonia is reddish-violet. It undergoes saponification with great ease. It forms the *salt*,  $C_{21}H_{16}O_4 \cdot AlCl_3$ , which is a cinnabar-red powder. The *salt*,  $C_{21}H_{16}O_4 \cdot SnCl_4$ , forms red flakes.

The absorption spectra of the tin double salts prepared are described.

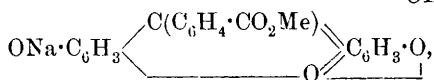
The red solutions of phenolphthalein alkali salts require such a large excess of alkali in order to be decolorised that the reaction cannot be clearly followed by conductivity measurements. Tetrabromophenolphthalein was, however, examined from this standpoint. A. McK.

**Constitution of the Phenolphthalein and Quinolphthalein Salts.** II. ARTHUR G. GREEN and PERCY E. KING (*Ber.*, 1907, 40, 3724—3734. Compare *Abstr.*, 1906, i, 670\*).—The scarlet compound described previously as the quinonoid methyl ester of phenolphthalein is found to be the hydrochloride of the ester. The *ester*, which is much

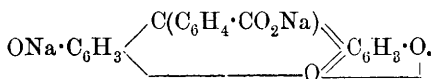
\* See also Proc., 1907, **23**, 228.

more stable than its hydrochloride, is obtained best by passing dry hydrogen chloride into a solution of phenolphthalein in methyl alcohol and 100% sulphuric acid, and, after keeping overnight, pouring the solution into ammonium hydroxide at 0°. After purification, it crystallises in orange, prismatic needles, and in alcoholic solution yields with hydrochloric acid a scarlet solution of the chloride which gradually loses its colour and yields phenolphthalein. The ester forms a violet-red solution in alkali hydroxides, from which the unchanged methyl ester is obtained by immediate acidification and phenolphthalein by postponed acidification. The methyl ester of quinolphthalein in the form of its chloride exhibits precisely analogous behaviour, and forms a bluish-purple solution in alkalis.

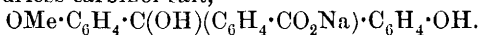
For these coloured alkali salts of the esters, the authors recommend the formulæ:  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}) : \text{C}_6\text{H}_4 : \text{O} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{OH} \end{smallmatrix}$  and



and from analogy the coloured salts of phenol- and of quinol-phthaleins must be represented by  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Na}) : \text{C}_6\text{H}_4 : \text{O} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{OH} \end{smallmatrix}$  and

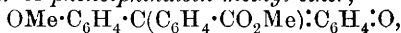


These conclusions, which accord with the behaviour of the salts of the phthaleins and their esters with excess of potassium hydroxide and with alcohol, the salts of the esters remaining coloured, are confirmed by a study of the lactonoid methyl and dimethyl ethers of phenolphthalein and quinolphthalein (Meyer and Spengler, Abstr., 1905, i, 440). The methyl ethers represented by the preceding quinonoid structures would not contain a phenolic hydroxyl group, and consequently should not form coloured alkali salts, and should yield esters insoluble in alkalis. This is actually the case. Phenolphthalein methyl ether has a double m. p. initially at 148—149°, and after resolidification at 80°; in alkalis, it yields a faintly red solution, the colour of which is weaker the purer the ether (Meyer and Spengler: m. p. 141—142°, red solution in alkalis). This solution probably contains the colourless carbinol salt,



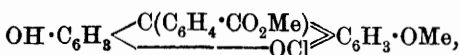
Quinolphthalein methyl ether separates from benzene in colourless prisms, m. p. 118—122°, and after removal of the benzene of crystallisation, m. p. 107—109°; it dissolves in alkalis forming a colourless solution of the carbinol salt (compare Nietzki and Burckhardt, Abstr., 1897, i, 225).

The methyl ester of phenolphthalein methyl ether,



obtained from the lactonoid methyl ether in a similar manner to the methyl ester of phenolphthalein, is an orange substance insoluble in alkalis; the hydrolysed compound yields the original lactonoid ether by acidification. The methyl ester of quinolphthalein methyl ether is obtained in the form of the chloride,

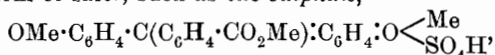




when dry hydrogen chloride is passed into a methyl-alcoholic solution of the lactonoid ether; it forms red plates, readily loses methyl chloride, is insoluble in aqueous alkalis, and yields the lactonoid ether by hydrolysis. The *chloride*,  $\text{OH} \cdot \text{C}_6\text{H}_3 \left\langle \frac{\text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})}{\text{OCl}} \right\rangle \text{C}_6\text{H}_3 \cdot \text{OMe}$ ,

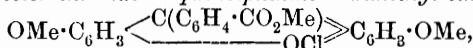
is prepared by passing hydrogen chloride into a glacial acetic acid solution of quinolphthalein methyl ether; it forms dark red, glistening crystals, and is instantaneously decomposed by water or moist ether.

The esters of dimethylated phenol- or quinol-phthalein are obtained only in the form of salts, such as the *sulphate*,



which is an unstable, scarlet substance. More stable is the red double salt,  $2[\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}) : \text{C}_6\text{H}_4 : \text{OMeCl}] \cdot \text{SnOCl}_2$ , which is decolorised by water, alcohol, or alkalis with regeneration of the lactonoid ether.

The *methyl ester chloride of quinolphthalein dimethyl ether*,



is isolated in the form of the double salt,  $2\text{C}_{22}\text{H}_{19}\text{O}_5\text{Cl} \cdot \text{ZnCl}_2$ , which is an orange-red substance. C. S.

#### Preparation of *o*-Carboxyphenylthioglycollic Acid.

KALLE & CO. (D.R.-P. 181658).—When diazotised anthranilic acid is treated with sodium monosulphide, a poor yield of thiosalicylic and salicylic acids is obtained, but when sodium polysulphide is employed a new sulphur derivative is obtained, which, unlike thiosalicylic acid, is insoluble in alcohol, and yields *o*-carboxyphenylthioglycollic acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , on treatment with an alkaline solution of sodium chloroacetate. G. T. M.

**Nitration of Benzoylvanillin.** JOAN POPOVICI (*Ber.*, 1907, 40, 3504—3506).—When benzoylvanillin is nitrated by cold concentrated nitric acid, one nitro-group only enters into the ring. It takes up the ortho-position relatively to the aldehyde group; this was proved by comparing the compound obtained with that resulting from the action of benzoyl chloride on (vic-) *o*-nitrovanillin; the phenylhydrazones are also identical.

*Benzoylvanillinphenylhydrazone* separates from glacial acetic acid in prisms, m. p. 209—210° (corr.).

(vic-) *o*-Nitrobenzoylvanillin,  $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{NO}_2)(\text{OMe}) \cdot \text{OBz}$  (1:2:3:4), separates from glacial acetic in colourless prisms, m. p. 97°. Its *phenylhydrazone* separates from glacial acetic acid in golden-yellow plates, m. p. 192°. A. McK.

**cyclobutanone.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 922—925. Compare Abstr., 1905, i, 355).—Further details are given for the preparation of pure cyclobutanone together with fresh determinations of some physical constants. *cyclobutanone*, b. p. 98.5—99°/745 mm.;  $D_4^{20}$  0.9548;  $D_4^{16}$  0.9382;  $n_D^{16}$  1.4220. The

semicarbazone of *cyclo*-butanone has m. p. 201° (decomp.). When boiled with lead oxide and water, 1 : 1-dibromocyclobutane is converted into *cyclobutanone* and an unsaturated bromide, probably  $\text{CH}_2\text{<}\begin{smallmatrix}\text{CH}_2 \\ \text{CH}\end{smallmatrix}\text{>CBr}$ , b. p. 93—95°.

Z. K.

*cyclo*Nonanone. RICHARD WILLSTÄTTER and TOKUHEI KAME-TAKA (*Ber.*, 1907, 40, 3876).—The authors confirm the observations of Zelinsky (this vol., i, 780) regarding the formation of *cyclononanone* from sebacic acid.

A. McK.

Terpenes and Ethereal Oils. LXXXVII. Nopinone. OTTO WALLACH and ARNOLD BLUMANN (*Annalen*, 1907, 356, 227—249).—Nopinone (Baeyer and Villiger, *Abstr.*, 1896, i, 622) has been prepared previously in such small amounts that only its b. p. has been determined. It was desirable therefore to attempt the preparation of larger quantities.

Nopic acid, m. p. 126°,  $[\alpha]_D - 15.64^\circ$ , is best isolated from the oxidation product of turpentine oil by conversion into its sparingly soluble sodium salt. Much better yields are obtained from dextro-rotatory American than from lævorotatory French turpentine oil.

Nopinone,  $\text{C}_9\text{H}_{14}\text{O}$ , is obtained in good yields by adding potassium permanganate and concentrated sulphuric acid to a hot aqueous solution of sodium nopate. It solidifies in a freezing mixture to a crystalline mass, m. p. slightly above 0°, b. p. 209°,  $D_{20} 0.981$ ,  $n_D^{20} 1.4787$ ,  $[\alpha]_D + 18.48^\circ$  when undiluted,  $+ 37.27^\circ$ — $+ 38.04^\circ$  in alcohol,  $+ 11.02^\circ$  in ether, or  $+ 10.79^\circ$ — $+ 10.95^\circ$  in benzene. When treated with hydrogen chloride in alcoholic solution, it condenses, forming the trichloride,  $\text{C}_{18}\text{H}_{29}\text{OCl}_3$ , which crystallises in stout prisms, decomp. 148° (evolving gas), and on prolonged boiling in solution or digestion with 1 mol. of sodium ethoxide is converted into the dichloride,  $\text{C}_{18}\text{H}_{28}\text{OCl}_2$ , crystallising in needles, m. p. 125—126°. The trichloride is again formed on treating the dichloride with hydrogen chloride in alcoholic solution; the ease with which it is formed together with its sparing solubility makes the trichloride suitable for the recognition of nopinone. On prolonged boiling with dilute sulphuric acid, nopinone is transformed into 1-isopropyl- $\Delta^2$ -cyclohexene-4-one (*Abstr.*, 1906, i, 195).

Reduction of nopinone with sodium in moist ethereal solution leads to the formation of two nopinols, probably *cis*- and *trans*-isomerides.  $\alpha$ -Nopinol,  $\text{C}_9\text{H}_{15}\cdot\text{OH}$ , sublimes in white needles, m. p. 102°, b. p. 204—205°,  $[\alpha]_D - 5.32^\circ$ , remains unchanged in contact with dilute sulphuric acid, and forms a phenylurethane,  $\text{NHPh}\cdot\text{CO}_2\cdot\text{C}_9\text{H}_{15}$ , m. p. 131—132°.  $\beta$ -Nopinol is obtained as a viscid mass,  $[\alpha]_D 15.03^\circ$ , forms a phenylurethane, m. p. 95—96°, and when heated with zinc chloride yields a small amount of nopinonene,  $\text{C}_9\text{H}_{14}$ , b. p. 157—160°.

Reduction of nopinone by means of sodium in alcoholic solution leads to the formation of the pinacone,  $\text{C}_{18}\text{H}_{30}\text{O}_2$ , which is obtained in crystals, m. p. 106—107°, b. p. 195—200°/11 mm.

Homopinol (methylnopinol, pinene hydrate),  $\text{C}_{10}\text{H}_{17}\cdot\text{OH}$ , prepared by the action of magnesium methyl iodide on nopinone, crystallises in needles, m. p. 58—59°, b. p. 204—205°,  $[\alpha]_D - 4.99^\circ$ , has an odour resembling camphor, is stable towards permanganate, and yields *cis*-

terpin hydrate when shaken with 5% sulphuric acid, or in less amount when treated with cold saturated oxalic acid. The action of formic acid on homonopinol leads to the formation of a mixture of products resulting probably from the primary formation of terpin and the further transformation of this into dipentene, terpinol, terpinene, and terpineol. Dipentene dihydrochloride is formed by the action of hydrogen chloride on homonopinol in glacial acetic acid solution.

When heated with zinc chloride, homonopinol yields polymerisation products together with small amounts of hydrocarbons, which boil chiefly at 170—180°, are volatile with steam, and have an odour of limonene. The action of potassium hydrogen sulphate on homonopinol at 130° leads to the formation of a *hydrocarbon*,  $C_{10}H_{16}$ , b. p. 163—164°.

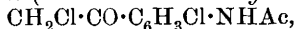
On treatment with phosphorus pentachloride in light petroleum, homonopinol yields a chloride,  $C_{10}H_{17}Cl$ , b. p. 95—105°/13 mm. or 200—205°/760 mm. evolving hydrogen chloride, which is isomeric with the chloride obtained by the action of hydrogen chloride on pinene, and on treatment with hydrogen chloride in glacial acetic acid solution yields dipentene dihydrochloride. The action of amyl nitrite and nitric acid on the chloride leads to the formation of a *nitrosate* containing chlorine; when treated with aniline, the chloride yields dipentene. This chloride may be formed as an intermediate product in the formation of dipentene by the action of hydrogen chloride on moist pinene.

G. Y.

[Alkylation of  $\psi$ -Ionone.] HAARMANN and REIMER (D.R.-P. 183855).— $\psi$ -Ionone, when mixed with five parts of methyl sulphate and the solution subsequently warmed at 40°, yields an alkylated product which is separated by distillation in steam. The alkyl derivative when freed from ionone by sodium hydrogen sulphite has the following properties: b. p. 135°/12 mm.,  $D^{20}_D$  0.945,  $n_D$  1.5150. It is, however, a mixture, the ketonic constituent of which when separated by means of semicarbazone has b. p. 120—128°/12 mm.,  $D^{20}_D$  0.940,  $n_D$  1.491—1.494. A semicarbazide,  $C_{13}H_{21}ON_3$ , was obtained, m. p. 182—183°. These results point to the production of a new methyl-ionone.

G. T. M.

**1-Chloroacetyl-2-chloro-4-aminobenzene** [ $\omega$ -2-Dichloro-4-aminoacetophenone] and its Derivatives. FRANZ KUNCKELL and A. RICHARTZ (*Ber.*, 1907, 40, 3394—3397).— $\omega$ -2-Dichloro-4-acetylaminacetophenone (3-chloro-4-chloroacetylacetanilide),



obtained by Friedel-Craft's synthesis from chloroacetyl chloride and *m*-chloroacetanilide in the presence of carbon disulphide, crystallises from benzene and melts at 146—147°.

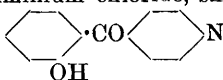
When oxidised with acidified permanganate, the ketone yields 1-chloro-2-acetylaminobenzoic acid,  $C_9H_8O_3NCl$ , m. p. 206—207°, and this on hydrolysis yields Tiemann's 2-chloro-4-aminobenzoic acid (*Abstr.*, 1891, 704).

$\omega$ -2-Dichloro-4-aminoacetophenone, obtained by hydrolysing the acetyl derivative, yields a *hydrochloride*,  $CH_2Cl \cdot CO \cdot C_6H_3Cl \cdot NH_2 \cdot HCl$ , in the form of yellowish-red needles, m. p. 278° (decomp.). The free amine melts at 95—97°.

J. J. S.

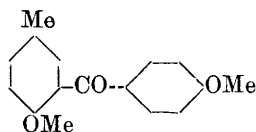
### Saponifiability of Ethers of Aromatic Hydroxy-ketones.

KARL AUWERS and ERICH RIETZ (*Ber.*, 1907, 40, 3514—3521).—It has been pointed out by Auwers (*Abstr.*, 1904, i, 67) that, by the condensation of phenetole with *p*-nitrobenzoyl chloride in the presence of aluminium chloride, small amounts of 4'-nitro-2-hydroxy-

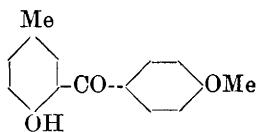
benzophenone, , are formed in addition to the

normal product, 4'-nitro-4-ethoxybenzophenone. The conclusion was drawn that the ethers of aromatic *o*-hydroxyketones are more readily saponified than the isomeric para-derivatives.

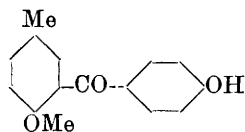
In support of this view, the authors have studied the behaviour of the ketone (I) on saponification with aluminium chloride; a mono-



(I.)



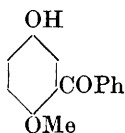
(II.)



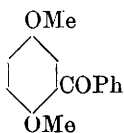
(III.)

methylated compound is formed which is not attacked by aluminium chloride even at 220°. The other methyl group, on the other hand, is eliminated with remarkable ease; in the synthesis of the dimethyl ether from *p*-cresol methyl ether and anisic chloride, the monomethyl ether is formed in about the same amount of the dimethyl ether. That the product of the partial saponification has the formula (II) was proved by the fact that the isomeric ether (III) is produced by the condensation of *p*-cresol methyl ether with *p*-nitrobenzoyl chloride and subsequent displacement of the nitro- by the hydroxy-group. The latter compound is saponified with great ease.

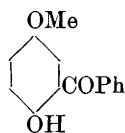
Kauffmann ascribed the formula (IV) to the substance obtained



(IV.)



(V.)



(VI.)

by the partial saponification of the compound (V). The authors conclude that the correct formula is (VI), since cryoscopic determinations in *p*-dibromobenzene solutions give normal values.

Similar results were obtained with ethers of another series of dihydroxy-ketones.

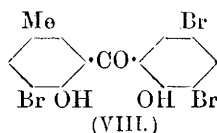
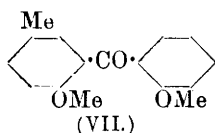
2 : 4'-Dimethoxy-5-methylbenzophenone,  $C_{16}H_{16}O_3$ , separates from light petroleum in colourless needles, m. p. 69—70°. 2-Hydroxy-4'-methoxy-5-methylbenzophenone,  $C_{15}H_{14}O_3$ , separates from dilute alcohol in yellow leaflets, m. p. 108—109°. Its dibromo-derivative,  $C_{15}H_{12}O_3Br_2$ , crystallises from glacial acetic acid in yellow needles, m. p. 168—169°.

4'-Nitro-2-methoxy-5-methylbenzophenone,  $C_{15}H_{13}O_4N$ , separates from light petroleum in golden, glistening leaflets, m. p. 101—102°.

4'-Amino-2-methoxy-5-methylbenzophenone,  $C_{15}H_{15}O_2N$ , obtained by the reduction of the preceding compound with ammonium sulphide, separates from benzene in tiny needles, m. p.  $152^\circ$ . 4'-Amino-2-hydroxy-5-methylbenzophenone,  $C_{14}H_{13}O_2N$ , separates from dilute acetic acid in leaflets, m. p.  $137^\circ$ .

4'-Hydroxy-2-methoxy-5-methylbenzophenone,  $C_{15}H_{14}O_3$ , obtained from 4'-amino-2-methoxy-5-methylbenzophenone by replacing the amino- by the hydroxy-group, crystallises from benzene in glistening leaflets, m. p.  $160^\circ$ . When saponified, it forms 2 : 4'-dihydroxy-5-methylbenzophenone,  $C_{14}H_{12}O_3$ , which crystallises from benzene in tiny, yellow needles, m. p.  $150$ — $151^\circ$ . The latter compound forms a tribromo-derivative,  $C_{14}H_9O_3Br_3$ , crystallising from glacial acetic acid in yellow needles, m. p.  $211.5$ — $202.5^\circ$ .

The ketone (VII), obtained from *o*-methoxybenzoyl chloride and



*p*-cresol methyl ether, was saponified at  $100^\circ$  with aluminium chloride and the product brominated, when the tribromo-compound (VIII) was obtained; it separates from glacial acetic acid in yellow crystals, melting indefinitely at  $190^\circ$ .  
A. McK.

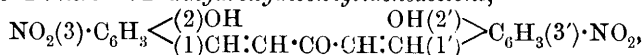
Dinitro- and Dibromo-2 : 2'-dihydroxydibenzylideneacetone.  
RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1907, 40, 3455—3461).—Compounds of the types  $CHR:CH \cdot CO \cdot CH:CHR$  and



have already been studied by Claisen and others; the authors have been interested in the effect of the substitution of nitro- or bromine groups on the behaviour as dyes of those types which possess the complex chromophore  $C:C \cdot CO \cdot C:C$ , are symmetrically constituted, and in which the two hydrogen atoms in the ortho-positions in each ring are substituted by hydroxyl groups.

It has been previously shown by Fabinyi (D.R.-P. 110521) that salicylaldehyde and acetone interact in alcoholic solution in the presence of concentrated sodium hydroxide to form the sodium salt of 2 : 2'-dihydroxydibenzylideneacetone, from which the latter compound itself is isolated when dilute mineral acid is added.

3 : 3'-Dinitro-2 : 2'-dihydroxydibenzylideneacetone,



obtained from *m*-(*vic*-)nitrosalicylaldehyde in an analogous manner, separates from alcohol in yellow needles, m. p.  $231$ — $232^\circ$  (decomp.). Its solution in concentrated sulphuric acid is yellowish-red and becomes colourless on the addition of water. The sodium salt forms glistening ruby-red crystals. The diacetyl derivative separates from glacial acetic acid in yellow crystals, m. p.  $228$ — $230^\circ$  (decomp.); the dibenzoyl derivative separates from nitrobenzene in tiny, yellow crystals, m. p.  $235$ — $238^\circ$  (decomp.).

5 : 5'-Dinitro-2 : 2'-dihydroxydibenzylidenacetone, obtained from *m*-(*as*-)nitrosalicylaldehyde, separates from alcohol in orange-yellow crystals, m. p. 212—214° (decomp.); its solution in concentrated sulphuric acid is orange-red; its sodium salt is reddish-brown. Its *diacetyl* derivative separates from glacial acetic acid in yellow scales, m. p. 203°.

4 : 4'-Dinitro-2 : 2'-dihydroxydibenzylidenacetone, obtained by the direct nitration of 2 : 2'-dihydroxydibenzylidenacetone, separates from alcohol in tiny needles, m. p. about 204° (decomp.); its solution in concentrated sulphuric acid is orange-red; its solution in alkali, cherry-red; its sodium salt is dark red. Its *diacetyl* derivative separates from glacial acetic acid in tiny leaflets, m. p. 196° (decomp.).

By the action of concentrated nitric acid on 2 : 2'-dihydroxydibenzylidenacetone, the more highly nitrated compound, *tetranitro*-2 : 2'-dihydroxydibenzylidenacetone,  $\text{CO}[\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OH}]_2$ , may be obtained under the conditions quoted; it separates from nitrobenzene in yellow needles; its solution in concentrated sulphuric acid is orange-coloured; it begins to decompose at 240°.

5 : 5'-Dibromo-2 : 2'-dihydroxydibenzylidenacetone, obtained from 5-bromosalicylaldehyde, crystallises from alcohol in yellow needles, m. p. 188° (decomp.); its solution in dilute aqueous sodium hydroxide is red, and the sodium salt is reddish-brown. Its solution in concentrated sulphuric acid is cherry-red; its solution in concentrated aqueous sodium hydroxide is bluish-violet. Its *diacetyl* derivative crystallises from glacial acetic acid in tiny, yellow needles, m. p. 187—188° (decomp.). The *dimethoxy*-derivative, obtained by the action of methyl iodide on the sodium salt, crystallises from alcohol in yellow leaflets, m. p. 137°; the *diethoxy*-derivative forms yellow leaflets, m. p. 131°. The *dibenzoyl* derivative crystallises from benzene in yellow crystals, m. p. 221° (decomp.).

2 : 2'-Diacetoxydibenzylidenacetone crystallises from glacial acetic acid or alcohol in yellow needles, m. p. 128°. 2 : 2'-Dimethoxydibenzylidenacetone separates from alcohol in glistening yellow leaflets, m. p. 124°. 2 : 2'-Diethoxydibenzylidenacetone forms glistening yellow leaflets, m. p. 89°. 2 : 2'-Dibenzoyloxydibenzylidenacetone forms yellowish-white crystals, m. p. 135°. A. McK.

**Duplobenzylidenethioacetone and the Oxonium Theory.** HANS VON LIEBIG (*J. pr. Chem.*, 1907, [ii], **76**, 277—280).—A criticism of Fromm and Höller's views as the constitution of the additive compounds of duplobenzylidenethioacetone (this vol., i, 710) from the standpoint of the present author's view of the nature of oxonium salts (this vol., i, 45). G. Y.

**Acetalation of Aldehydes and Ketones.** LUDWIG CLAISEN (*Ber.*, 1907, **40**, 3903—3914).—In consequence of the criticisms of many investigators, the author publishes the details of his process for obtaining acetals in nearly quantitative yield from aldehydes or ketones by means of ethyl orthoformate. The aldehyde, or ketone (1 mol.), and ethyl orthoformate (1.1 mols.) are dissolved in alcohol (not less than 3 mols.) and the mixture, in the presence of a catalyst, such as a

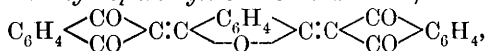
mineral acid, ferric chloride, or ammonium chloride, is kept at the ordinary temperature or is gently warmed.

*o*-Ethers of  $\beta$ -diketones and of the esters of ketonic acids are also obtained by this method. Benzoylacetone yields the *ether*,  $\text{COPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{OEt}$ , b. p.  $162-164^\circ$ ,  $D^{15}_D$  1.058, which is converted by hydroxylamine into 3-phenyl-5-methylisooxazole, m. p.  $42-43^\circ$ .

If too large a quantity of the catalyst is used in the process, or if the time is unduly prolonged, the yield of the acetal may diminish to zero.

Arbusoff's experiments on the acetalation of acetone and acetophenone by ethyl orthoformate and alcohol without a catalyst (this vol., i, 749) have been repeated, and not a trace of the acetal has been obtained. C. S.

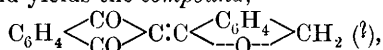
**Condensation of Diketohydrindene [1:3-Indandione] with Phthalic Anhydride.** CARMELO MARCHESE (*Gazzetta*, 1907, 37, ii, 303-309).—*Anhydrophthalylbis-1:3-indandione*,



prepared by the condensation of phthalic anhydride with 1:3-indandione or ethyl 2-sodio-1:3-diketohydrindene-2-carboxylate in presence of acetic anhydride, crystallises from xylene or nitrobenzene in yellow needles, m. p.  $325^\circ$ , and dissolves in alkali hydroxides, giving intensely red solutions.

*Phthalylbis-1:3-indandione*,  $\text{C}_6\text{H}_4[\text{CO}\cdot\text{CH}:(\text{CO})_2\cdot\text{C}_6\text{H}_4]_2$ , obtained by boiling the preceding compound with alcoholic potassium hydroxide solution, separates from ethyl acetate in faintly yellow, shining crystals, m. p.  $198^\circ$ , and dissolves readily in nitrobenzene and sparingly in alcohol, benzene, xylene, or acetic acid. The salts of the alkali metals and of calcium are intensely red and readily soluble in water; the *barium* salt,  $\text{C}_{26}\text{H}_{12}\text{O}_6\text{Ba}\cdot 11\text{H}_2\text{O}$ , was analysed.

Reduction of *anhydrophthalylbis-1:3-indandione* by means of zinc dust and acetic acid yields the *compound*,



m. p.  $275^\circ$ , which dissolves in acetic acid or ethyl acetate and, to a slight extent, in alcohol, water, benzene, or xylene.

An attempt to condense camphoric anhydride with 1:3-indandione in presence of acetic anhydride yielded 2-acetyl-1:3-indandione (compare Schwerin, *Abstr.*, 1894, i, 194). T. H. P.

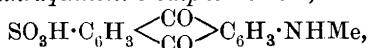
**New Anthraquinone Derivatives.** EDUARD LAUBÉ (*Ber.*, 1907, 40, 3562-3567).—1-*p*-Bromoanilinoanthraquinone, prepared by condensing aminoanthraquinone with *p*-dibromobenzene in presence of potassium carbonate and copper powder, is a dark red powder, m. p.  $308^\circ$ , dissolving in concentrated sulphuric acid with a green coloration which changes to a scarlet-red on the addition of a drop of dichromate. *p*-Phenylenebis-1-aminanthraquinone, obtained at the same time as the above compound, separates from chloroform as a blackish violet powder giving a violet, metallic, glistening mark on porcelain, m. p. above  $320^\circ$ . 2-*p*-Bromoanilinoanthraquinone forms ball-like, scarlet-

red crystals, m. p.  $242^{\circ}$ , dissolving in sulphuric acid with a cornflower-blue coloration. *p*-Phenylenebis-2-aminoanthraquinone is a dark brown powder, m. p.  $300^{\circ}$ , giving a greenish-blue coloration with sulphuric acid.

1-Iodoanthraquinone reacts more easily with carbazole and with diphenylamine than the corresponding chloro-compound. *N*-Anthraquinonylcarbazole crystallises in well-formed, ruby-red crystals, m. p.  $252\text{--}254^{\circ}$ , dissolving in sulphuric acid with an emerald-green coloration which, on warming, changes through olive-green to brown. It gives rise to a yellowish-red solution with green fluorescence when reduced with zinc and acetic acid. 1-Diphenylaminoanthraquinone is a blackish-red powder, dissolving with an olive-green coloration in sulphuric acid. E. F. A.

[Preparation of Amino-, Alkylamino-, and Arylamino-derivatives of Anthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 181722. Compare this vol., i, 224).—The sulphonic groups in 1:5- and 1:8-anthraquinonedisulphonic acids may be partially or completely replaced by amino-, alkylamino-, or arylamino-groups by heating the alkali salts of these acids with ammonia, an alkylamine, or an aromatic amine.

1-Methylaminoanthraquinone-5-sulphonic acid,



is produced together with a small amount of *s*-dimethyl-1:5-diaminoanthraquinone,  $\text{NHMe}\cdot\text{C}_6\text{H}_3\left\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{NHMe}$ , by heating potassium 1:5-anthraquinonedisulphonate with aqueous methylamine at  $150^{\circ}$ ; the *potassium* salt crystallises from water in violet-brown needles.

1-Methylaminoanthraquinone-8-sulphonic acid, 1-aminoanthraquinone-5-sulphonic acid, and 1-aminoanthraquinone-8-sulphonic acid are similarly obtained, and their tinctorial properties are described in the patent.

*s*-1:5-*p*-Ditolylaminoanthraquinone may be prepared from 1:5-anthraquinonedisulphonic acid and *p*-toluidine. G. T. M.

Preparation of Trichloroanthraflavic Acid. R. WEDEKIND (D.R.-P. 181659).—The chlorine additive product of anthraflavic acid ("hexachloroanthraflavic acid"), when heated with phenol or some other solvent of high boiling point, such as xylene or nitrobenzene, loses hydrogen chloride and furnishes a *trichloroanthraflavic acid*, which separates in lustrous, yellow needles. This compound, which is employed in the preparation of dyes of the anthracene series, is insoluble in water, and yields a sparingly soluble *sodium* salt.

G. T. M.

Preparation of Dianthraquinonyl and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 184495).—The following is an alternative method of preparing dianthraquinonyl and its derivatives. 1-Amino-2-methylanthraquinone is diazotised in sulphuric acid and the dry diazo-sulphate suspended in acetic anhydride



and treated with copper powder, when 2:2'-dimethyl-1:1'-dianthraquinonyl is obtained (compare this vol., i, 539). G. T. M.

**Preparation of a Chlorine Additive Compound of Anthraflavic Acid.** R. WEDEKIND (D.R.-P. 179916).—Anthraflavic acid does not absorb chlorine in acidified water at 100°, but, when the boiling temperature is raised by the addition of sulphuric acid, substitution occurs with the formation of the dichloro-derivatives; when, however, this acid is suspended in concentrated calcium or magnesium chloride solution and treated at 110° with a mixture of sodium chlorate and hydrochloric acid, a yellow substance having the composition of a *hexachlorodihydroxyanthraquinone* is obtained. This compound is moderately stable towards acids, but is decomposed by aniline and dilute alkalis. When heated in phenol or cresol, this additive product loses hydrogen chloride and a well-defined trichloro-anthraflavic acid is produced. G. T. M.

**Benzanthrone Derivatives of the Naphthanthraquinone Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 181176. Compare Abstr., 1906, i, 889, and this vol., i, 324).—Naphthanthraquinone resembles anthraquinone in reacting with glycerol to yield benzanthrone derivatives, which on heating with alkali hydroxides furnish blue colouring matters suitable for vat dyeing.

Benzonaphthanthrone,  $C_{21}H_{12}O$ , m. p. 186—188°, was prepared in the following ways: (1) by heating naphthanthraquinone with glycerol, aniline sulphate, and concentrated sulphuric acid at 150°, or by warming its dihydro-derivative with these reagents at 110°; (2) by heating the quinone or naphthanthranol with glycerol and zinc chloride at 200 to 210°. G. T. M.

**Linalool is a Tertiary Alcohol.** ROURE-BERTRAND FILS (*Chem. Zentr.*, 1907, ii, 464; from *Wiss. u. ind. Ber. Roure-Bertrand Fils*, [ii], 5, 3—5).—Experiments on the formation of esters of geraniol and linalool have shown that linalool is a tertiary alcohol. The alcohols were mixed with acetic acid (6 mols.) and kept at a constant temperature. The quantities which had entered into combination after different periods are given below:

	hours.		days.					months.	
	6.	24.	3.	10.	15.	24.	45.	5.	12.
Geraniol .....	2.7	5.5	12.6	29.2	35.7	45.0	62.3	85.6	90.0%
Linalool .....	—	0.4	—	0.6	—	1.1	—	3.9	5.3%

E. W. W.

**Terpenes and Ethereal Oils. LXXXVI. Compounds of the Terpinene Series.** OTTO WALLACH and FRIEDRICH BOEDECKER [and, in part, FRITZ MEISTER] (*Annalen*, 1907, 356, 197—226. Compare this vol., i, 64).—This paper contains a further account of the compounds of the terpinene series and their relationships to other terpenes. Part of the details have been already published (this vol., i, 227, 228, 229); the following are new.

In addition to the methods of preparation described previously, terpinene dihydrochloride, m. p.  $52^{\circ}$ , has now been formed from terpineneterpin, from the saturated alcohol,  $C_{10}H_{17}\cdot OH$ , from sabinene hydrate, and from the monohydrochloride.

Terpinene monohydrochloride,  $C_{10}H_{17}Cl$ , b. p.  $85-95^{\circ}/11$  mm., prepared by the action of hydrogen chloride on the terpinene in carbon disulphide solution, forms the dihydrochloride when treated with hydrogen chloride in glacial acetic acid. The monohydrochloride obtained from sabinene (this vol., i, 229) does not solidify in a mixture of solid carbon dioxide and ether, and is more stable towards potassium hydroxide than is limonene monohydrochloride.

The terpin, *terpineneterpin*,  $C_{10}H_{18}(OH)_2$  (this vol., i, 229), is prepared by shaking thujene or terpineol with sulphuric acid. Terpineol is formed as an intermediate product in the preparation of the terpin from sabinene. The terpin crystallises and sublimes in white leaflets, m. p.  $137-138^{\circ}$ , b. p.  $250^{\circ}$  (slight decomp.), is markedly volatile with steam, is more readily soluble than *cis*-terpin hydrate, forms mixed crystals, m. p. about  $108^{\circ}$ , with anhydrous *cis*-terpin, and with hydrogen chloride in glacial acetic acid forms terpinene dihydrochloride.

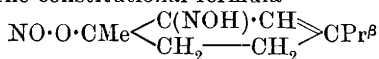
When distilled with a saturated solution of oxalic acid, terpineneterpin yields terpineol and *terpinene-cineol*, which is obtained as a colourless oil, b. p.  $172-173^{\circ}$ ,  $D_{20} 0.897$ ,  $n_D 1.4485$ , has an odour resembling cineol, does not solidify in a mixture of solid carbon dioxide and ether, and is volatile with steam. On treatment with hydrogen bromide in light petroleum solution, it forms terpinene dihydrobromide, gives a light red, crystalline precipitate with bromine in light petroleum, and on oxidation yields products different from those obtained from cineol.

The terpineol obtained from cardamom and majorana oils must have the constitution  $CMe \begin{array}{c} \diagup CH_2 \cdot CH_2 \diagdown \\ \diagdown O \diagup \\ \diagup CH_2 \cdot CH_2 \diagdown \end{array} CPr^{\beta}$ , since the trihydroxyterpane, m. p.  $114-116^{\circ}$ , obtained on oxidation with potassium permanganate, yields carvenone when heated with hydrochloric acid. The trihydroxyterpane,  $OH \cdot CMe \begin{array}{c} \diagup CH(OH) \cdot CH_2 \diagdown \\ \diagdown CH_2 \diagup \\ \diagup CH_2 \diagdown \end{array} CPr^{\beta} \cdot OH$ , on oxidation with chromic acid, yields a small amount of a ketone which forms a semicarbazone,  $C_{10}H_{19}ON_3$ , m. p.  $146^{\circ}$ , and may be thujaketone. The trihydroxyterpane is oxidised by potassium permanganate in alkaline solution, forming two isomeric acids. The acid,  $C_{10}H_{18}O_6$ , m. p.  $205-206^{\circ}$ , which is the main product, loses water when heated or when boiled with acids, forming a lactone,  $C_{10}H_{14}O_4$ , m. p.  $63-64^{\circ}$ . This is volatile with steam, and on treatment with alkalis again forms the acid, m. p.  $205-206^{\circ}$ . The isomeric acid, m. p.  $188-189^{\circ}$ , yields a lactone,  $C_{10}H_{14}O_4$ , m. p.  $72-73^{\circ}$ , from which it is regenerated by the action of alkalis.

The terpineol from sabinene has  $[\alpha]_D +25.4'$ , and on oxidation yields a trihydroxyterpane,  $[\alpha]_D +21.21'$ . Optically inactive terpineol, which on oxidation yields the acid, m. p.  $188-189^{\circ}$ , is obtained from terpinene dihydrochloride and from the fractions of commercial terpineol boiling at low temperatures. The terpineol from terpinene-

terpin is oxidised to the acid, m. p. 188—189°, and probably contains small amounts of  $\Delta^4$ -menthene-1-ol together with the  $\Delta^1$ -menthene-4-ol.

The reduction of terpinene nitrosite in alkaline solution leads to the formation of a mixture of carvenone and tetrahydrocarvenone (compare Wallach and Laufler, Abstr., 1901, i, 89; Amenomiya, Abstr., 1905, i, 603). The constitutional formula



is ascribed to the nitrosite, which, however, in view of its chemical behaviour and in spite of the results of molecular weight determinations, is considered to be bimolecular.

The paper concludes with a discussion of the constitution of terpinene. G. Y.

**Sesquiterpenes. I. Caryophyllene.** ERNST DEUSSEN and ARNOLD LEWINSOHN (*Annalen*, 1907, 356, 1—23).—A study of caryophyllene was undertaken in continuation of the investigation of West Indian sandalwood oil (Abstr., 1900, ii, 579; 1902, i, 552).

Caryophyllene nitrosochloride (m. p. 161—163°: Wallach and Walker, Abstr., 1893, i, 101; 158—160°: Schreiner and Kremers, Abstr., 1900, i, 106) is found to be a mixture; on extraction with alcohol containing 10% of ethyl acetate,  $\alpha$ -caryophyllene nitrosochloride remains unchanged, and on recrystallisation from chloroform separates in glistening crystals, m. p. 177° if slowly or 179° if quickly heated; it is optically inactive, is stable, remaining unchanged when boiled with concentrated hydrochloric or nitric acids, and forms solutions in chloroform and benzene which are colourless at the ordinary temperature and become blue when heated. The alcohol-ethyl acetate extract contains  $\beta$ -caryophyllene nitrosochloride, which crystallises in needles, m. p. 159°,  $[\alpha]_D - 98.07^\circ$ , is moderately soluble in hot light petroleum, and may be bimolecular, and a substance,  $\text{C}_{15}\text{H}_{23}\text{O}_2\text{N}$ , which crystallises in prismatic needles, m. p. 162.5—163.5°,  $[\alpha]_D + 217.2^\circ$ , is sparingly soluble in light petroleum, and decolorises bromine, but does not react with benzylamine.  $\alpha$ -Caryophyllene nitrosochloride reacts with benzylamine forming Schreiner and Kremers'  $\beta$ -base, m. p. 126—128° (*loc. cit.*), which therefore is  $\alpha$ -caryophyllenenitrolbenzylamine. The *hydrochloride*,  $\text{NO} \cdot \text{C}_{15}\text{H}_{24} \cdot \text{NH} \cdot \text{CH}_2\text{Ph} \cdot \text{HCl}$ , crystallises in glistening leaflets, m. p. 195°, and is optically inactive.  $\beta$ -Caryophyllenenitrolbenzylamine, Schreiner and Kremers'  $\alpha$ -base, m. p. 167°, is formed by the action of benzylamine on the  $\beta$ -nitrosochloride; it crystallises from chloroform and alcohol in needles, m. p. 172—173°,  $[\alpha]_D^{16} + 217.87^\circ$ , and yields a laevorotatory *hydrochloride*.

$\alpha$ -Nitrosocaryophyllene,  $\text{C}_{15}\text{H}_{23}\text{ON}$ , formed by reducing the  $\alpha$ -nitrosochloride with sodium and methyl alcohol, crystallises in rhomboids, m. p. 116°, is optically inactive, and yields a crystalline *additive* compound with bromine.

$\beta$ -Nitrosocaryophyllene, formed by reduction of the nitrosochlorides, crystallises in needles, m. p. 120—121°,  $[\alpha]_D + 61.77^\circ$ .

The blue caryophyllene nitrosite, m. p. 115°,  $[\alpha]_D + 102.95^\circ$ , when treated successively with potassium hydroxide and acetic acid in

alcoholic solution, is converted into a unimolecular *isomeride*, which crystallises in colourless needles, m. p. 139—139·5°,  $[\alpha]_D^{18} + 120\cdot0^\circ$ , forms greenish-blue solutions in glacial acetic acid or alcohol, decolorises bromine in glacial acetic acid solution, and if heated with glacial acetic acid forms a crystalline *substance* resembling nitrocaryophyllene.

If the solution of the blue nitrosite in alcoholic potassium hydroxide is acidified with acetic acid only after four hours, it yields d-nitrosocaryophyllene,  $C_{15}H_{23}ON$ , crystallising in needles, m. p. 162—163°,  $[\alpha]_D^{18} + 209\cdot2^\circ$ ; this substance is unimolecular, and decolorises bromine in glacial acetic acid solution or more slowly in carbon tetrachloride solution.

When the blue nitrosite is boiled with light petroleum in a current of carbon dioxide, the solution becomes green and finally yellow, evolves nitric oxide, and deposits a voluminous precipitate containing (a) a *substance*,  $C_{15}H_{23}O_6N_4$  or  $C_{15}H_{23}O_7N_3$ , which crystallises from acetone on addition of light petroleum in silky needles, m. p. 159° (decomp.), and dissolves in aqueous potassium hydroxide, but is optically inactive and does not decolorise bromine, and (b) a *nitrosite*,  $C_{15}H_{22}O_4N_2$ , which crystallises in flat needles, m. p. 130·5°, decolorises bromine in glacial acetic acid solution, and is optically inactive.

The action of boiling alcohol on the blue nitrosite leads to the formation of a *substance* crystallising in needles, m. p. 128°.

A new *sesquiterpene*,  $C_{15}H_{24}$ , is obtained from the light petroleum mother-liquor from the preparation of blue caryophyllene nitrosite as an oil, b. p. 123—124°/14·5 mm.,  $[\alpha]_D - 25\cdot03^\circ$ ,  $D^{20}_D 0\cdot8990$ ,  $n^{20}_D 1\cdot49617$ , and with nitrosyl chloride forms a *nitrosochloride*, m. p. 122°, together with traces of  $\alpha$ -caryophyllene nitrosochloride, derived probably from a small admixture of caryophyllene, and an *oil*,  $[\alpha]_D - 17^\circ$ , which distils in a current of steam. Whether the new sesquiterpene is formed during the preparation of the nitrosite or is present originally in the caryophyllene remains undecided.

The resemblance of the reactions of  $\alpha$ -caryophyllene nitrosochloride to those of caryophyllene alcohol suggests that these substances are closely related in their constitutions. G. Y.

**Components of Ethereal Oils. Sesquiterpene Cedrene.** FRIEDRICH W. SEMMLER and ALFRED HOFFMANN (*Ber.*, 1907, 40, 3521—3528. Compare Rousset, *Abstr.*, 1898, i, 595).—Cedrene, b. p. 124—126°/12 mm.,  $D^{15}_D 0\cdot9354$ ,  $\alpha_D - 55^\circ$  (100 mm. tube),  $n_D 1\cdot50233$ , yields, on oxidation with potassium permanganate, *cedreneglycol*,  $C_{15}H_{26}O_2$ , which separates from acetone in centimetre-long columnar prisms, m. p. 160°, b. p. 186—187°/11 mm.,  $D^{15}_D 1\cdot053$ ; it is very resistant towards permanganate and only reacts very slowly with acetic anhydride. Another product of the oxidation is *cedrene-ketoaldehyde* or *diketone*,  $C_{15}H_{24}O_2$ , b. p. 165°/10 mm.,  $D^{15}_D 1\cdot055$ , the *disemicarbazone* of which has m. p. 234°. The chief product is *cedrene-ketonic acid*,  $C_{15}H_{24}O_3$ , b. p. 215—222°/11 mm.; the *semicarbazone* has m. p. 245°; the *oxime*, m. p. about 60°, whilst the *methyl ester*, b. p. 160—165°/8 mm.,  $D^{15}_D 1\cdot054$ ,  $n_D 1\cdot484$ , forms a *semicarbazone*, m. p. 180°. *Methyl cedrenedicarboxylate* has b. p. 165—173°,  $n_D 1\cdot47936$ ,  $D^{15}_D 1\cdot081$ .

**Cedrone**,  $C_{15}H_{22}O$ , formed by oxidation of cedrene with chromic acid, is a slightly yellow oil with an intense odour of cedarwood, b. p. 147—150°,  $D^{12.5}_D$  1.011,  $n_D$  1.51202,  $\alpha_D$  -91°30' (100 mm. tube), and forms a semicarbazone, m. p. 242—243°. The reduction product, *dihydroisocedrol*,  $C_{15}H_{26}O$ , shows b. p. 148—151°/9.5 mm.,  $D^{18}_D$  1.007,  $n_D$  1.51202,  $[\alpha]_D$  -20°30'. In addition to cedrone, another ketone is formed, b. p. 148—152°/10 mm.,  $D^{16}_D$  1.005,  $\alpha_D$  -40°. Crude cedrone forms an *oxime*, b. p. 160—180°/11 mm., and this gives rise to an *amine*, b. p. 145—150°,  $D^{15}_D$  0.979,  $n_D$  1.5097,  $\alpha_D$  -20°36'.

**Dihydrocedrene**,  $C_{15}H_{23}$ , has b. p. 116—122°/10 mm.,  $D^{15}_D$  0.9052,  $n_D$  1.48721. E. F. A.

**First Runnings from Finnish Turpentine Oil.** OSSIAN ASCHAN (*Zeitsch. angew. Chem.*, 1907, 20, 1811—1816. Compare Atterberg, Abstr., 1880, 663; Harries, Abstr., 1898, i, 232; Aschan, Abstr., 1906, i, 442, 686).—The yellowish-brown colour and characteristic suffocating odour of the turpentine oil obtained by the distillation of the roots of Finnish pines and firs, *Pinus abies* and *P. sylvestris*, is chiefly due to the presence of diacetyl and its homologues, and the quinones derived from these compounds by condensation. In addition to these compounds, the fraction, b. p. 20—160°, obtained from Finnish turpentine oil, was found on investigation to contain simple aldehydes, furan, sylvan, benzene, toluene, *m*-xylene, methyl esters of fatty acids, furfuraldehyde, unsaturated compounds (probably hydrocarbons), and probably 2:5-dimethylfuran. The fraction, b. p. 100—105°, obtained from the fraction, b. p. 20—160°, gave a red coloration with a pine shaving moistened with hydrochloric acid similar to that obtained with pyrrole. However, the fraction contains no nitrogen, so that this reaction cannot be employed as a test for pyrrole in distillation products obtained from wood. W. H. G.

**American Colophony.** PAUL LEVY (*Ber.*, 1907, 40, 3658—3660).—The statement made that the abietin obtained by the distillation of abietic chloride (Abstr., 1906, i, 870) is identical with Kraemer and Spilker's substance from colophony (Abstr., 1900, i, 150) has been confirmed by a careful fractionation of the crude oil from the dry distillation of American colophony.

Abietic acid is indifferent to molten alkali and to the usual reducing agents, although it forms with hydrogen bromide an additive product pointing to this acid containing two ethylenic linkings.

W. R.

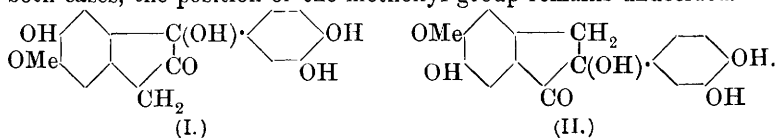
**Chemical Examination of Eriodictyon Glutinosum. II.** GUSTAV MOSSLER (*Monatsh.*, 1907, 28, 1029—1039. Compare Power and Tutin, Abstr., 1906, ii, 885; Trans., 1907, 91, 887).—Eriodictyonone has  $[\alpha]^{20}_D$  -28.21°. It is now found that eriodictyonone tetra-acetate does not form an additive compound with bromine, and; further, that the supposed tetrabromide is a *dibromo*-derivative,  $C_{16}H_{12}O_6Br_2$ ; hence eriodictyonone cannot contain an ethylene linking. The presence of a carbonyl group is confirmed by the formation in alcoholic-acetic acid solution of a *phenylhydrazone*,  $C_{16}H_{14}O_5 \cdot N_2HPh$ , which separates in yellow crystals, m. p. 184—186°. Neither eriodictyonone nor its tetra-acetate is oxidised by potassium per-

manganate in neutral solution; in presence of an alkali, there is obtained the resin formed by the action of alkalis alone.

When heated with fuming hydrochloric acid in a sealed tube at 120°, eriodictyonone yields catechol and an *oil*, which gives a green coloration with alcoholic ferric chloride, and is probably an impure *homocatechol*,  $C_6H_3Me(OH)_2$ .

The action of diazomethane on eriodictyonone leads to the formation of a *methyl ether*,  $C_{15}H_{10}O_4(OMe)_2$ , which crystallises in prisms, m. p. 160°, reduces ammoniacal silver solution, forms a red resin when heated with aqueous alkalis, and gives a red coloration with alcoholic ferric chloride. On further treatment with an excess of diazomethane, this ether yields the *tetramethyl ether*,  $C_{15}H_8O_2(OMe)_4$ , which crystallises in yellow needles, m. p. 162°, is insoluble in aqueous alkalis, and does not give a coloration with ferric chloride. When fused with potassium hydroxide, the tetramethyl ether forms protocatechuic acid.

In the light of these results, it is considered that the constitution of eriodictyonone must be represented by the formula I or II. In both cases, the position of the methoxyl group remains undecided.



(see also Power and Tutin, *Proc.*, 23, 243).

G. Y.

**Spectrophotometry of the Chlorophyllins and the Energetics of Chlorophyll.** M. TSVETT (*Ber. deut. bot. Ges.*, 1907, 25, 388—397. Compare this vol., i, 787).—Results obtained with an alcoholic solution of chlorophyllin show that the absorption is greater in the blue portion of the spectrum than in the red. The band  $\lambda$  460—475 can be distinguished in solutions so diluted that the band in the red portion is no longer visible.

N. H. J. M.

**Phylloxanthin.** M. TSVETT (*Biochem. Zeitsch.*, 1907, 6, 373—378).—A reply to Marchlewski's criticism (this vol., i, 867) of the conclusions drawn by the author (this vol., i, 787). The spectrum of phylloxanthin is very similar to that of  $\beta$ -chlorophyllan; neither substance can be transformed into phyllocyanin.

G. B.

**New Method of Preparing Azophenin.** WLADIMIR SCHAPOSCHNIKOFF (*Zeitsch. Farb.-Ind.*, 1907, 6, 289—291).—Details are given for preparing quinonedichlorodi-imine by the action of a solution of bleaching powder on *p*-phenylenediamine or its hydrochloride; by the method used, a pure white product is readily obtained. It is best converted into azophenin by adding aniline to its solution in benzene; other substances are also formed, but azophenin is the principal product (2.8 grams of azophenin from 3.5 grams of quinonedichlorodi-imine), and can be easily separated in a pure state.

W. A. D.

**Oxidation of Aromatic Amines by Means of Manganese Salt with Formation of Dyes.** FRITZ CRONER (*Chem. Zeit.*, 1907, 31, 948—949).—If 10 c.c. of a 0.2% aqueous solution of atoxyl

[monosodium *p*-aminophenylarsonate] are treated with 10 drops of an 8% manganous chloride solution free from iron and three drops of 20% ammonia, and the resulting precipitate dissolved by addition of a moderate excess of sulphuric acid to the mixture, there is obtained an intense red solution. The red substance is not extracted by shaking with amyl alcohol. The coloration is not produced if the precipitate and reaction liquid are treated with acid separately. Colorations are obtained in the same manner with primary or secondary aromatic amines, but not with tertiary amines, nitroamines, or acylamines. These results confirm Ehrlich and Berthelm's formula for atoxyl (this vol., i, 812). Descriptions are given of the colorations obtained with numerous aromatic amino- and diamino-compounds; where the resulting substance is soluble in amyl alcohol, the colour of the extract is also given.

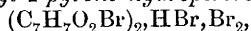
The amount of dye formed is proportional to the manganese salt and not to the alkali added. The colour reaction takes place in presence of mercuric chloride or arsenious acid, but is diminished in intensity by addition of small amounts of hydrogen cyanide or thiocyanate, and is suppressed completely when these are present in molecular proportion to the manganese salt. Similar colour reactions are obtained in this manner, but only in isolated cases with ferrous chloride; nickel, chromium, and copper salts do not give colorations. G. Y.

**Methylfurfuraldoxime.** Correction. WILHELM MEIGEN (*Ber.*, 1907, 40, 3567—3568. Compare this vol., i, 232).—The compound, m. p. 51—52°, previously regarded as a mixture of the *syn*- and *anti*-forms of the oxime, is now shown to be pure methylfurfuraldoxime. E. F. A.

**Hydroperbromides of Negatively-Substituted 4-Pyrones.** FRANZ FEIST (*Ber.*, 1907, 40, 3647—3652. Compare *Abstr.*, 1905, i, 914; 1906, i, 974).—Contrary to Hantzsch and Denstorff's view that only oxides having relatively strong basic properties are capable of forming hydroperbromides, crystalline, more or less stable hydroperbromides have been prepared from 4-pyrones with feeble or no basic properties.

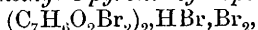
Hydroperbromides of bromo- and dibromo-2 : 6-dimethyl-4-pyrones were shown previously to exist in the crude product of the action of undiluted bromine on 2 : 6-dimethyl-4-pyrone; the composition of this crude product is found now to have undergone little change in two years. The pure hydroperbromides are prepared by the action of bromine and hydrogen bromide on bromo- and dibromo-2 : 6-dimethyl-4-pyrones.

*3-Bromo-2 : 6-dimethyl-4-pyrone hydroperbromide,*



forms a yellow, crystalline powder, decomp. 150°.

*3 : 5-Dibromo-2 : 6-dimethyl-4-pyrone hydroperbromide,*

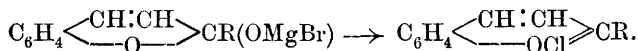
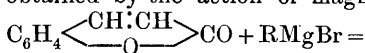


decomp. 147—148° when freshly prepared, decomposes only slowly at

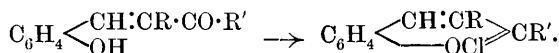
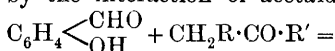
the ordinary temperature, and can be recrystallised repeatedly from chloroform containing traces of bromine, from which it separates in glistening crystals.

Ethyl chelidonate and ethyl dibromochelidonate form *hydroperbromides*,  $C_{11}H_{12}O_6 \cdot HBr \cdot Br_7$  and  $C_{11}H_{10}OHBr_2 \cdot HBr \cdot Br_5$ , respectively, which crystallise in reddish-brown needles or prisms, but are less stable than the hydroperbromides of the brominated dimethylpyrones, decomposing when washed with ether or light petroleum or on exposure to air, evolving fumes of bromine and hydrogen bromide. G. Y.

**Synthesis of Benzopyrylium Derivatives.** HERMAN DECKER and THEODOR VON FELLENBURG (*Ber.*, 1907, 40, 3815—3818).—Benzopyrylium derivatives may be prepared by the method employed by Bünzly and Decker (*Abstr.*, 1904, i, 912) in the synthesis of xanthonium compounds; thus, 2-substituted benzopyrylium compounds are obtained by the action of magnesium alkyl bromides on coumarin:



They also result from the ring-condensation of the products obtained by the interaction of acetaldehyde or ketones and salicylaldehyde:



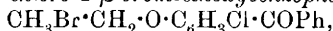
Hydrogen chloride passed into a mixture of resorcyaldehyde, and acetophenone precipitates 7-hydroxy-2-phenylbenzopyrylium chloride,  $OH \cdot C_6H_3 \begin{array}{c} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{OCl} \end{array} CPh$ , identical with the compound obtained by Bülow and Sicherer (*Abstr.*, 1902, i, 113) from benzoylacetaldehyde and resorcinol. The compounds obtained by Bülow (*Abstr.*, 1901, i, 400, 559; 1902, i, 113) from 1:3-diketones and dihydroxybenzenes are therefore hydroxybenzopyrylium salts. The formulæ of these compounds must consequently contain 1 mol. of water less than is present in the formulæ assigned to them by Bülow; this mol. of water is really present as water of crystallisation.

7-Hydroxy-2-phenylbenzopyrylium picrate loses its water of crystallisation at 100° without undergoing decomposition as stated by Bülow and Sicherer (*loc. cit.*). W. H. G.

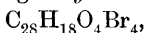
**Synthesis of Leuco-coumaranketones.** STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and CH. MARSCHALK (*Ber.*, 1907, 40, 3660—3669).—The synthesis of *p*-benzoylcoumarans was attempted in order to throw further light on the constitution of catechin (compare this vol., i, 73). Two methods were tried: (1) the conversion of *p*-hydroxybenzophenone into the corresponding coumaran derivative, (2) interaction of aromatic acid chlorides in the presence of aluminium chloride



on coumaran and its substitution derivatives. The first method did not yield the desired result. By the condensation of 3-chloro-4-hydroxybenzophenone and ethylene dibromide in the presence of sodium methoxide, 3-chloro-4- $\beta$ -bromoethoxybenzophenone,



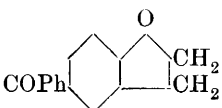
is formed as chief product. It crystallises in small, white plates, m. p. 79—80°. There is also formed the sparingly soluble 4:4'-ethylene-dioxy-bis-3-chlorobenzophenone,  $\text{C}_2\text{H}_4(\text{O} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{COPh})_2$ , crystallising in white needles, m. p. 224—226°. All attempts, however, to close the coumaran ring by the Wurtz reaction were unsuccessful, and the same remark applies to the bromo-derivatives. 3-Bromo-4- $\beta$ -bromoethoxybenzophenone,  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{Br}_2$ , crystallises in white leaflets from dilute alcohol, m. p. 96—97°; the 4:4'-ethylenedioxy-bis-3 bromobenzophenone,  $\text{C}_{28}\text{H}_{20}\text{O}_4\text{Br}_2$ , m. p. 229—230°. 3:5-Dibromo-4- $\beta$ -bromoethoxybenzophenone,  $\text{C}_{15}\text{H}_{11}\text{O}_2\text{Br}_3$ , crystallises in white plates, m. p. 106—107°; the corresponding ethylenedioxy-derivative,



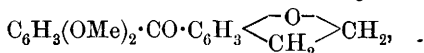
has m. p. 217—218°.

4- $\beta$ -Bromoethoxybenzophenone,  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}$ , which crystallises in prisms from alcohol, m. p. 72°, does not yield *p*-benzoylcoumaran on treatment with aluminium chloride; the product obtained is *p*-benzoylphenol. The corresponding ethylenedioxy-compound,  $\text{C}_{28}\text{H}_{22}\text{O}_4$ , has m. p. 195°.

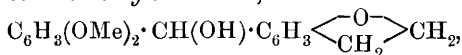
Coumaran itself reacts easily with aromatic acid chlorides in the presence of aluminium chloride and from analogy to the phenol ethers, the conclusion is drawn that substitution occurs in the para-position to the oxygen atom.

4-Benzoylcoumaran, , m. p. 44°, crystallises

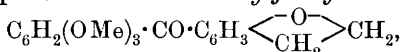
from light petroleum in the triclinic system [ $a : b : c = 1.4568 : 1 : 1.8354$ ;  $\alpha 101^\circ 32'$ ,  $\beta 109^\circ 45'$ ,  $\gamma 103^\circ 9'$ ]. By reduction of an alcoholic solution, the *leuco-p*-benzoylcoumaran was obtained as a viscous oil; it is conjectured to be the parent substance of catechin. 4-Veratroylcoumaran,



crystallises in stout, white prisms, m. p. 136—137°, and gives on reduction *leuco*-4-veratroylcoumaran,



stout prisms, m. p. 97—98°. 2-Trimethylgalloylcoumaran,



forms needles, m. p. 110—111°, and its *leuco*-compound,  $\text{C}_{18}\text{H}_{20}\text{O}_3$ , forms leaflets, m. p. 108—109°.

Chroman also combines with acid chlorides to form similar derivatives. 6-Benzoylchroman,  $\text{C}_{16}\text{H}_{14}\text{O}_2$ , is an oil, b. p. 365°/710 mm., solidifying to a crystalline mass in a cold mixture. 6-Veratroyl-

*chroman*,  $C_6H_3(OMe)_2 \cdot CO \cdot C_6H_3 \begin{smallmatrix} \diagup O-CH_2 \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix}$ , crystallises in white needles, m. p. 103—104°; its *leuco*-compound,  $C_{18}H_{20}O_4$ , forms prisms, m. p. 115—116°.

The following compounds are also described: *p-veratroyl-o-ethyl-anisole*,  $C_6H_3(OMe)_2 \cdot CO \cdot C_6H_3Et \cdot OMe$ , which crystallises in white needles, m. p. 103—104°, and its *leuco*-derivative,  $C_{18}H_{22}O_4$ , white needles, m. p. 84—85°; *p-trimethylgalloyl-o-ethylanisole*,  $C_{19}H_{22}O_5$ , m. p. 105°, the *leuco*-compound has m. p. 86—88°. W. R.

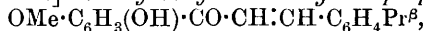
**Further Synthesis in the Flavone Group.** STANISLAUS VON KOSTANECKI (*Ber.*, 1907, 40, 3669—3677).—[With M. KOLKER.]—*6-Hydroxy-4'-isopropylflavone*,  $C_{19}H_{20}O_3$ , prepared by the interaction of quinacetophenone monomethyl ether, cumenol, and sodium hydroxide, crystallises from alcohol in colourless leaflets, m. p. 90°. *3-Bromo-6-methoxy-4'-isopropylflavanone*,  $OMe \cdot C_6H_3 \begin{smallmatrix} \diagup O-CH \cdot C_6H_4Pr^\beta \\ \diagdown CO \cdot CHBr \end{smallmatrix}$ , obtained

by brominating the corresponding methoxyisopropylflavanone in carbon disulphide, forms white needles, m. p. 125—127°. Like all 3-bromoflavanones when treated with concentrated potassium hydroxide in alcoholic solution, hydrogen bromide is eliminated and

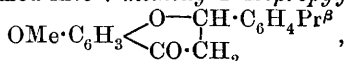
*6-methoxy-4'-isopropylflavone*,  $OMe \cdot C_6H_3 \begin{smallmatrix} \diagup O-C \cdot C_6H_4Pr^\beta \\ \diagdown CO \cdot CH \end{smallmatrix}$ , is obtained;

it crystallises from dilute alcohol in white leaflets, m. p. 135°. On heating with hydriodic acid, *6-hydroxy-4'-isopropylflavone*,  $C_{18}H_{16}O_3$ , is formed, and from alcohol gives pale yellow needles, m. p. 182—183°.

[With A. TOBLER.]—*2'-Hydroxy-4'-methoxy-4-isopropylchalkone*,



prepared by condensing cumenol with paeonol, crystallises from alcohol in yellow leaflets, m. p. 104°. When an alcoholic solution of this compound is heated with dilute hydrochloric acid for twenty-four hours, it is transformed into *7-methoxy-4'-isopropylflavanone*,



which crystallises in prisms, m. p. 75°. Amyl nitrite and hydrochloric acid convert the flavanone into the *isonitroso*-derivative, which, however, is unstable, and there results *7-methoxy-4'-isopropyl-*

*flavanol*,  $OMe \cdot C_6H_3 \begin{smallmatrix} \diagup O-C \cdot C_6H_4Pr^\beta \\ \diagdown CO \cdot C \cdot OH \end{smallmatrix}$ ; it crystallises in pale yellow,

glistening leaflets, m. p. 201°. Like all flavanols, the yellow *sodium* salt is sparingly soluble; the *acetate*,  $C_{21}H_{20}O_5$ , has m. p. 163—164°. Reduction of the methoxyisopropylflavanol with hydriodic acid gives rise to *7-hydroxy-4'-isopropylflavanol*,  $C_{18}H_{16}O_4$ , which forms almost colourless leaflets, m. p. 243°; the *diacetate*,  $C_{22}H_{20}O_6$ , crystallises in white needles, m. p. 124°.

[With H. RABINOWITSCH.]—*2'-Hydroxy-3':4'-dimethoxy-4-isopropyl-chalkone*,  $OH \cdot C_6H_2(OMe)_2 \cdot CO \cdot CH : CH \cdot C_6H_4Pr^\beta$ , prepared from gallacetophenone dimethyl ether and cumenol in the presence of

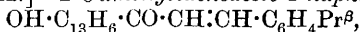
50% sodium hydroxide, crystallises in yellow leaflets, m. p. 114°, and forms the starting point for the preparation of the 7:8-dihydroxyisopropylflavanol in a similar manner to that of the 7-hydroxy-compound.

7:8-Dimethoxy-4'-isopropylflavanone,  $C_{20}H_{22}O_4$ , forms small, white, granular crystals, m. p. 92°. The isonitroso-derivative,  $C_{20}H_{21}O_5N$ , is stable and has m. p. 173°.

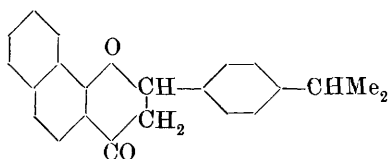
7:8-Dimethoxy-4'-isopropylflavanol,  $C_{20}H_{20}O_5$ , forms pale yellow needles, m. p. 162°, and yields an intensely yellow sodium salt; the acetate,  $C_{22}H_{22}O_6$ , white needles, m. p. 152°.

7:8-Dihydroxy-4'-isopropylflavanol,  $C_{18}H_{16}O_5$ , crystallises in glistening leaflets, m. p. 265°; the diacetate,  $C_{24}H_{22}O_8$ , forms white needles, m. p. 152°.

[With G. STENZEL.]—2-Cumenyldieneaceto-1-naphthol,



prepared from cumenol and 2-aceto-1-naphthol under similar conditions to the benzylidene compound (compare Abstr., 1898, i, 369), crystal-



lises from alcohol in orange-red prisms, m. p. 98°; the acetate,  $C_{24}H_{20}O_3$ , is pale yellow, m. p. 88—89°. 4'-isoPropyl- $\alpha$ -naphthylflavanone (annexed formula) forms colourless prisms, m. p. 134—135°; the corresponding flavanol,

$C_{22}H_{18}O_3$ , crystallises in pale yellow needles, m. p. 211—212°; the acetate,  $C_{24}H_{20}O_4$ , is white, m. p. 157°.

W. R.

**Preparation of Santalyl Esters.** CHEMISCHE FABRIK VON HEYDEN (AKTIEN-GESELLSCHAFT) (D.R.-P. 182627. Compare Abstr., 1906, i, 972).—The santalyl esters of the higher fatty acids from valeric acid onwards do not possess the unpleasant odour and irritating properties of free santalol and its esters with acetic acid and its immediate homologues.

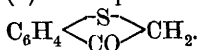
*Santalyl stearate*, a clear yellow oil, is prepared by mixing santalol and stearyl chloride and completing the reaction on the water-bath; it separates on the addition of alcohol.

*Santalyl valerate* and *santalyl oleate* resemble the preceding compound, and are prepared respectively in a similar manner from valeryl and oleyl chlorides and santalol.

G. T. M.

**Preparation of Thionaphthen Derivatives.** KALLE & CO. (D.R.-P. 184469).—*o*-Aminophenylthioglycollic acid, prepared from *o*-thioaniline and chloroacetic acid, when diazotised and treated with potassium cuprocyanide furnishes *o*-cyanophenylthioglycollic acid, yellowish needles, m. p. 142°. This substance on hydrolysis with aqueous sodium hydroxide yields 3-amino-(1)-thionaphthen-2-carboxylic acid, which on further treatment with alkali gives rise to 3-hydroxy-

(1)-thionaphthen-2-carboxylic acid and 3-hydroxy-(1)-thionaphthen,

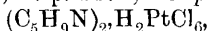


G. T. M.

**Some New Alkaloids from Plants.** AMÉ PICTET and G. COURT (*Ber.*, 1907, 40, 3771—3783; *Bull. Soc. chim.*, 1907, [iv], 1, 1001—1016).—The hypothesis put forward by Pictet (*Abstr.*, 1905, i, 541) receives support from the fact that alkaloids of simple structure are obtained by steam distillation from plants which have been treated with dilute sodium carbonate solution.

The concentrated aqueous extract of tobacco leaves ("raw nicotine") yields, when distilled at 80—120°, an alkaline distillate from which pyrrolidine and 1-methylpyrrolidine were isolated and identified by means of their auri- and platini-chlorides. 1-Methylpyrrolidine *picrolonate* crystallises in yellow prisms, m. p. 222° (decomp.).

Black pepper yields a distillate which does not contain piperidine as stated by Johnstone (*Abstr.*, 1889, 298), but a *base* which is probably a *C*-methylpyrrolidine,  $\text{C}_5\text{H}_9\text{N}$ ; the *aurichloride*,  $\text{C}_5\text{H}_9\text{N}, \text{HAuCl}_4$ , crystallises in yellow leaflets or flat needles, m. p. 182°; the *picrolonate* is a yellow, crystalline powder, m. p. 217°; the *platinichloride*,



m. p. 203°, forms microscopic, orange prisms.

The distillate from carrot leaves was found to contain pyrrolidine and a new base, *daucine*,  $\text{C}_{11}\text{H}_{18}\text{N}_2$ , a colourless, oily liquid with a nicotine-like odour, b. p. 240—250°,  $[\alpha]_D + 7.74^\circ$  in ether. The *hydrochloride* forms long needles; no precipitate is produced on adding auric, platinic, or mercuric chloride to a solution of the hydrochloride. The hydrochloride when heated with zinc dust does not give a coloration with a pine shaving. The *base* obtained from carrot seeds is not identical with *daucine*, since it gives the pyrrole reaction and its *aurichloride*, m. p. 172—175° (decomp.), is insoluble.

The leaves of parsley yield a *base*, the crystalline *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust; no precipitate is obtained on adding auric or platinic chloride to a solution of the hydrochloride; the *picrolonate* forms yellow, microscopic needles, m. p. 210°.

Coca leaves yield a *base*, the *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust. No precipitate is formed on adding picric acid, auric or platinic chloride to a solution of the hydrochloride; picronic acid produces a yellow, flocculent precipitate.

The authors consider that, since the above bases, with the exception of *daucine*, belong to the pyrrole group, they are probably derived from the plant albumin.

W. H. G.

**Cinchona Alkaloids. VII. A New Oxidation Product of Cinchonine.** PAUL RABE [with ERNST ACKERMANN and W. SCHNEIDER] (*Ber.*, 1907, 40, 3655—3658).—An intermediate product of the oxidation of cinchonine by chromic acid in either sulphuric acid or glacial acetic acid has been isolated in small quantity. It is a *base*,

$C_{19}H_{20}ON_2$ , containing two atoms of hydrogen less than cinchonine, and crystallises in pale yellow needles, m. p. 126—127°,  $[\alpha]_D^{20} + 68.8^\circ$  in 3.3% alcoholic solution. Although a strong base, it also dissolves in aqueous alkali hydroxides, from which it is precipitated by carbon dioxide. It is oxidised by chromic acid to cinchonic acid and meroquinine; potassium permanganate and bromine are, however, without action. The *hydrochloride*,  $C_{19}H_{20}ON_2 \cdot HCl$ , crystallises in white needles, m. p. 245—247°; the *methiodide*, has m. p. 232—233°, and the *dihydroiodide* is oily. The base combines with hydroxylamine.

W. R.

**True and False (Pseudo-) Commercial Tannates of Quinine.** PIETRO BIGINELLI (*Gazzetta*, 1907, 37, ii, 205—226).—Tannic acid is capable of forming, with the ordinary salts of quinine, additive compounds which are usually yellow. Such compounds, containing variable proportions of tannic acid, are always obtained when solutions of tannic acid act on quinine salts. Many of the commercial quinine tannates are compounds of this nature, retaining some of the qualities of the quinine salts from which they have been prepared, and are hence termed pseudo- or false tannates. Quinine pseudo-tannates of constant composition can be prepared under constant conditions. The percentage of quinine in these compounds varies from 18 to 39. Tannic acid is not capable of displacing sulphuric or hydrochloric acid from its combination with quinine. True quinine tannates can only be prepared by mixing solutions of the base and acid in proportions varying according to the tannate required.

The following compounds have been prepared and analysed.

- (1) True quinine tannates:  $C_{20}H_{24}O_2N_2, C_{14}H_{10}O_9, 3H_2O$ ;  
 $C_{20}H_{24}O_2N_2, 2C_{14}H_{10}O_9, 6H_2O$ ;  $C_{20}H_{24}O_2N_2, 3C_{14}H_{10}O_9, 10H_2O$ .  
 (2) False or pseudo-tannates:  $4(C_{20}H_{24}O_2N_2, H_2SO_4), 5C_{14}H_{10}O_9, 13H_2O$ ;  
 $2(C_{20}H_{24}O_2N_2, H_2SO_4), 5C_{14}H_{10}O_9, 20H_2O$ ;  
 $2(C_{20}H_{24}O_2N_2, H_2SO_4), 7C_{14}H_{10}O_9, 25H_2O$ ;  
 $2C_{20}H_{24}O_2N_2, H_2SO_4, 5C_{14}H_{10}O_9, 20H_2O$ ;  
 $2(C_{20}H_{24}O_2N_2, 2HCl), 5C_{14}H_{10}O_9, 13H_2O$ ;  
 $C_{20}H_{24}O_2N_2, 2HCl, 5C_{14}H_{10}O_9, xH_2O$ .

T. H. P.

**A Base Obtained in the Working Up of the Alkaloids Occurring with Cocaine.** CARL LIEBERMANN (*Ber.*, 1907, 40, 3602—3603).—Anhydroecgonine ethyl ester (Einhorn, *Abstr.*, 1887, 741; Willstätter, *Abstr.*, 1901, i, 649) has been found in the ecgonine residues obtained in the separation of the subsidiary alkaloids of crude cocaine. It is formed probably by esterification of anhydroecgonine during the process of separation. The ethyl ester, b. p. 130—132°/11 mm.,  $[\alpha]_D - 51.33'$ , is hydrolysed by boiling hydrochloric acid, D 1.125, forming anhydroecgonine. The *picrate*,  $C_{11}H_{17}O_2N, C_6H_3O_7N_3$ , crystallises in yellow leaflets, m. p. 168°; the *platinichloride*, m. p. 217° (211°: Einhorn, *loc. cit.*); the *aurichloride*,  $C_{11}H_{17}O_2N, HAuCl_4$ , forms lemon-yellow granules, m. p. 124°.

G. Y.

**isoConiine.** ALBERT LADENBURG (*Ber.*, 1907, 40, 3734—3736. Compare Abstr., 1906, i, 692).—In consequence of Löffler's suggestion that the high rotatory power of synthetic coniine is due to the presence of allylpiperidine, the author has attempted to prepare the alkaloid by a method which excludes the formation of the unsaturated base. Methylpicolylalkine is reduced by hydriodic acid and amorphous phosphorus at 125°, the product treated with zinc dust and cold water, and the resulting propylpyridine reduced by sodium and alcohol to propylpiperidine, which is resolved by tartaric acid. The liberated base is pure *isoconiine*, and has  $[\alpha]_D^{18.5} + 17.85^\circ$ . C. S.

**Morphine.** XIV. *allo-ψ-Codeine, a New Isomeride of Codeine.* LUDWIG KNORR, HEINRICH HÖRLEIN, and CLEMENS GRIMME (*Ber.*, 1907, 40, 3844—3851).—It has been lately pointed out by Knorr and Hörlein (this vol., i, 789) that, of the two compounds, *ψ-codeine* and *isocodeine*, quoted in the literature as being isomeric with codeine, *ψ-codeine* is a structural isomeride of codeine. Uncertainty exists, however, regarding Schryver and Lees' "*isocodeine*" (*Trans.*, 1901, 79, 576), which is a mixture containing appreciable amounts of *ψ-codeine*, the presence of the latter doubtless accounting for the *ψ-codeinone* obtained by the oxidation of "*isocodeine*." In attempting to prepare pure *isocodeine*, the authors have obtained a new base, isomeric with codeine; crude *isocodeine* appears to contain *isocodeine*, *ψ-codeine*, and small amounts of this new base, which, for the present, is termed *allo-ψ-codeine*. When this new base is oxidised with chromic acid in sulphuric acid solution, it forms *ψ-codeinone*, and accordingly contains the alcoholic hydroxyl group in position 8.

The melting points and specific rotations of the isomeric morphines, codeines, and methylmorphimethines are quoted in tabular form, and also the melting points and specific rotations of the corresponding methiodides.

From the products of the hydrolysis of chloromorphide, *γ-isomorphine*, a new isomeride of morphine, has been isolated. This compound has m. p. 278°,  $[\alpha]_D^{15} - 94^\circ$  (solvent not stated), and its methiodide has m. p. 295° and  $[\alpha]_D^{15} - 51^\circ$ ; when methylated, it forms *ψ-codeine* [compare, however, Lees (*Trans.*, 1907, 91, 1408), who has also lately studied the hydrolysis of chloromorphide and obtained, as one of the products, *neoisomorphine*, which seems to be identical with the above-mentioned *γ-isomorphine*].

*allo-ψ-Codeine* is possibly identical with Lees' *β-isocodeine*. It is prepared as follows from the mixture of bases obtained by the method of Schryver and Lees by the hydrolysis of bromocodeide. Potassium iodide is added to the solution of this crude *isocodeine* in dilute acetic acid, when a mixture of *ψ-codeine* and *allo-ψ-codeine* hydriodides gradually separates and may be separated by means of absolute alcohol. As an alternative method, crude *isocodeine* is acetylated by means of boiling acetic anhydride and the mixture of acetyl derivatives separated by means of absolute alcohol, in which acetyl *allo-ψ-codeine* is soluble with difficulty, and separates in tiny needles, m. p. 194—195°.

*allo-ψ-Codeine*, obtained either from the hydriodide or the acetyl derivative, is an oil with a bluish-violet fluorescence; it has not yet been obtained crystalline. In absolute alcohol, it has  $[\alpha]_D^{15} - 228^\circ$  ( $c = 4.5$ ). Its *hydriodide* separates from water in spear-shaped crystals decomposing at  $280-285^\circ$ ; in aqueous solution, it has  $[\alpha]_D^{15} - 153^\circ$  ( $c = 1.967$ ). It differs from *ψ-codeine hydriodide*, which crystallises from water in glistening leaflets, contains  $1\text{H}_2\text{O}$ , has m. p.  $260-265^\circ$  (decomp.), and  $[\alpha]_D^{15} - 57^\circ$ .

When *allo-ψ-codeine* is oxidised, it forms *ψ-codeinone*.

*Acetylallo-ψ-codeine* crystallises from absolute alcohol in needles, m. p.  $194-195^\circ$ , and differs from acetyl-*ψ-codeine*, which is an oil, and from acetylcodeine, which has m. p.  $133.5^\circ$ . Its *methiodide*,  $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}, \text{MeI}, \text{EtOH}$ , separates from absolute alcohol in leaflets, m. p. about  $260^\circ$  (decomp.).

*allo-ψ-Codeine methiodide*,  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}, \text{MeI}$ , crystallises from methyl alcohol in rectangular leaflets, m. p. about  $215^\circ$  (decomp.). In aqueous solution, it has  $[\alpha]_D^{15} - 142^\circ$  ( $c = 1.728$ ). When boiled with sodium hydroxide, it forms a methine base which, for the present, is termed *ξ-methylmorphimethine*; it is apparently related to ε-methylmorphimethine in the same manner as *allo-ψ-codeine* is related to *ψ-codeine*. The new base has  $[\alpha]_D^{15} - 174^\circ$  ( $c = 8.91$ ) in alcoholic solution (after treatment with alcoholic potassium hydroxide); when dried until constant in weight, it gave  $[\alpha]_D^{15} - 178^\circ$  ( $c = 10.955$ ) in alcoholic solution. Its *methiodide*,  $\text{C}_{19}\text{H}_{23}\text{O}_3\text{N}, \text{MeI}$ , is a colourless powder, m. p. about  $180^\circ$  (indefinite); in aqueous solution, it has  $[\alpha]_D^{15} - 148^\circ$  ( $c = 2.486$ ).

A. McK.

### Morphine. XV. Dioxycodine and Deoxydihydrocodine.

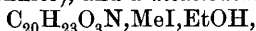
LUDWIG KNORR and RUDOLF WAENTIG (*Ber.*, 1907, 40, 3860—3868). —In continuation of the work of Knorr and Hörlein (this vol., i, 235), it is found that deoxycodine is best prepared by the reduction of bromocodine or chlorocodine with zinc dust and alcohol in the absence of acid. The reduction product, obtained by means of sodium and alcohol, is, however, not identical, as was formerly supposed, with the product obtained by the action of zinc and hydrochloric acid or of zinc dust and alcohol; it is levorotatory, whereas the other products are dextrorotatory.

From the dextrorotatory deoxycodine of Knorr and Hörlein, the levorotatory base, deoxydihydrocodine, is obtained by the action of sodium and alcohol.

Deoxycodine melts at about  $126^\circ$  and crystallises from dilute methyl alcohol in glistening, hexagonal or rhombic leaflets. In alcoholic solution, it has  $[\alpha]_D^{15} + 119-121^\circ$  ( $c = 4.9215$ ).

*Deoxycodine hydrochloride*,  $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}, \text{HCl}, \text{EtOH}$ , crystallises from absolute alcohol in glistening prisms, which soften at about  $165^\circ$ , and have m. p. about  $270^\circ$  (decomp.); in aqueous solution, it has  $[\alpha]_D^{15} + 84-87^\circ$ . The *hydriodide*,  $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}, \text{HI}$ , separates from water in needles, m. p. about  $265^\circ$  (decomp.). The *benzoate* crystallises from water in tiny, prismatic needles, m. p. about  $188^\circ$ ; in absolute alcohol, it has  $[\alpha]_D^{15} + 106^\circ$  ( $c = 5.53$ ). The *acetyl* derivative is an oil, and forms

an *hydriodide*,  $C_{20}H_{23}O_3N, HI$ , which separates from water in silky needles, m. p.  $230^\circ$  (indefinite), and a *methiodide*,



which crystallises from absolute alcohol in yellow needles, m. p. about  $270^\circ$ .

Deoxycodine forms a glassy methiodide, from the aqueous solution of which a brown oil separates on boiling with sodium hydroxide; when this oil is crystallised from absolute alcohol, it forms yellow prisms, m. p.  $162-164^\circ$ , and is the methine base of deoxycodine. It is readily oxidised even at the ordinary temperature by the air; its *nitrate*,  $C_{19}H_{23}O_3N, HNO_3$ , is, however, more stable and separates from acetic acid in silky needles, m. p.  $202^\circ$ .

*Methyldeoxycodine methiodide*,  $C_{19}H_{23}O_2N, MeI$ , obtained by the methylation of deoxycodine in alkaline solution with methyl sulphate and interaction of the product with potassium iodide, crystallises in glistening leaflets, m. p.  $251-252^\circ$ , with preliminary softening. It has  $[\alpha]_D^{15} + 108^\circ$  ( $c = 2.290$ ) in alcoholic solution.

When the aqueous solution of methyldeoxycodine methiodide is boiled with sodium hydroxide, an oil separates, which is very unstable; it decomposes in hydrochloric acid solution giving dimethylmorphol.

*Deoxydihydrocodeine*,  $C_{18}H_{23}O_2N, \frac{1}{2}H_2O$ , crystallises from dilute methyl alcohol in glistening leaflets, m. p. about  $132^\circ$ ; the anhydrous compound has  $[\alpha]_D^{15} - 24^\circ$  ( $c = 5.171$ ) in absolute alcoholic solution. Its *hydrochloride*,  $C_{18}H_{23}O_2N, HCl, EtOH$ , has m. p. about  $155^\circ$  (decomp.), and  $[\alpha]_D^{15} - 17^\circ$  ( $c = 5.289$ ) in aqueous solution. The *benzoate* separates from ethyl acetate in tetrahedra, m. p. about  $180^\circ$ , and has  $[\alpha]_D^{15} - 9^\circ$  ( $c = 5.145$ ).

*Methyldeoxydihydrocodeine methiodide*,  $C_{19}H_{25}O_2N, MeI$ , obtained by methylating deoxydihydrocodeine with methyl sulphate and then causing the product to react with potassium iodide, separates from water in leaflets and from alcohol in needles, m. p.  $248-249^\circ$  (indefinite), and has  $[\alpha]_D^{15} - 12^\circ$  ( $c = 2.773$ ) in 99% alcoholic solution.

A. McK.

#### Preparation of Narceine and Homonarceine Derivatives.

KNOLL & Co. (D.R.-P. 183589. Compare this vol., i, 236).—Narceine and homonarceine were formerly alkylated by treatment with alkyl sulphates, and it is now found that the same derivatives are obtained by the action of alkyl iodides, methyl phosphate, and methyl nitrate.

Ethylnarceine hydrochloride, m. p.  $231^\circ$ , may be obtained from the product of the interaction of ethyl bromide on the potassium derivative of narceine.

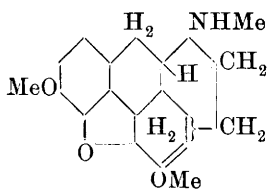
Methylnarceine hydrochloride, m. p.  $243^\circ$ , is produced by treating the potassium derivative of narceine with methyl phosphate and combining the resulting base with hydrochloric acid.

G. T. M.

**The Action of Ozone on Thebaine.** ROBERT PSCHORR and HANS EINBECK (*Ber.*, 1907, 40, 3652—3654).—Morphine bases are converted into [phenanthrene derivatives by treatment with ozone,



the side-ring containing nitrogen undergoing rupture. Thebaine, however, behaves differently, the nitrogen ring remains intact, a 60% yield of  $\alpha$ -thebaizone,  $C_{19}H_{21}O_5N$ , leaflets, m. p. 125—126° (corr.), is obtained containing two atoms of oxygen more than thebaine. This new compound contains two methoxyl groups like thebaine, and the presence of a carbonyl group is shown by the formation of a *mono-semicarbazone*,  $C_{20}H_{24}O_5N_4$ , which crystallises in flat rods, m. p. 262°

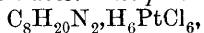


(corr.). On dissolution of the thebaizone in dilute sodium hydroxide solution, hydrolysis of one methoxyl group occurs, and the conclusion is drawn that one of the methoxy-groups exists as the ester. The fifth oxygen atom is indifferent. These results, taken in conjunction with those already known about thebaine, lead to the constitution annexed,

the grouping  $\cdot C(OMe):C:$  being converted into that represented by  $CO_2Me \cdot C:O$ .

W. R.

**A New Base from the Solanaceæ.** RICHARD WILLSTÄTTER and WOLFGANG HEUBNER (*Ber.*, 1907, 40, 3869—3875) —The new *alkaloid*,  $C_8H_{20}N_2$ , obtained from *Hyoscyamus muticus* in addition to hyoscyamine and other products, is a colourless liquid, b. p. 169° (corr.), and with  $D^{15}_D$  0.7941; it is miscible with water in all proportions, has a strongly alkaline reaction, and is easily volatile with steam. It exhibits the behaviour of a saturated, ditertiary base. It is quite stable towards permanganate in cold sulphuric acid solution, and does not react with benzenesulphonic chloride and alkali. In moderate doses, it has no poisonous action. The *hydrochloride*,  $C_8H_{20}N_2 \cdot 2HCl$ , crystallises in triangular prisms, m. p. 273° (decomp.), is deliquescent, and very readily soluble in water. Its *platinichloride*,

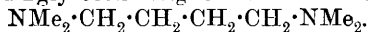


has m. p. 234° (decomp.); its *aurichloride* decomposes at 206—207°.

The *compound*,  $C_4H_8(NMe_3I)_2$ , forms hygroscopic leaflets or tiny needles, m. p. 305—308° (decomp.). By the distillation of the ammonium base, obtained from the iodide by means of silver oxide, an aqueous distillate was obtained and a gas, which was identified as butadiene by means of the sparingly soluble  $\alpha$ -bromide, m. p. 117°, and the more easily soluble bromide, m. p. 39°. The aqueous distillate contained, in addition to trimethylamine, tetramethyldiaminobutane, which was identified by means of its aurichloride.

The preparation of 1:4-diaminobutane from succinaldoxime is described, the method used being a modification of the method of Ciamician and Zanetti. The methylation of 1:4-diaminobutane is described, hexamethyltetramethylenediammonium chloride being obtained. When the latter compound is distilled, the main product is the monoamine, 1-methylpyrrolidine. 1-Methylpyrrolidine methiodide,  $C_6H_{14}NI$ , crystallises in prisms, which decompose above 300°; the *aurichloride*,  $C_6H_{14}NCl_4Au$ , crystallises in hexagonal prisms with pyramidal ends, m. p. 286° (decomp.).

The product of the methylation of tetramethylenediamine, in the form of its chloride, aurichloride, platinichloride, and picrate, was compared with the quaternary derivatives of the solanaceous base investigated, the agreement being complete. The following constitution has accordingly been assigned to the alkaloid:

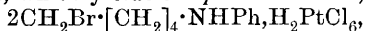


*Hexamethyltetramethylenediammonium chloride*,  $\text{C}_4\text{H}_{12}(\text{NMe}_3)_2\text{Cl}_2$ , crystallises from alcohol in prisms; its *picrate* has m. p.  $285^\circ$  (decomp.); its *platinichloride* has m. p.  $279^\circ$  (decomp.); its *aurichloride* decomposes at  $304\text{--}309^\circ$ . A. McK.

**Rupture of Cyclic Bases by Cyanogen Bromide.** JULIUS VON BRAUN (*Ber.*, 1907, 40, 3914—3933).—The action of cyanogen bromide on cyclic bases either breaks the ring (Abstr., 1900, i, 430) or replaces the alkyl or aryl group attached to the nitrogen atom by the cyanogen group (Abstr., 1902, i, 365). A third alternative is represented by the scheme  $\text{X} \diamond \text{N} \cdot \text{R} + \text{Br} \cdot \text{CN} = \text{Br} \cdot \text{X} \cdot \text{NR} \cdot \text{CN}$ . The improved

methods for the preparation of  $\alpha\delta$ -dibromobutane and  $\alpha\epsilon$ -dibromopentane (Abstr., 1904, i, 841) have enabled the author to prepare numerous derivatives of pyrrolidine and piperidine, by means of which he has shown that the rupture of a cyclic base is more easily accomplished by cyanogen bromide than by any other method, a brominated cyanamide being formed in accordance with the preceding scheme.

The reaction between 1-phenylpiperidine and cyanogen bromide leads, after several hours, to the formation of *phenyl- $\omega$ -bromoamylcyanamide*,  $\text{CH}_2\text{Br} \cdot [\text{CH}_2]_4 \cdot \text{NPh} \cdot \text{CN}$ , and the quaternary bromide,  $\text{C}_5\text{NH}_{10}\text{PhBr} \cdot [\text{CH}_2]_5 \cdot \text{NPh} \cdot \text{CN}$ . The latter is a brown oil which is identified by conversion into the *platinichloride*,  $(\text{C}_{23}\text{H}_{30}\text{N}_3)_2\text{PtCl}_6$ , m. p.  $121\text{--}122^\circ$ . The former is an oil which is soluble in concentrated acids, and by prolonged boiling with 48% hydrobromic acid is converted into the oily  *$\omega$ -bromoamylaniline hydrobromide*, from an aqueous solution of which the *picrate* is obtained as a yellowish-green powder which sinters at  $137^\circ$  and has m. p.  $141^\circ$ . The *base* is a faintly-coloured, feebly-smelling oil, which yields the *platinichloride*,



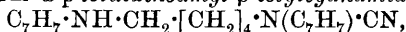
m. p.  $117\text{--}118^\circ$ , in reddish-yellow crystals, and by warming changes quantitatively to 1-phenylpiperidine hydrobromide, m. p.  $235^\circ$ . 1-Phenylpiperidine picrate has m. p.  $148^\circ$ .

Piperidine in excess and phenyl- $\omega$ -bromoamylcyanamide react to form  *$\omega$ -piperidinoamylphenylcyanamide*,  $\text{C}_5\text{NH}_{10} \cdot \text{CH}_2 \cdot [\text{CH}_2]_4 \cdot \text{NPh} \cdot \text{CN}$ , b. p.  $230\text{--}232^\circ/9\text{ mm.}$ , of which the *picrate*, m. p.  $112^\circ$ , forms yellow leaflets, and the *methiodide*, m. p.  $101^\circ$ , white leaflets.

*Phenylmethylpiperidinium iodide* has m. p.  $146^\circ$ ; distillation of the hydroxide does not cause a rupture of the ring, but regenerates 1-phenylpiperidine.

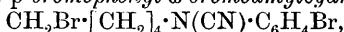
1-*p*-Tolylpiperidine, prepared from *p*-toluidine and  $\alpha\epsilon$ -dibromopentane, has b. p.  $268\text{--}269^\circ$  (compare Lellmann and Just, Abstr., 1891, 1244; Scholtz and Wassermann, this vol., i, 339), and behaves with cyanogen bromide in a similar manner to 1-phenylpiperidine. The *bromide*,  $\text{C}_7\text{H}_7 \cdot \text{C}_5\text{NH}_{10}\text{Br} \cdot [\text{CH}_2]_5 \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{CN}$ , m. p.  $124\text{--}125^\circ$ ,

forms hygroscopic, white leaflets. *p*-Tolyl- $\omega$ -bromoamylcyanamide,  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{CN}$ , is an oil which reacts with an excess of *p*-toluidine to form  $\omega$ -*p*-toluidinoamyl-*p*-tolylcyanamide,



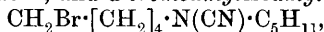
m. p.  $87^\circ$ , the hydrochloride and hydrobromide of which have m. p.  $153$ — $154^\circ$  and  $149^\circ$  respectively. The preceding cyanamide is hydrolysed by 30% sulphuric acid, yielding *s*-di-*p*-tolylpentamethylenediamine,  $\text{C}_3\text{H}_6(\text{CH}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$ , m. p.  $60^\circ$ , of which the hydrochloride, platnichloride, hydrobromide, and sulphate are mentioned; the dinitroso-derivative is a yellow, crystalline powder, m. p.  $70$ — $71^\circ$ , which yields a bishydrazine derivative by reduction. Dicyanodi-*p*-tolylpentamethylenediamine,  $\text{C}_3\text{H}_6[\text{CH}_2\cdot\text{N}(\text{CN})\cdot\text{C}_7\text{H}_7]_2$ , prepared from the diamine and cyanogen bromide in ethereal solution, has m. p.  $92^\circ$ .

1-*p*-Bromophenylpiperidine reacts somewhat slowly with cyanogen bromide, and yields *p*-bromophenyl- $\omega$ -bromoamylcyanamide,



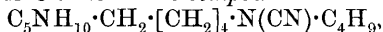
m. p.  $53^\circ$ , which by boiling with sodium phenoxide in alcoholic solution forms the ether,  $\text{OPh}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Br}$ , m. p.  $60^\circ$ , b. p.  $270$ — $280/10$  mm.

1-isoAmylpiperidine and cyanogen bromide yield isoamylpiperidine hydrobromide, m. p.  $255^\circ$ , and  $\omega$ -bromoamylisoamylcyanamide,



which reacts with piperidine to form  $\omega$ -piperidinoamylisoamylcyanamide,  $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{N}(\text{CN})\cdot\text{C}_5\text{H}_{11}$ , b. p.  $213$ — $215^\circ/12$  mm., of which the picrate, platnichloride, aurichloride, methiodide, and methochloride are oils: the platnichloride of the last-mentioned, however, forming red crystals, m. p.  $145^\circ$ , sintering at  $137^\circ$ . The preceding cyanamide is hydrolysed by heating with concentrated hydrochloric acid at  $130^\circ$  for fifteen to twenty hours, and yields  $\omega$ -piperidinoamylisoamylamine,  $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{NH}\cdot\text{C}_5\text{H}_{11}$ , b. p.  $170$ — $172^\circ/9$  mm., of which the picrate has m. p.  $152^\circ$ .

1-Butylpiperidine,  $\text{C}_5\text{NH}_{10}\cdot\text{C}_4\text{H}_9$ , b. p.  $175$ — $176^\circ$ , is obtained from butylamine and  $\alpha$ -dibromopentane in 85—90% yield; the picrate has m. p.  $132^\circ$ . Butyl- $\omega$ -bromoamylcyanamide,  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{N}(\text{CN})\cdot\text{C}_4\text{H}_9$ , reacts with piperidine to form the compound



b. p.  $206$ — $207/12$  mm.

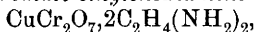
C. S.

**Compounds of Dichromates of Bivalent Metals with Organic Bases.** NICOLA PARRAVANO and A. PASTA (*Gazzetta*, 1907, 37, ii, 252—264).—The normal dichromates of bivalent metals, when obtainable, are unstable, but they yield with organic bases well-defined additive compounds which are stable and can be prepared relatively easily.

The compounds prepared by the authors were obtained by adding the organic base to a solution containing potassium dichromate (1 mol.) and the metallic sulphate (1 mol.), or in the case of cadmium, the nitrate.

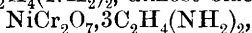
The copper dichromate pyridine compound,  $\text{CuCr}_2\text{O}_7\cdot 4\text{C}_5\text{NH}_5$ , forms a green, pulverulent precipitate and dissolves readily in ammonia, giving an intensely green liquid from which can be isolated: (1) the compound,  $\text{CuCr}_2\text{O}_7\cdot 4\text{NH}_3\cdot 2\text{H}_2\text{O}$ , in shining, black, prismatic crystals, and (2) the compound,  $\text{CuCrO}_4\cdot 4\text{NH}_3$ , in small, green prisms; both these compounds

are decomposed by water. The *copper dichromate aniline* derivative,  $\text{CuCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , forms a tobacco-coloured powder decomposable by water. The *copper dichromate ethylenediamine* compound,

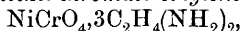


crystallises from water in chestnut-red laminæ.

The *nickel dichromate pyridine* compound,  $\text{NiCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$ , forms pale chestnut prisms; the *aniline* compound,  $\text{NiCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , a bright red, crystalline crust decomposable by water; the *ethylenediamine* compounds,  $\text{NiCr}_2\text{O}_7 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$ , almost black crystals, and



pale red crystals. The *nickel chromate ethylenediamine* compound,



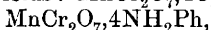
is extremely stable and forms small, dirty yellow prisms.

Cobalt dichromate forms the *compounds*:  $\text{CoCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$ , minute, black crystals;  $\text{CoCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , minute, brick-red crystals decomposable by water. The *compound*,  $\text{CoCrO}_4 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$ , forms silky, golden-yellow needles.

*Cadmium dichromate* gives:  $\text{CdCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$ , forming an orange-yellow, crystalline precipitate;  $\text{CdCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , as minute, yellow crystals decomposed by water;  $\text{CdCr}_2\text{O}_7 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2$ , as minute, orange-yellow crystals.

*Zinc dichromate* forms:  $\text{ZnCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$ , which resembles the corresponding cadmium compound, but is not altered by light;  $\text{ZnCr}_2\text{O}_7 \cdot 3\text{NH}_2\text{Ph} \cdot \text{H}_2\text{O}$ , which resembles the analogous cadmium derivative in appearance and properties.

*Manganese dichromate* yields:  $\text{MnCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$  and



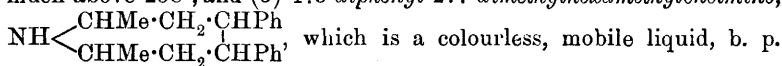
both forming dark chestnut crystals.

All these compounds are in accord with Werner's theory of coordination (*Zeitsch. anorg. Chem.*, 1893, 3, 267; Abstr., 1893, ii, 379).

The solubility of the pyridine derivatives of the dichromates increases, whilst the stability decreases, continuously in the series: copper, nickel, cobalt, cadmium, zinc, manganese. The conductivity of these compounds increases in the order: nickel, cobalt, cadmium, zinc.

T. H. P.

**Diphenyldimethylhexamethyleneimine.** GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 344—349. Compare Harries and de Osa, Abstr., 1903, i, 815).—Reduction of benzyldeneacetoxime with aluminium amalgam yields: (1)  $\gamma$ -amino- $\alpha$ -phenylbutane (Harries and de Osa, *loc. cit.*); (2) a substance, b. p. much above  $238^\circ$ , and (3) 4:5-diphenyl-2:7-dimethylhexamethyleneimine,



$235\text{--}238^\circ$ , with an odour recalling that of piperidine and forming strongly alkaline solutions. Its *benzoyl* derivative,  $\text{C}_{20}\text{H}_{24}\text{NBz}$ , crystallises from aqueous alcohol in white needles, m. p.  $101\text{--}102^\circ$ , and has the normal molecular weight in freezing benzene. The *picrate*,  $\text{C}_{20}\text{H}_{25}\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises from benzene or water in yellow needles, m. p.  $143\text{--}144^\circ$ ; the *oxalate* crystallises from alcohol in uacreous scales, or from aqueous alcohol in slender needles, m. p.

212—213°; the *hydrochloride*,  $C_{20}H_{25}N, HCl$ , forms white needles, m. p. 154—155°; the *platinichloride*,  $(C_{20}H_{25}N)_2, H_2PtCl_6$ , crystallises from water in microscopic, pale yellow, rhombic plates, m. p. 185—187°, and the *aurichloride*,  $C_{20}H_{25}N, HAuCl_4$ , crystallises from water in shining, yellow needles, m. p. 162—163°, and dissolves readily in alcohol.

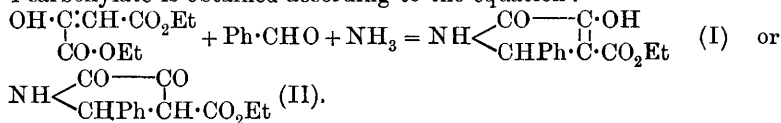
T. H. P.

[Preparation of Isatin.] KALLE & Co. (D.R.-P. 184693, 184694).—*o*-Nitromandelic acid, when reduced with zinc dust in an alkaline or ammoniacal solution containing ammonium chloride and the filtered solution treated with excess of concentrated hydrochloric acid, furnishes a yellow, crystalline product, m. p. 162°, which is probably an *anhydride* of *o*-hydroxylaminomandelic acid,  $OH \cdot NH \cdot C_6H_4 \cdot CH(OH) \cdot CO_2H$ , and may be represented by the formula  $C_6H_4 \cdot \underset{NH}{\overset{C(OH)}{\text{<}}} \cdot CO_2H$ . When

this anhydride is melted either alone or preferably with a dehydrating agent, such as acetic anhydride, it gives rise to isatin or acetylisatin respectively. Isatin is also produced when the anhydride is dissolved in aqueous sodium carbonate or hydroxide and the solution subsequently acidified.

G. T. M.

**Action of Ethyl Oxalacetate on Aldehydes in Presence of Ammonia and Primary Amines: a New General Reaction of Aldehydes.** LOUIS J. SIMON and A. CONDUCHÉ (*Ann. Chim. Phys.*, [viii], 12, 5—58).—Ethyl oxalacetate readily condenses with aldehydes in presence of ammonia, forming derivatives of 2:3-diketopyrrolidine; thus, in the case of benzaldehyde, ethyl 2:3-diketo-5-phenylpyrrolidine-4-carboxylate is obtained according to the equation:



If a primary amine is used in place of ammonia, a compound containing the group NR instead of the NH of the pyrrolidine nucleus is obtained. Some of the substances obtained in this way have been described already (Abstr., 1904, i, 521 and 812; 1905, i, 887 and 888; this vol., i, 725). The following facts are new.

The diketopyrrolidine derivatives, as liberated from their ammonium salts by adding acid, contain  $1H_2O$ ; as this water is not present in the ammonium salts which are derived from the enolic formula (I) above, it is probably combined with the carbonyl group in position 3 in formula II, thus:  $NH \cdot \underset{CHPh \cdot \underset{CO_2Et}{\overset{C}{\text{>}}}}{\overset{CO \text{---} \overset{C(OH)_2}{\text{>}}}{\text{<}}} \quad (III)$ . This water can be

expelled by heating in a vacuum at 100°; the anhydrous substance remaining sometimes takes up water again from the atmosphere (salicylic and piperonylic derivatives), but in other cases does not do so. The substance decomposing at 185°, obtained from benzaldehyde and previously given the formula I above (Abstr., 1904, i, 522), is really the hydrated substance (III); when dehydrated, it decomposes at the

same temperature, 185°. The *ammonium* salt,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{C}(\text{ONH}_4) \\ \text{CHPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ , decomposes at 175°; the analogous *aniline* salt melts at 160°, and the *p-toluidine* salt decomposes at 173°; the last two substances, when heated at 120—130°, lose the whole of the combined base, leaving the anhydrous compound (I).

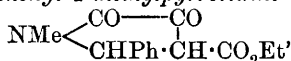
The *ammonium* salt,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{C} \cdot \text{ONH}_4 \\ \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ , of the compound from salicylaldehyde, ethyl oxalacetate and ammonia, decomposes at 190°; the *copper* salt crystallises with 4H<sub>2</sub>O. The *ammonium* salt of the compound from anisaldehyde decomposes at 175°. The compound  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{CH}(\text{CO}_2\text{Et}) \cdot \text{C} \cdot \text{CO} \end{smallmatrix}$ , prepared from vanillin, crystallises in rhombic prisms with 2H<sub>2</sub>O; the *ammonium* salt decomposes at 175°. The compound from piperonal gives an *ammonium* salt decomposing at 185°; the *copper* salt,  $(\text{C}_{14}\text{H}_{12}\text{NO}_6)_2\text{Cu} \cdot \text{C}_2\text{H}_4\text{O}_2$ , forms yellowish-green needles.

Furfuraldehyde condenses with ethyl oxalacetate and ammonia to form the compound  $\text{C}_4\text{OH}_3 \cdot \text{CH} \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\ \text{CO} \text{---} \text{CO} \end{smallmatrix}$ . From acetaldehyde,

the compound  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CO} \\ \text{CHMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$  (m. p. 146°) is obtained similarly; it is anhydrous and has a definite melting point, differing in these respects from all the other compounds of a similar type; a second form of this substance (m. p. 132°), also anhydrous, is produced with it, the two compounds being probably the racemic and meso-forms which should exist owing to the presence of two asymmetric carbon atoms. The *copper* salt crystallises with 1H<sub>2</sub>O.

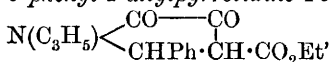
The compound  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CO} \\ \text{CH}(\text{C}_6\text{H}_{13}) \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$  (m. p. 128°), prepared from heptaldehyde, ethyl oxalacetate, and ammonia, is also anhydrous, melts without decomposing, and appears to exist in two forms; the *ammonium* salt, which decomposes at 146°, the *potassium*, and *silver* salts are crystalline.

*Ethyl 2:3-diketo-5-phenyl-1-methylpyrrolidine-4-carboxylate*,



prepared from ethyl oxalacetate, benzaldehyde, and methylamine, crystallises in white needles, is anhydrous, decomposes at 162°, and gives a crystalline *methylamine* salt,  $\text{C}_{14}\text{H}_{15}\text{O}_4\text{N} \cdot \text{NH}_2\text{Me}$ , which decomposes at 155°.

*Ethyl 2:3-diketo-5-phenyl-1-allylpyrrolidine-4-carboxylate*,



prepared similarly by using allylamine, crystallises from alcohol in slender needles, m. p. 146°; the *allylamine* salt forms silky prisms and decomposes at 142°.

*Ethyl 2:3-diketo-5-phenyl-1-benzylpyrrolidine-4-carboxylate*, prepared

by using benzylamine, crystallises in white needles, m. p.  $190^{\circ}$  with decomposition; the *benzylamine* salt, m. p.  $140^{\circ}$ , is crystalline.

Ethyl 2:3-diketo-1:5-diphenylpyrrolidine-4-carboxylate, obtained from ethyl oxalacetate, benzaldehyde, and aniline (compare Abstr., 1904, i, 812), is also formed when ethyl oxalacetate is left at the ordinary temperature in ethereal solution with benzylideneaniline. The *potassium* salt,  $C_{19}H_{16}O_4NK, 3\frac{1}{2}H_2O$ , the *barium*, *copper*, and *silver* salts are described; it does not form a salt with aniline.

In the introduction to the paper, the relationship of the substances described with compounds containing the same fundamental nucleus is discussed at length.

W. A. D.

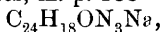
**2'- and 4'-Nitro-6'-methyl- $\alpha$ -stilbazole.** FELIX B. AHRENS and AUGUST LUTHER (*Ber.*, 1907, 40, 3400—3406).—2'-Nitro-6-methyl- $\alpha$ -stilbazole,  $C_{14}H_{12}O_2N_2$ , obtained by heating *o*-nitrobenzaldehyde with 2:6-lutidine and zinc chloride at  $180$ — $190^{\circ}$  for ten hours, crystallises from dilute alcohol in slender, pale yellow needles, m. p.  $55$ — $57^{\circ}$ . The following salts have been prepared. *Hydrochloride*,  $C_{14}H_{12}O_2N_2, HCl$ , glistening needles, m. p.  $235$ — $275^{\circ}$  (decomp.); *hydrobromide*, slender, yellow needles, m. p.  $240$ — $241^{\circ}$  (decomp.); *hydriodide*, yellow plates, m. p.  $198$ — $199^{\circ}$ ; *nitrate*, pale yellow needles, m. p.  $148$ — $149^{\circ}$ ; *picrate*,  $C_{20}H_{15}O_9N_5$ , m. p.  $227$ — $228^{\circ}$  (decomp.) after sintering at  $210^{\circ}$ ; *mercurichloride*,  $C_{14}H_{12}O_2N_2, HCl, HgCl_2$ , m. p.  $147$ — $148^{\circ}$ ; *aurichloride*, m. p.  $191$ — $192^{\circ}$ ; *platinichloride*, yellow plates; *hydrogen sulphate*, yellow needles, m. p.  $130$ — $131^{\circ}$ ; *stannichloride*,

$C_{14}H_{12}O_2H_2, HCl, SnCl_2$ , yellow needles, m. p.  $225$ — $226^{\circ}$ ;  $C_{14}H_{12}O_2N_2, HCl, ZnCl_2$ , m. p.  $195$ — $196^{\circ}$ ;  $C_{14}H_{12}O_2N_2, HCl, BaCl_2$ , long, yellow needles decomposing at  $238^{\circ}$ .

The isomeric 4'-nitro-6-methyl- $\alpha$ -stilbazole crystallises from dilute alcohol in long needles, m. p.  $131$ — $132^{\circ}$ . The salts prepared are: *hydrochloride*,  $C_{14}H_{12}O_2N_2, HCl$ , long yellow needles, m. p.  $221$ — $222^{\circ}$ ; *nitrate*, pale yellow plates, m. p.  $162$ — $163^{\circ}$ ; *platinichloride*, decomposes at  $255^{\circ}$ ; *aurichloride*, m. p.  $225$ — $226^{\circ}$ ; *mercurichloride*, yellow needles.

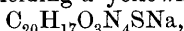
When reduced with tin and hydrochloric acid, the *o*-nitro-compound yields 2'-amino-6-methyl- $\alpha$ -stilbazole,  $C_{14}H_{14}N_2$ , in yellow, glistening needles, m. p.  $136$ — $137^{\circ}$ . This readily absorbs carbon dioxide from the air, yielding the *carbonate*,  $(C_{14}H_{14}N_2)_2 \cdot H_2CO_3$ . The *hydrochloride*,  $C_{14}H_{14}N_2, 2HCl$ , crystallises in pale yellow plates, m. p.  $234$ — $235^{\circ}$ ; the *stannichloride*,  $C_{14}H_{14}N_2, 2HCl, 2SnCl_2$ , forms orange-coloured needles, m. p.  $278^{\circ}$ , and the *mercurichloride*, similar needles, m. p.  $164^{\circ}$ . The *platinichloride* has not been obtained in a crystalline form. The diazotised amino-compound yields an *azo-dye*,  $C_{24}H_{18}ON_3K$ , with an alkaline solution of  $\beta$ -naphthol; it crystallises from alcohol in red plates, m. p.  $157$ — $158^{\circ}$ , and dyes wool or silk.

4'-Amino-5-methyl- $\alpha$ -stilbazole forms pale brown needles, m. p.  $139$ — $140^{\circ}$ . The *hydrochloride* decomposes at  $265^{\circ}$ ; the *mercurichloride* crystallises in reddish-brown needles, m. p.  $260^{\circ}$  (decomp.); the *stannichloride* forms brown needles, m. p.  $188$ — $189^{\circ}$ . The *azo-dye*,

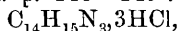


obtained from the diazotised base and an alkaline solution of  $\beta$ -naphthol, crystallises in dark reddish-brown plates, m. p. 248—249°, and dyes silk and wool red.

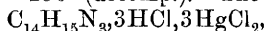
2'-Amino-6-methyl- $\alpha$ -stilbazole couples with diazotised sulphanilic acid in alkaline solution yielding a yellowish-brown *dye*,



which is readily reduced to sulphanilic acid and *diamino-6-methyl- $\alpha$ -stilbazole*,  $\text{C}_{14}\text{H}_{15}\text{N}_3$ , the latter of which crystallises from dilute alcohol in long needles, m. p. 148—149°. The *hydrochloride*,



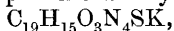
forms needles, m. p. 249—250° (decomp.). The *mercurichloride*,



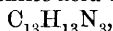
crystallises in yellow needles, m. p. 179—180°; the *stannichloride* forms glistening yellowish-brown needles, m. p. 245—246° (decomp.).

The bisdiazio-derivative of the base couples with an alkaline solution of  $\beta$ -naphthol yielding a pale red *dye*,  $\text{C}_{34}\text{H}_{23}\text{O}_2\text{N}_5\text{Na}_2$ , which crystallises from alcohol in plates, m. p. 180—181°. With  $\beta$ -naphtholdisulphonic acid (R-acid), a brownish-red *dye*,  $\text{C}_{34}\text{H}_{23}\text{O}_{14}\text{N}_5\text{S}_4\text{Na}_4$ , is obtained; it crystallises from water in plates.

4'-Amino-6-methyl- $\alpha$ -stilbazole yields a *dye*,  $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_4\text{SNa}$ , with diazotised sulphanilic acid; it crystallises from alcohol in yellowish-brown plates, and dyes silk, wool, and cotton yellow. 4'-Amino- $\alpha$ -stilbazole and diazotised sulphanilic acid yield a yellow *dye*,



which can be reduced to sulphanilic acid and *diamino- $\alpha$ -stilbazole*,



the latter of which crystallises in long, yellow needles, m. p. 126—127°. Its *hydrochloride*,  $\text{C}_{13}\text{H}_{13}\text{N}_3 \cdot 3\text{HCl}$ , forms yellowish-red, glistening needles; its *mercurichloride*, red needles, and its *stannichloride*, long, red needles, m. p. 240—241°.

J. J. S.

**New Process for the Preparation of Aromatic 3-Hydroxy-5-pyrazolones or Pyrazolidones.** AUGUST MICHAELIS and KONRAD SCHENK (*Ber.*, 1907, 40, 3568—3569).—Malonic acid and acetylphenylhydrazine condense in presence of phosphorus trichloride to 3-hydroxy-1-phenyl-5-pyrazolone previously described by Michaelis and Burmeister (*Abstr.*, 1892, 1004). In a similar manner, dimethylmalonic acid condenses to 3-hydroxy-1-phenyl-4:4-dimethyl-5-pyrazolone,  $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{CMe}_2 \\ \diagdown \quad \diagup \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$ , separating in colourless crystals, m. p. 176°.

Similarly, acetyl-*p*-bromophenylhydrazine and malonic acid condense to 3-hydroxy-1-*p*-bromophenyl-5-pyrazolone, crystallising in plates, m. p. 217°, and forming a red condensation product with benzaldehyde. The method appears to be generally applicable.

E. F. A.

**Thionpyrazolones.** RICHARD STOERMER and D. JOHANNSEN (*Ber.*, 1907, 40, 3701—3703).—The action of phosphorus pentasulphide on pyrazolones yields thionpyrazolones and is therefore analogous to that on pyrrolidone (compare Tafel and Lawaczek, this vol., i, 720).

The pyrazolone, obtained from ethyl dimethylacetoacetate, when



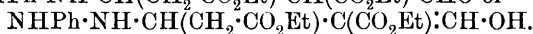
heated at  $140^{\circ}$  with phosphorus pentasulphide yields 1-phenyl-3:4:4-trimethyl-5-thionpyrazolone,  $\text{NPh} \begin{smallmatrix} \text{CS}-\text{CMe}_2 \\ \text{N}=\text{CMe} \end{smallmatrix}$ , which crystallises in long, yellow prisms, m. p.  $45-46^{\circ}$ , b. p.  $187-190^{\circ}/12$  mm. Methyl iodide gives a dimethiodide, m. p.  $210-215^{\circ}$ , which with silver chloride yields a methochloride, the platinichloride of which has m. p.  $235-237^{\circ}$ .

1-Phenyl-3-methyl-4:4-diethyl-5-thionpyrazolone,  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{S}$ , yellow prisms, m. p.  $80^{\circ}$ , and 1-phenyl-3-methyl-5-thionpyrazolone,  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}$ , or m. p.  $133^{\circ}$ , are best prepared in xylene solution. W. R.

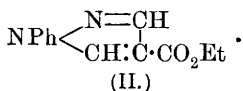
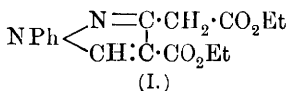
### Action of Phenylhydrazine on Ethyl Formylglutaconate.

WILHELM WISLICENUS and ERNST BREIT (*Annalen*, 1907, 356, 32-44).

—The action of phenylhydrazine on ethyl formylglutaconate has been again studied with the object of throwing light on certain points in the reaction left indefinite by the investigations of Wislicenus and Bindemann (*Abstr.*, 1901, i, 361) and Hesse (*Diss.*, Würzburg, 1902). The first product of the reaction is now found to be an additive compound,  $\text{NPh} \cdot \text{NH} \cdot \text{CH}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CHO}$  or



This condenses, forming ethyl 1-phenylpyrazole-3-acetate-4-carboxylate (I) or ethyl 1-phenylpyrazole-4-carboxylate (II), depending on the conditions. The latter product is formed when the additive compound is heated in absence of air, which explains its formation on distillation of ethyl formylacetate-phenylhydrazone (*loc. cit.*):



The additive compound,  $\text{C}_{16}\text{H}_{22}\text{O}_5\text{N}_2$ , formed by mixing ethyl formylglutaconate and phenylhydrazine in cold ethereal solution, crystallises in needles, m. p.  $70^{\circ}$ , and on exposure to air in ethereal solution forms ethyl 1-phenylpyrazole-3-acetate-4-carboxylate, m. p.  $89-90^{\circ}$ . 1-Phenylpyrazole-3-acetic-4-carboxylic acid,  $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_2$ , decomp.  $221^{\circ}$ , is formed by boiling the ester with aqueous baryta, evolves carbon dioxide on prolonged heating at  $140^{\circ}$ , forming 1-phenyl-3-methylpyrazole-4-carboxylic acid, and yields the ester, m. p.  $89-90^{\circ}$ , when boiled with alcoholic hydrogen chloride. The barium,  $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_2\text{Ba} \cdot 2\text{H}_2\text{O}$ , and silver,  $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_2\text{Ag}_2$ , salts were analysed.

When heated at  $60-70^{\circ}$  in presence of air, the additive compound yields a mixture of the above ester and ethyl 1-phenylpyrazole-4-carboxylate, m. p.  $96-97^{\circ}$ , together with ethyl acetate. In the absence of air, ethyl 1-phenylpyrazole-4-carboxylate and ethyl acetate only are formed.

When *p*-bromophenylhydrazine is added to an ethereal solution of ethyl formylglutaconate, the additive compound does not separate, but after some time the solution deposits ethyl 1-*p*-bromophenylpyrazole-3-acetate-4-carboxylate,  $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_2\text{Br}$ , m. p.  $128-129^{\circ}$ , which does not give a coloration with potassium dichromate in concentrated sulphuric

acid solution. But if the ethereal solution is rapidly evaporated, the additive compound separates, and if heated at  $140^{\circ}$  in a current of carbon dioxide, loses water and ethyl acetate forming *ethyl 1-p-bromophenylpyrazole-4-carboxylate*,  $C_{12}H_{11}O_2N_2Br$ , which crystallises in needles, m. p.  $133-134^{\circ}$ . G. Y.

**The Hydrazones of Ethyl Formylacetate.** WILHELM WISLICENUS and H. W. BYWATERS (*Annalen*, 1907, 356, 45—50. Compare preceding abstract; Wislicenus and Bindemann, *Abstr.*, 1901, i, 361).—The phenylhydrazone of ethyl formylacetate yields the same condensation products as are obtained from the additive compound of phenylhydrazine and ethyl formylglutaconate.

Ethyl 1-phenylpyrazole-3-acetate-4-carboxylate is formed when the phenylhydrazone is treated with hydrogen chloride in cold absolute alcoholic solution, whilst ethyl 1-phenylpyrazole-4-carboxylate is obtained on distillation of the phenylhydrazone.

The *p*-bromophenylhydrazone of ethyl formylacetate,  $C_{11}H_{13}O_2N_2Br$ , crystallises in slightly yellow prisms, m. p.  $80-81^{\circ}$ , is more stable than the corresponding phenylhydrazone, and gives a dark violet coloration with concentrated sulphuric acid, or a brownish-red with alcoholic ferric chloride. On treatment with hydrogen chloride in absolute alcoholic solution, it condenses, forming ethyl 1-*p*-bromophenylpyrazole-3-acetate-4-carboxylate (preceding abstract), which distils in a vacuum with partial decomposition, and gives the pyrazoline reaction after reduction. 1-*p*-Bromophenylpyrazole-3-acetic-4-carboxylic acid,  $C_{12}H_9O_4N_2Br$ , crystallises in colourless needles, m. p.  $229-230^{\circ}$ ; the silver salt, m. p.  $270^{\circ}$  (decomp.). When distilled in a vacuum, the *p*-bromophenylhydrazone of ethyl formylacetate yields ethyl 1-*p*-bromophenylpyrazole-4-carboxylate, m. p.  $131-132^{\circ}$ .

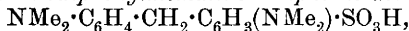
The semicarbazone of ethyl formylacetate,  $C_6H_{11}O_3N_3$ , crystallises in almost colourless prisms, m. p.  $147-148^{\circ}$ , and when heated at  $160^{\circ}$  in a sealed tube decomposes, forming alcohol, hydrazodicarbonamide, and a resin, which is soluble in alcohol and forms a silver salt.

G. Y.

**Preparation of a *p*-Aminodiphenylaminesulphonic Acid.** ERNST ERDMANN (D.R.-P. 181179).—Although diphenylamine itself is not easily converted into a monosulphonic acid, one sulphonic group is readily introduced into the molecule of *p*-aminodiphenylamine, providing that the sulphuric acid contains a certain proportion of sulphur trioxide and that the sulphonation is effected at about  $110-130^{\circ}$ , the temperature required being dependent on the amount of trioxide present. The time required to complete the reaction varies from one to three hours. *p*-Aminodiphenylaminesulphonic acid, which is purified by dissolving in alkali and reprecipitating by mineral acid, is sparingly soluble in hot water, and crystallises from this solvent in clusters of fine needles. Its sodium and potassium salts crystallise from water, and the diazo-derivative separates as a yellow, crystalline product. The new acid differs from its isomerides in the coloration it furnishes with chromic acid and ferric chloride. G. T. M.

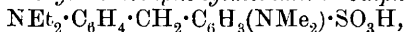
**Preparation of Tetra-alkyldiaminodiphenylmethanesulphonic Acids.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 183793).—The direct sulphonation of tetramethyldiaminodiphenylmethane does not lead readily to the formation of a mono-sulphonic acid. The product is contaminated by coloured by-products and by substances of the sulphone type. It has now been found that the monosulphonic acids of this series may be synthesised in good yield by condensing formaldehyde with dimethyl- or diethyl-aniline and dimethylaniline-*m*-sulphonic acid.

*Tetramethyldiaminodiphenylmethane-m-sulphonic acid,*



crystallises from aqueous solutions, and its *sodium* salt may be salted out in the form of slender needles.

*Dimethylaminodiethylaminodiphenylmethane-m-sulphonic acid,*



resembles its lower homologue.

G. T. M.

**Action of Hydrazine Hydrate on Nitro-compounds. I.** THEODOR CURTIUS (*J. pr. Chem.*, 1907, [ii], 76, 233—237).—A short account of the chief results of the study of the action of hydrazine hydrate on nitro-compounds previously unpublished or published only in dissertations.

Rothenberg showed (Abstr., 1893, i, 701) that whilst the action of hydrazine hydrate on oximes leads to substitution, *p*-nitrobenzene, *p*-nitro-*o*-dimethylaniline, and diphenylnitrosoamine are reduced by hydrazine hydrate forming aniline, *p*-aminodimethylaniline, and *as*-diphenylhydrazine respectively. It has since been found that the action of hydrazine hydrate on *p*-nitrosodimethylaniline leads also to the formation of traces of dimethylamine, whilst if the action is moderated by dilution of the hydrazine hydrate, tetramethyldiaminoazoxybenzene is formed.

Bollenbach (*Diss.*, Heidelberg, 1902), who obtained *o*- and *p*-aminophenols by reduction of the nitrophenols with hydrazine hydrate, was unable to reduce *m*- or *p*-nitrobenzoic acid in this manner, and found that *m*-dinitrobenzene is reduced only to *m*-nitroaminobenzene. On the other hand, Hoesch (*Diss.*, Heidelberg, 1904) has obtained

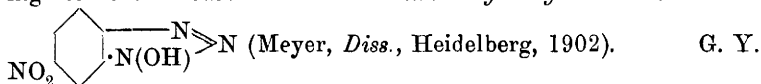
*β* aminophthalhydrazide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{NH}$ , by reduction of ethyl

*β*-nitrophthalate by means of hydrazine hydrate.

The action of hydrazine hydrate on ethyl 3:5-dinitrobenzoate (Reidel, *Diss.*, Heidelberg, 1902; see following abstract) leads to the formation of 3:5-dinitrobenzohydrazide, which is reduced by an excess of hydrazine hydrate forming 3-nitro-5-aminobenzohydrazide. Similarly, 3:5-dinitrobenzoic acid forms the hydrazine salts of 3:5-dinitro- and 3-nitro-5-amino-benzoic acids. The second nitro-group, as in the case of *m*-dinitrobenzene, cannot be reduced in this manner.

Bollenbach (*loc. cit.*) found that 2:4-dinitrobenzoic acid reacts in analogous manner to hydrazine hydrate, forming 2-nitro-4-aminobenzoic acid. 2:4-Dinitrophenylhydrazine, on the contrary, is not reduced by hydrazine hydrate, which functions merely as an alkali, the reaction lead-

ing to the formation of 6-nitro-1-hydroxy-1:2:3-benzotriazole,

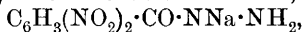


G. Y.

## Action of Hydrazine Hydrate on Nitro-compounds. II.

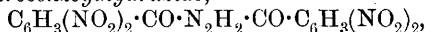
### Action of Hydrazine Hydrate on Ethyl 3:5-Dinitrobenzoate.

THEODOR CURTIUS and ADOLF RIEDEL (*J. pr. Chem.*, 1907, [ii], 76, 238—263. Compare preceding abstract).—3:5-Dinitrobenzohydrazide,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , prepared in a 63.7—69% yield by boiling ethyl 3:5-dinitrobenzoate with a limited amount of hydrazine hydrate in alcoholic solution, crystallises in yellow, prismatic needles, m. p. 158°, reduces ammoniacal silver nitrate and Fehling's solutions when heated, and forms crystalline condensation products with aldehydes and ketones. The crystalline sodium derivative,



was analysed. The benzylidene derivative,  $\text{C}_7\text{H}_4\text{O}_5\text{N}_2 \cdot \text{CHPh}$ , crystallises in slightly brown needles, m. p. 262°. The propylidene derivative,  $\text{C}_7\text{H}_4\text{O}_5\text{N}_2 \cdot \text{CMe}_2$ , forms slightly yellow needles, m. p. 213.5°. The acetyl derivative,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NHAc}$ , crystallises in yellowish-white needles, m. p. 201.5°. When treated with sodium nitrite in glacial acetic acid solution, the hydrazide forms 3:5-dinitrobenzoyl-azoimide,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CO} \cdot \text{N}_3$ , which is obtained in small, white crystals, detonates slightly when heated, and yields 3:5-dinitrobenzoic acid when boiled with aqueous sodium hydroxide. 3:5-Dinitrobenzanilide,  $\text{C}_{13}\text{H}_9\text{O}_5\text{N}_3$ , formed by boiling the azoimide with aniline, crystallises in brown needles, m. p. 234°. Ethyl 3:5-dinitrophenylcarbamate,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$  (?), prepared by boiling the azoimide with absolute alcohol, is obtained as a viscid, red oil, which yields 3:5-dinitroaniline when boiled with concentrated hydrochloric acid. 3:5-Dinitroacetanilide,  $\text{C}_8\text{H}_7\text{O}_5\text{N}_3$ , crystallises in yellowish-white needles, m. p. 191°. The action of boiling methyl alcohol on the azoimide leads to the formation of methyl 3:5-dinitrobenzoate and azoimide. *s*-Bis-3:5-dinitrophenylcarbamide, m. p. 265°, formed together with 3:5-dinitroaniline by boiling 3:5-dinitrobenzoylazoimide with water, is probably identical with Struve and Radenhausen's tetranitrocarb-anilide (*Abstr.*, 1896, i, 35).

#### Bis-3:5-dinitrobenzoylhydrazide,



prepared by the action of iodine on 3:5-dinitrobenzoylhydrazide in boiling alcoholic solution, is obtained in a 30% yield as a yellow powder, m. p. 276°, and dissolves unchanged in concentrated sulphuric acid, being reprecipitated on addition of water. When heated with alcoholic hydrogen chloride at 100° in a sealed tube, it is decomposed, yielding *m*-dinitrobenzene and hydrazine. The crystalline disodium derivative,  $\text{N}_2\text{Na}_2[\text{CO} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2]_2$ , is described.

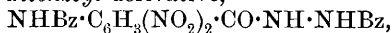
3-Nitro-5-aminobenzoylhydrazide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , is formed in a 60% yield together with a reddish-grey, crystalline powder, m. p. 283—284°, having the composition of bisdinitrobenzoylhydrazide, when ethyl 3:5-dinitrobenzoate is boiled in concentrated alcoholic solution with an excess of hydrazine hydrate. 3-Nitro-

5-aminobenzoylhydrazide is formed also by boiling ethyl 3-nitro-5-aminobenzoate with hydrazine hydrate in alcoholic solution. It crystallises in yellowish-red leaflets, m. p.  $221^{\circ}$ , and reduces ammoniacal silver nitrate and Fehling's solutions when heated.

*Hydrazonium 3:5-dinitrobenzoate*,  $C_6H_3(NO_2)_2 \cdot CO_2H \cdot N_2H_4$ , formed by heating 3:5-dinitrobenzoic acid with a limited amount of hydrazine hydrate in alcoholic solution, crystallises in yellowish-brown needles, m. p.  $168^{\circ}$ , reduces ammoniacal silver nitrate and Fehling's solutions in the cold, yields benzaldazine and 3:5-dinitrobenzoic acid when shaken with benzaldehyde in aqueous solution, and is converted into ethyl 3:5-dinitrobenzoate when heated with alcoholic hydrogen chloride.

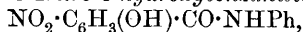
*Hydrazonium 3-nitro-5-aminobenzoate*,  $NH_2 \cdot C_6H_3(NO_2)_2 \cdot CO_2H \cdot N_2H_4$ , prepared by boiling 3:5-dinitrobenzoic acid or its hydrazonium salt with an excess of hydrazine hydrate in alcoholic solution, crystallises in reddish-yellow needles, m. p.  $207^{\circ}$  (decomp.), reduces ammoniacal silver nitrate and Fehling's solutions in the cold, and when shaken with benzaldehyde yields benzaldazine and 3-nitro-5-aminobenzoic acid.

The following substances derived from 3-nitro-5-aminobenzoylhydrazide are described. The *hydrochloride*,  $C_7H_8O_3N_4 \cdot 2HCl$ , brown crystals, m. p.  $221-222^{\circ}$ . The *benzylidene* derivative,  $C_{14}H_{12}O_3N_4$ , yellow, prismatic needles, m. p.  $247-248^{\circ}$ . The *m-hydroxybenzylidene* derivative,  $C_{14}H_{12}O_4N_4$ , reddish-brown leaflets, m. p.  $242^{\circ}$ . The *m-nitrobenzylidene* derivative,  $C_{14}H_{11}O_5N_5$ , yellow needles, m. p.  $240^{\circ}$ . The *propylidene* derivative,  $C_{10}H_{12}O_3N_4$ , golden needles, m. p.  $208^{\circ}$ . The *triacetyl* derivative,  $NHAc \cdot C_6H_3(NO_2)_2 \cdot CO \cdot NAc \cdot NHAc$ , yellow nodules, m. p.  $256^{\circ}$ . The *dibenzoyl* derivative,



slightly brown needles, m. p.  $236^{\circ}$ .

*3-Nitro-5-hydroxybenzoylazoimide*,  $NO_2 \cdot C_6H_3(OH) \cdot CO \cdot N_3$ , prepared by the action of sodium nitrite on 3-nitro-5-aminobenzoylhydrazide in acetic acid solution, is obtained as a reddish-yellow, flocculent substance, which becomes brown when dried in a desiccator and detonates when heated. It dissolves in aqueous sodium hydroxide with slight evolution of gas, forming a dark red solution, and on addition of sulphuric acid yields azoimide. *3-Nitro-5-hydroxybenzanilide*,



formed by boiling the azoimide with aniline, crystallises in white needles, m. p.  $232^{\circ}$ . The *urethane*,  $NO_2 \cdot C_6H_3(OH) \cdot NH \cdot CO_2Et$ , formed by boiling the azoimide with absolute alcohol, is obtained as a viscid, red oil, and, when heated with sodium hydroxide and hydrogen chloride successively, yields 3-nitro-5-aminophenol.

When heated with water, 3-nitro-5-hydroxybenzoylazoimide forms *s-di-3-nitro-5-hydroxyphenylcarbamide*,  $CO[NH \cdot C_6H_3(OH) \cdot NO_2]_2$ , and small amounts of 3-nitro-5-aminophenol. The carbamide is obtained as a brittle mass, decomp.  $260-270^{\circ}$ , and is decomposed by boiling concentrated sodium hydroxide forming 3-nitro-5-aminophenol.

*s-Di-3-nitro-5-aminobenzoylhydrazide*,  $N_2H_2[CO \cdot C_6H_3(NH_2) \cdot NO_2]_2$ , prepared by boiling 3-nitro-5-aminobenzoylhydrazide with iodine in alcoholic solution, is obtained as a yellow, granular powder, m. p.  $263-264^{\circ}$ , and is hydrolysed, forming hydrazine, by alcoholic hydrogen chloride at  $100^{\circ}$ .

G. Y.

**Preparation of 5:5-Dialkylbarbituric Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 183628).—The dialkylbarbituric acids are obtained by heating the dialkylmalonyldiurethanes, produced from the dialkylmalonyl chlorides and alkylurethanes, either alone or in the presence of carbamide, phenyl carbonate, or a similar compound. G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** E. MERCK (D.R.-P. 183857).—The ethyl dialkylmalonates yield 5:5-dialkylbarbituric acids when heated either with biuret or an alkylallophanate. Ethyl dialkylmalonates, when heated with either biuret or ethyl allophanate in alcoholic sodium ethoxide, furnish 5:5-dialkylbarbituric acids (compare Abstr., 1906, i, 461). G. T. M.

**Preparation of 4:6-Dioxy-2-thio-5:5-dialkylpyrimidines.** EMANUEL MERCK (D.R.-P. 182764).—4:6-Dioxy-2-thio-5:5-diethylpyrimidine may be produced by heating diethylmalonyl chloride with thiocarbamide at 100°, and 4:6-dioxy-2-thio-5:5-dipropylpyrimidine is similarly prepared from dipropylmalonyl chloride. These substances are readily oxidised to the corresponding 5:5-dialkylbarbituric acids by dilute nitric acid or alkaline permanganate. G. T. M.

**Pyrimidines. XXIII. Uracil-4-carboxylic Acid.** HENRY L. WHEELER (*Amer. Chem. J.*, 1907, 38, 358—366).—By the condensation of carbamide with ethyl oxalacetate, Müller (Abstr., 1897, i, 549) obtained a compound which he regarded as ethyl uracil-4-carboxylate,  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$ .

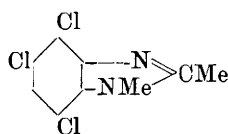
As no evidence was adduced to prove that the substance had this pyrimidine structure, it seemed possible that it might be the ester of the acid,  $\text{CO} \begin{smallmatrix} \diagup \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{CO} \end{smallmatrix}$ , obtained by Gabriel (Abstr., 1906, i, 636) by the action of bromine on maly lureide. Müller's ester has therefore been prepared and studied, and it has been found that on hydrolysis it yields an acid, which is not identical with Gabriel's acid, and on treatment with bromine is converted into dibromobarbituric acid. It is proved, therefore, that Müller's ester has the structure originally assigned to it, that Gabriel was right in concluding that his acid was not a pyrimidine, and that maly lureide has the constitution,  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , proposed by Guareschi (Abstr., 1877, i, 458), and not  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$ , as suggested by Grimaux (Abstr., 1875, 752).

*Uracil-4-carboxylic acid*,  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ ,  $\text{H}_2\text{O}$ , m. p. 347° (decomp.), crystallises from water in prisms; the *methyl* ester, m. p. 230°, forms colourless needles; the *potassium* and *barium* salts are described.

An attempt to prepare ethyl uracil-4-carboxylate by treating ethyl oxalacetate with ethyl- $\psi$ -thiocarbamide hydrobromide resulted in the formation of an additive compound,  $C_{11}H_{20}O_5N_2S$ , m. p. 133—134°, which crystallises in colourless needles and when boiled with hydrochloric acid yields a substance, m. p. 206—207°, which contains sulphur, but not nitrogen. When ethyl cyanoacetylacetate is treated in the same way, an additive compound,  $C_{10}H_{17}O_3N_2S$ , m. p. 159°, is produced, which separates from alcohol in colourless, flat prisms. Ethyl oxalamalonate, under similar conditions, yields an additive compound,  $C_{17}H_{32}O_7N_4S_2$ , m. p. 181° (decomp.), which crystallises from alcohol in lustrous scales.

E. G.

[Properties of Substituted Amidines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 180126).—The amidines derived from the



aromatic orthodiamines may be employed as substitutes for camphor in the production of celluloid.

Methylbenziminazole, m. p. 113—115°, trichloro-2-methyl-1-ethylbenziminazole, m. p. 116—117° (from ethyl aceto-*o*-nitrotrichloro-

anilide), and 4:5:7-trichloro-1:2-dimethylbenziminazole, m. p. 120—121°, can be worked up with nitrocellulose in the presence of alcohol.

G. T. M.

**3-Amino-2-methylquinoline.** O. STARK (*Ber.*, 1907, 40, 3425—3433).—When the oxime of 3-acetyl-2-methylquinoline is heated with sulphuric acid at 180°, the Beckmann reaction occurs, followed by hydrolysis, and the elimination of the acetyl group, and the final product is 3-amino-2-methylquinoline:  $C_9NH_5Me \cdot CMe \cdot NOH \rightarrow C_9NH_5Me \cdot NH \cdot COMe \rightarrow C_9NH_5Me \cdot NH_2$ .

A 92% yield of 3-acetyl-2-methylquinoline may be obtained by heating an alcoholic solution of *o*-aminobenzaldehyde and acetylacetone with a few drops of piperidine. It melts at 78—79° (compare Eliasberg and Friedländer, *Abstr.*, 1892, 1106). The *semicarbazone*,  $C_{13}H_{14}ON_4$ , crystallises from alcohol in small, colourless needles, m. p. 208°.

3-Amino-2-methylquinoline crystallises from ether in long, yellow needles, m. p. 159—160°, or from light petroleum in brilliant golden needles. The *hydrochloride*,  $C_{10}H_{10}N_2 \cdot 2HCl$ , obtained by passing dry hydrogen chloride into an absolute ethereal solution of the base, forms a yellowish-white, crystalline powder; the *platinichloride*,  $2C_{10}H_{10}N_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , forms glistening golden needles, and darkens when heated to 220—230°; the *picrate*,  $C_{10}H_{10}N_2 \cdot C_6H_3O_7N_3$ , also forms golden needles, and decomposes at about 235°. The *acetyl* derivative,  $C_9NH_5Me \cdot NHAc$ , crystallises from ether in needles, m. p. 164°. The solutions of the acetyl derivative do not fluoresce until hydrolysis has begun. The same acetyl derivative may also be obtained by the action of a phosphorus oxychloride solution of phosphorus pentachloride on the oxime.

When oxidised with permanganate, the aminomethylquinoline yields

water with  $2\text{H}_2\text{O}$ , but if a solution of the compound saturated at  $60\text{--}65^\circ$  is boiled, anhydrous crystals separate. When reduced with hydrogen iodide in acetic acid solution, 3-amino-4-hydroxy-2-methylquinoline yields quinaldine (2-methylquinoline), and not aminoquinaldine as stated by Conrad, Limpach, and Eckhardt (Abstr., 1888, 1111). J. J. S.

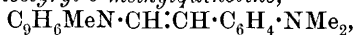
**Fluorescence of 3-Amino-2-methylquinoline and 3-Amino-4-hydroxy-2-methylquinoline.** Use of 3-Amino-2-methylquinoline as an Indicator. O. STARK (Ber., 1907, 40, 3434).—Pure aqueous solutions of 3-amino-2-methylquinoline and of 3-amino-4-hydroxy-2-methylquinoline do not fluoresce even in very dilute solutions. The former compound fluoresces in acid solutions only, and the latter in both acid and alkaline solution, thus indicating the relationship between fluorescence and dissociation. A pure aqueous solution of the hydroxy-derivative is best obtained by distillation in steam; it is then non-fluorescent, but the addition of the minutest trace of acid on alkali produces fluorescence.

3-Amino-2-methylquinoline is an excellent indicator in acidimetry, and can replace methyl-orange. An alcoholic solution is the best to use. J. J. S.

**Some Methineammonium Dyes.** A. PORAI-KOSCHITZ [with P. SOLODOWINKOFF and M. TROITZKI] (Zeitsch. Farb. Ind., 1907, 6, 291—295. Compare Rupe and Porai-Koschitz, Abstr., 1906, i, 754; Nölting and Witte, *ibid.*, 886).—2-m-Aminostyryl-6-methylquinoline,  $\text{C}_9\text{NH}_6\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , prepared by reducing with stannous chloride and hydrochloric acid the corresponding nitro-compound prepared from *m*-nitrobenzaldehyde and 2:6-dimethylquinoline (Gasda, Abstr., 1906, i, 41), crystallises from benzene in slightly yellow needles, m. p.  $160.5^\circ$ , and gives a yellow hydrochloride,  $\text{C}_{18}\text{H}_{16}\text{N}_2\cdot 2\text{HCl}$ .

2-p-Nitrostyryl-6-methylquinoline,  $\text{C}_9\text{NH}_6\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , prepared by condensing *p*-nitrobenzaldehyde with 2:6-dimethylquinoline, crystallises from pyridine as a bright green powder, m. p.  $177^\circ$ ; its reduction gives 2-p-aminostyryl-6-methylquinoline, which crystallises from dilute alcohol in bright yellow leaflets, m. p.  $173^\circ$  after darkening at  $164^\circ$ ; the hydrochloride,  $\text{C}_{18}\text{H}_{16}\text{N}_2\cdot\text{HCl}$ , is purple-red, and the benzoyl derivative forms an orange, crystalline powder, m. p.  $224^\circ$ .

2-p-Dimethylaminostyryl-6-methylquinoline,



obtained from *p*-dimethylaminobenzaldehyde and 2:6-dimethylquinoline, crystallises from dilute alcohol or pyridine in long, yellow needles, m. p.  $198^\circ$ ; the hydrochloride,  $\text{C}_{20}\text{H}_{20}\text{N}_2\cdot\text{HCl}$ , is a purple, crystalline powder.

5-m-Aminostyrylacridine,  $\text{C}_{13}\text{NH}_8\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , prepared by reducing 5-m-nitrostyrylacridine (Friedländer, Abstr., 1905, i, 829) with stannous chloride and hydrochloric acid, crystallises from pyridine in short, yellow needles, m. p.  $232\text{--}234^\circ$ ; its salts are vermilion-red.

5-p-Nitrostyrylacridine, prepared by heating *p*-nitrobenzaldehyde

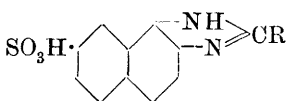


with 5-methylacridine and zinc chloride at 140—150°, crystallises from alcohol in small, bright yellow needles, m. p. 212°; its salts are sparingly soluble in water. 5-*p*-Aminostyrylacridine, obtained by reducing the foregoing, or by heating aminobenzaldehyde with 5-methylacridine and zinc chloride at 120°, crystallises from alcohol as a yellow powder, m. p. 209°. 5-*p*-Dimethylaminostyrylacridine, prepared by fusing *p*-dimethylbenzaldehyde with 5-methylacridine and zinc chloride during six hours at 135°, crystallises from alcohol; m. p. 238—239·5°; the *hydrochloride*,  $C_{23}H_{20}N_2 \cdot HCl$ , is blue; the *dihydrochloride*, yellow and unstable.

The foregoing *p*-aminobenzylidene compounds, derived from 6-methylquinaldine and 5-methylacridine, dye wool, silk, and mordanted cotton darker shades (orange to red) than the corresponding benzylidene compounds; on the other hand, the *m*-aminobenzylidene compounds either do not possess tinctorial properties or are only feebly yellow.

W. A. D.

**Preparation of 2-Derivatives of 6-Hydroxy- $\alpha\beta$ -naphthiminazole-8-sulphonic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 181178. Compare Abstr., 1906, i, 713).—



The naphthiminazole derivatives, derived from 1 : 2-diaminonaphthalene-5 : 7-disulphonic acid on fusion with alkali hydroxides, lose the sulphonic group in position 5, and become converted into 6-hydroxy- $\alpha\beta$ -naphthiminazole-8-sulphonic acids having the annexed general formula.

G. T. M.

**Action of Ethylamine on Isatin.** C. HASLINGER (*Ber.*, 1907, 40, 3598—3601. Compare this vol., i, 657).—Whilst the action of aromatic amines and diamines, and of pyrrole and piperidine on isatin, has been investigated exhaustively, of the aliphatic amines that of anylamine only has been studied (Schiff, *Annalen*, 1867, 144, 53). Ethylamine is now found to react with dibromoisatin yielding a yellow, a colourless, and a green product, depending on the conditions of the reaction. Under similar conditions, isatin and bromoisatin yield each only a yellow and a colourless product. All three classes of compounds dissolve in concentrated sulphuric acid, the yellow compounds forming a red to reddish-violet, the green compound forming a blue, solution from which the corresponding isatin is precipitated on addition of water; the colourless compounds form colourless solutions and are reprecipitated unchanged on dilution. With fuming hydrochloric acid, the yellow compounds form red solutions, which slowly become orange-yellow and deposit the isatin; the blue compound gives the same reaction, but more slowly, whilst the colourless compounds remain undissolved.

3-Ethyliminoisatin,  $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{C(NEt)} \end{smallmatrix} > C \cdot OH$ , prepared by treating isatin with an equal amount of 33% alcoholic ethylamine solution, crystallises in yellow needles and intumesces at 152°, forming a violet mass which dissolves in alcohol to a reddish-violet solution.

3:3-Diethylamino-1-ethyl- $\psi$ -isatin,  $C_6H_4 \begin{smallmatrix} \text{NEt} \\ \diagup \quad \diagdown \\ \text{C}(\text{NHEt})_2 \end{smallmatrix} \text{CO}$ , prepared by treating isatin with four times its weight of 33% alcoholic ethylamine solution, separates from ethyl acetate in white crystals and rapidly decomposes, losing ethylamine, in solution.

5-Bromo-3-ethyliminoisatin,  $C_{10}H_9ON_2Br$ , forms yellow crystals and intumesces at about  $167^\circ$ , forming a violet mass; the potassium derivative,  $C_{10}H_8ON_2BrK$ , crystallises in red needles.

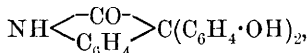
5:7-Dibromo-3-ethyliminoisatin,  $C_{10}H_8ON_2Br_2$ , is yellow, and decomposes about  $175^\circ$ .

5:7-Dibromo-3:3-diethylamino-1-ethyl- $\psi$ -isatin,  $C_{14}H_{19}ON_3Br_2$ , forms white needles, and is stable towards solvents.

5:7-Dibromo-2-ethylaminoisatin (5:7-dibromo-2-ethylimino- $\psi$ -isatin),  $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C} \cdot \text{NHet}$  or  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C} \cdot \text{NEt}$ , prepared by prolonged action of an excess of ethylamine on dibromoisatin, forms green crystals.

Dichloroisatin yields the three corresponding derivatives with ethylamine. G. Y.

**Oxidation of Phenolisatin.** CARL LIEBERMANN and N. DANAILA (*Ber.*, 1907, 40, 3588—3597).—In connexion with the study of indigotin-like colouring matters from isatin (this vol., i, 657), the authors have investigated the constitution of the dye formed by oxidation of phenolisatin. Baeyer and Lazarus (*Abstr.*, 1886, 155) showed phenolisatin to have the constitution



and considered the deep red dye formed by oxidation of this with potassium ferricyanide in alkaline solution to be aminobenzaurin,

$\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH}) \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$ . It is found now that this dye is

2-aminoaurin,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH}) \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$ , only traces of aminobenzaurin being formed.

The name diphenolisatin is to be preferred to phenolisatin as more in agreement with the constitution. Diphenolisatin, m. p.  $260-261^\circ$  ( $220^\circ$ : Baeyer and Lazarus, *loc. cit.*), forms stable compounds with ether, m. p.  $70-80^\circ$ , and chloroform, decomp.  $110^\circ$ . Contrary to Baeyer and Lazarus' statement, diphenolisatin forms a triacetate,  $C_{20}H_{12}O_3Na_3$ , which separates from alcohol in white, microscopic crystals, m. p.  $201-202^\circ$ .

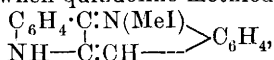
Halogenated diphenolisatins are prepared from halogenated isatins in the same manner as diphenolisatin from isatin. Bromodiphenolisatin,  $\text{NH} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3\text{Br} \end{smallmatrix} \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2$ , crystallises in white needles,

m. p.  $235-236^\circ$ , and forms a triacetate,  $C_{20}H_{11}O_3NBrAc_3$ , m. p.  $217^\circ$ . Dibromodiphenolisatin,  $\text{NH} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2\text{Br}_2 \end{smallmatrix} \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2$ , forms a diacetate,  $C_{20}H_{11}O_3NBr_2Ac_2$ , m. p.  $237-238^\circ$ . Chlorodiphenolisatin, m. p.  $237-238^\circ$ . Dichlorodiphenolisatin, m. p.  $276-277^\circ$ .

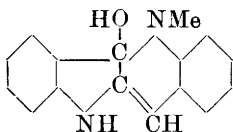
Diphenolisatins are oxidised to aminoaurins by potassium ferricyanide in alkaline solution or by potassium persulphate. The action of iodine on diphenolisatins in alkaline solution leads to the formation of a bluer colour. The aminoaurins are obtained in orange, amorphous powders, insoluble in water or benzene, but readily soluble in cold alcohol or glacial acetic acid; the absorption bands in the spectra of the cherry-red, alkaline solutions lie nearer to the D line than those in the aurin spectrum. The coloration with concentrated sulphuric acid is redder with aminoaurin than with aurin.

The following aminoaurins have been analysed: 2-aminoaurin (*isatin-red*),  $C_{19}H_{15}O_3N$ ; 5-bromo-2-aminoaurin,  $C_{19}H_{14}O_3NBr$ ; 3:5-dibromo-2-aminoaurin,  $C_{19}H_{13}O_3NBr_2$ ; 5-chloro-2-aminoaurin,  $C_{19}H_{14}O_3NCl$ ; dichloro-2-aminoaurin,  $C_{19}H_{13}O_3NCl_2$ . G. Y.

**Methylquindolanol.** FRIEDRICH FICHTER and HANS PROBST (*Ber.*, 1907, 40, 3478).—It was shown by Fichter and Boehringer (this vol., i, 92) that, when quindoline methiodide,



is treated with sodium hydroxide, it forms a  $\psi$ -base, *methylquindolanol*, which, it is now found, has the annexed formula; it crystallises from methyl alcohol in tiny needles. The application of the Zeisel method showed that no methoxy-groups were present. A. McK.



**Preparation of Aromatic Monoacetyltriamines.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 183843).—The aromatic monoacetyltriamines have hitherto not been obtained by the reduction of aromatic 2:4-dinitroacylamines owing to the resultant condensation between the contiguous amino- and acylamino-groups leading to the production of the anhydro-bases of the iminoazole series. It has now been found that reduction without condensation can be effected by the use of mild reducing agents, such as iron and dilute acetic or mineral acids.

4-Acetyl-amino-*m*-phenylenediamine,  $NHAc \cdot C_6H_3(NH_2)_2$ , prismatic crystals, m. p. 158—159°, results from the mild reduction of 2:4-dinitroacetanilide; when heated above its melting point or when boiled with glacial acetic acid, it loses water, forming aminomethylbenziminazole.

2-Acetyl-amino-3:5-tolylenediamine,  $NHAc \cdot C_6H_3Me(NH_2)_2$ , yellow needles, m. p. 210—211°, is less soluble than the preceding base, and is obtained from 3:5-dinitroaceto-*o*-toluidide in a similar manner. Favourable results are obtained by substituting these new bases for the ordinary meta-diamines in the production of azo-dyes.

G. T. M.

[Preparation of Triaminotriphenylethylene.] GEORGES IMBERT and CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 180011).—Trichloro- or tribromo-ethylene or acetylene tetrachloride, or the

corresponding tetrabromide, when mixed with aniline and heated with a solution of alkali hydroxide or carbonate, furnishes an excellent yield of triaminotriphenylethylene, a base which is of use in pharmaceutical chemistry and the colour industry. G. T. M.

**Oxazine Dyes.** RUDOLF NIETZKI and VICTOR BECKER (*Ber.*, 1907, 40, 3397—3400).—1:4-Diamino-2-naphthol forms a stable *hydrochloride*,  $C_{10}H_{10}ON_2 \cdot 2HCl$ , which attacks the mucous membrane. The free base rapidly turns brown on exposure to the air. A blue oxazine dye, *diaminonaphthoxazone*,  $NH_2 \cdot C_{10}H_5 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C_{10}H_5 \cdot NH$ , is obtained when an alcoholic solution of this hydrochloride is boiled with crystallised sodium acetate while a current of air is passed through the solution. It forms well-developed, glistening crystals. A crystalline *hydrochloride*,  $C_{20}H_{14}ON_3Cl$ , is formed when the base is dissolved in phenol, precipitated with alcohol and hydrochloric acid, and dried at  $100^\circ$ . It dyes cotton mordanted with tannin, and its alcoholic and acetic acid solutions exhibit a brilliant red fluorescence. When the aminosulphonic acid, known as eikonogen, is used in place of the diaminonaphthol, a *disulphonic acid* derivative of the above dye is obtained.

1:4-Diamino- $\beta$ -naphthol-6-sulphonic acid yields a *diaminonaphthoxazonedisulphonic acid*, which dyes wool in an acid-bath a blue colour. J. J. S.

**Synthesis of Iminoazolyethylamine** [4- $\beta$ -Aminoethylglyoxaline]. ADOLF WINDAUS and W. VOGT (*Ber.*, 1907, 40, 3691—3695).—The recognition that glyoxaline radicles are contained in the alkaloid pilocarpine (Jowett, *Trans.*, 1903, 83, 438) and in substances derived from proteins like histidine (Pauly, *Abstr.*, 1904, i, 1068) has suggested the synthesis of these natural products. As a step in this direction, glyoxaline-4-propionic acid (*Abstr.*, 1905, i, 834) has been converted into 4- $\beta$ -aminoethylglyoxaline,  $\begin{smallmatrix} NH \cdot CH \\ | \\ CH=N \end{smallmatrix} \gg C \cdot CH_2 \cdot CH_2 \cdot NH_2$ , by means of Curtius' method.

*Ethyl glyoxalinepropionate* is a colourless oil, obtained by esterification and purification by means of the *oxalate*, which crystallises in rhombic plates, m. p.  $158^\circ$ ; the *picrolonate* forms light yellow needles, m. p.  $226^\circ$  (decomp.). The *hydrazide*,  $C_6H_{10}ON_4$ , obtained by the interaction of the ester and 50% hydrazine hydrate, has m. p.  $142^\circ$ . The *hydrochloride* of aminoethylglyoxaline is obtained in 55% yield by treating an alcoholic solution of the hydrazide with amyl nitrite and hydrochloric acid to form the azoimide, decomposing this to obtain the urethane, and finally hydrolysing the urethane. It crystallises in prisms, m. p.  $240^\circ$  (decomp.). No sparingly soluble salts are given by ammoniacal zinc or silver hydroxides in contradistinction to other glyoxaline compounds. The *platinichloride* is orange, blackens towards  $200^\circ$ , but does not melt; *picrate*, m. p.  $239^\circ$  (decomp.); *picrolonate* is characteristic, m. p.  $266^\circ$  (decomp.).

By treating the aminoethylglyoxaline with benzoyl chloride and

sodium hydroxide, the ring is ruptured and *tribenzoylbutenetriamine*,  $\text{NHBz} \cdot \text{CH} : \text{C}(\text{NHBz}) \cdot [\text{CH}_2]_2 \cdot \text{NHBz}$ , is obtained as glistening needles, m. p.  $191^\circ$ . W. R.

### Behaviour of Hydrogen Cyanide towards Phenylcarbimide.

II. WALTER DIECKMANN and HEINRICH KÄMMERER (*Ber.*, 1907, 40, 3737—3743. Compare Abstr., 1905, i, 874).—By the action of sodium ethoxide, diphenylparabanimide is converted into the isomeric *as-oxalyl*diphenylguanidine,  $\text{NPh} : \text{C} \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NH} - \text{CO} \end{smallmatrix}$ , m. p.  $225^\circ$ , which

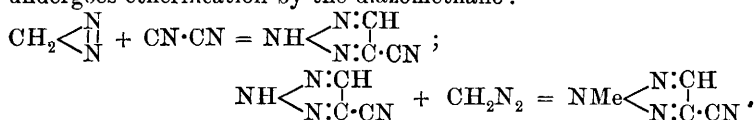
forms colourless prisms, has acid properties, and is hydrolysed by concentrated hydrochloric acid yielding aniline and *phenylparabanic acid*, m. p.  $209$ — $210^\circ$ . The two new compounds are also obtained by the condensation of ethyl oxalate with diphenylguanidine and phenylcarbamide respectively in the presence of sodium ethoxide.

Melanoximide (*s-oxalyl*diphenylguanidine), m. p.  $225^\circ$ , which is obtained most conveniently by warming diphenylguanidine cyanide with dilute acetic acid, is also converted by sodium ethoxide into *as-oxalyl*diphenylguanidine.

With phenylcarbimide at  $120^\circ$ , diphenylparabanimide yields the *carbanilide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{N} : \text{C} \begin{smallmatrix} \text{CO} - \text{NPh} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$ , m. p.  $233^\circ$ , which is therefore the final product of the action of hydrogen cyanide on phenylcarbimide (*loc. cit.*). By prolonged heating with glacial acetic acid, the carbanilide yields diphenylparabanic acid, whereas hydrolysis by a mixture of hydrochloric and glacial acetic acids forms in addition phenylcarbamide.

Phenylcarbamide is hydrolysed by boiling acetic acid yielding diphenylcarbamide and small quantities of aniline and acetanilide; by dilute hydrochloric acid giving ammonium chloride, aniline hydrochloride, and carbon dioxide, and by boiling water forming diphenylcarbamide, ammonia, aniline, and carbon dioxide. C. S.

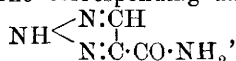
**Action of Diazo-derivatives of Aliphatic Hydrocarbons on Cyanogen and its Derivatives. I and II. Cyanogen.** ALBERTO PERATONER and E. AZZARELLO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 237—243; 318—328. Compare Azzarello, Abstr., 1905, i, 867).—An ethereal solution of cyanogen reacts violently with a 2—5% ethereal solution of diazomethane or diazoethane, forming a cyanoderivative of osotriazole, which, unless special precautions are taken, undergoes etherification by the diazomethane:



In order to prevent the etherification, a very small amount of the diazo-compound must be treated with a large excess of cyanogen in cold ethereal solution. The fact that only one of the CN groups in the cyanogen molecule reacts with the diazo-hydrocarbon, no com-

pound consisting of two triazole nuclei joined by their carbon atoms being formed, would indicate a structure other than  $\text{N}:\text{C}:\text{C}:\text{N}$  for cyanogen. The balance of evidence, which the authors review, is, however, in favour of the above formula.

3-Cyano-osotriazole,  $\text{NH} \begin{smallmatrix} \text{N}:\text{CH} \\ \diagdown \\ \text{N}:\text{C}:\text{CN} \end{smallmatrix}$ , separates from benzene in small, white crystals, m. p. 113—114°, and gives precipitates with salts of many heavy metals. The corresponding *amide*,



prepared by the action of alcoholic potassium hydroxide on the cyano-compound, is deposited from alcohol in small, white crystals, m. p. 256—257°. When treated with 40% alcoholic potassium hydroxide solution, or with concentrated hydrochloric acid, it yields the osotriazole-carboxylic acid described by Baltzer and von Pechmann (Abstr., 1891, 1116), and this, when heated at 230—240°, is converted into the osotriazole prepared by these authors.

3-Cyano-1-methylsotriazole,  $\text{NMe} \begin{smallmatrix} \text{N}:\text{CH} \\ \diagdown \\ \text{N}:\text{C}:\text{CN} \end{smallmatrix}$ , is a colourless, neutral liquid, b. p. 95°/30 mm., having a fruity odour. When heated with 40% alcoholic potassium hydroxide, it is converted quantitatively into the potassium derivative of 1-methylsotriazole-3-carboxylic acid,

$\text{NMe} \begin{smallmatrix} \text{N}:\text{CH} \\ \diagdown \\ \text{N}:\text{C}:\text{CO}_2\text{H} \end{smallmatrix}$ , which is deposited from acetone or benzene in small, white crystals, m. p. 141—142°. The *potassium*,  $\text{C}_4\text{H}_4\text{O}_2\text{N}_3\text{K}$ , *barium*,  $(\text{C}_4\text{H}_4\text{O}_2\text{N}_3)_2\text{Ba}\cdot 3\frac{1}{2}\text{H}_2\text{O}$ , and *calcium* salts, and the *ethyl ester*,  $\text{C}_2\text{N}_3\text{HMe}\cdot\text{CO}_2\text{Et}$ , b. p. 115°/60 mm., were prepared.

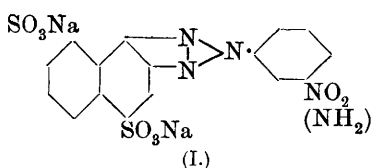
4-Cyano-3-methylsotriazole,  $\text{NH} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagdown \\ \text{N}:\text{C}:\text{CN} \end{smallmatrix}$ , separates from benzene in small, white crystals, m. p. 84°, b. p. 160°/30 mm., has the normal molecular weight in freezing acetic acid, and, in aqueous solution, has an acid reaction. The *silver* derivative,  $\text{C}_4\text{H}_3\text{N}_4\text{Ag}$ , is a white powder stable towards light.

3-Methylsotriazole-4-carboxylic acid,  $\text{NH} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagdown \\ \text{N}:\text{C}:\text{CO}_2\text{H} \end{smallmatrix}$ , separates from water in shining, acicular crystals, m. p. 214° (decomp.); the *calcium* salt,  $(\text{C}_4\text{H}_4\text{O}_2\text{N}_3)_2\text{Ca}$ , was prepared.

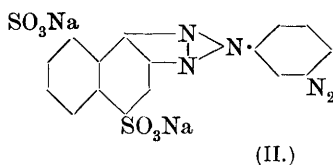
4-Cyano-3-methyl-1-ethylsotriazole,  $\text{NEt} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagdown \\ \text{N}:\text{C}:\text{CN} \end{smallmatrix}$ , is an oily, neutral liquid, b. p. 105°/28 mm. 3-Methyl-1-ethylsotriazole-4-carboxylic acid,  $\text{NEt} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagdown \\ \text{N}:\text{C}:\text{CO}_2\text{H} \end{smallmatrix}$ , crystallises from benzene in shining, white needles, m. p. 131°; its *calcium* salt,  $(\text{C}_6\text{H}_3\text{N}_3\text{O}_2)_2\text{Ca}$ , was prepared.

T. H. P.

[3' - Aminophenyl -  $\alpha\beta$  - naphthatriazole - 5 : 9 - sulphonic Acid.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D R.-P. 174548).—Sodium-3'-nitrophenyl -  $\alpha\beta$  - naphthatriazole - 5 : 9-sulphonate,



(I) was prepared by coupling *m*-nitrodiazobenzene chloride with  $\alpha$ -naphthylamine-3:8-disulphonic acid in sodium carbonate solution, and then, after 20 hours, warming the liquid to 70–75° and adding aqueous sodium hypochlorite. The



product was salted out and reduced with iron filings and water acidified with hydrochloric acid; the solution was rendered alkaline with sodium carbonate and 3-aminophenyl- $\alpha\beta$ -naphthatriazole-4:9-disulphonic acid (I) precipitated from the filtrate by adding hydrochloric acid and sodium chloride. The *azo*-derivative (II), obtained by coupling the aminotriazole with  $\beta$ -naphthol-3:6-disulphonic acid, when dissolved in water and treated with a solution of barium chloride and a paste of aluminium hydroxide, yields a brilliant reddish-lake which is remarkably stable to light.

G. T. M.

**The Mechanism of the Indamine and Azine Synthesis.** Willstätter's Paper on Aniline-Black. HANS TH. BUCHERER (*Ber.*, 1907, 40, 3412–3419. Compare this vol., i, 641).—The syntheses of indamines, azines, thiazines, and oxazines are represented by a single scheme, based on the two following facts. (1) The readiness with which *o*- and *p*-diamines, -aminophenols, dihydroxy-derivatives, and the corresponding sulphur compounds are oxidised. (2) The readiness with which monoimines, di-imines, quinols, and the corresponding sulphur compounds form additive compounds. In addition, attention is drawn to the readiness with which groups attached to nitrogen, oxygen, or sulphur wander into the nucleus. The two reactions, which occur alternately in the case of a *p*-diamine, may be represented as (a) *p*-diamine + O  $\rightarrow$  *p*-di-imide and (b) *p*-di-imide + HX  $\rightarrow$  *p*-diamine with the X group attached to nitrogen.

Several examples are worked out in detail, more especially the formation of safranin, methylene-blue, and Meldola's blue. Also the formation of 2:2'-diaminoazobenzene from *o*-quinonedi-imine and of di-aminoazodiphenyl from the oxidation product of benzidine.

Willstätter's formula for aniline-black is criticised.

J. J. S.

**Action of Hydroxylamine on Safranones.** OTTO FISCHER and FRITZ RÖMER (*Ber.*, 1907, 40, 3406–3411. Compare Fischer and Arntz, this vol., i, 94; Kehrmann and Prager, *ibid.*, 447).—Kehrmann and Prager's view of the constitution of the aminoisorosindone, obtained by the action of hydroxylamine on isorosindone, is confirmed, since the ethers obtained by the action of alkyl iodides and potassium hydroxide on the corresponding hydroxyisorosindone are not identical with the ethers of naphthasafranin. The ortho-position of the methoxy-

group in the methyl ether has been established by the synthesis of the ether from nitrosoguaiacol and  $\beta$ -phenylnaphthylamine.

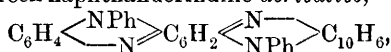
It appears that only those safranones yield amino-derivatives with hydroxylamine which are free from substituents in the two ortho-positions with respect to the quinone oxygen. Thus rosindone, *o*-methoxyisorosindone, and  $\beta$ -*o*-methylisorosindone (Abstr., 1901, i, 417) do not yield amino-derivatives.

Safranol does not yield an amino-derivative with hydroxylamine, but safranol ethyl ether yields *o*-aminosafranol ethyl ether,  $C_{20}H_{17}O_2N_3$ , which crystallises from alcohol in brilliant brown plates, m. p. about  $250^\circ$ . The addition of concentrated hydrochloric acid to the alcoholic or acetic acid solution produces a yellowish-green coloration. The corresponding methyl ether is less soluble in alcohol.

*o*-Anilinoisorosindone,  $C_{28}H_{19}ON_3$ , obtained by heating *o*-aminoisorosindone with aniline and aniline hydrochloride at  $150^\circ$ , crystallises from alcohol in bronze-coloured needles, m. p.  $282-284^\circ$ .

A naphthafluorindine,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6H_2 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NPh} \end{smallmatrix} C_{10}H_6$ , is obtained when *o*-aminoisorosindone, *o*-phenylenediamine, and its hydrochloride are heated with ethyl alcohol at  $140-150^\circ$  for three hours; it crystallises from pyridine in golden-bronze, glistening plates, which dissolve in glacial acetic acid yielding a pure blue solution. The same product is formed when isorosindone is used instead of its amino-derivative, and even more readily from isorosinduline salts and *o*-phenylenediamine (compare Fischer and Hepp, Abstr., 1896, i, 323).

*o*-Aminoisorosindone, or isorosindone, when heated with *o*-amino-diphenylamine, its hydrochloride, and absolute alcohol at  $150^\circ$  for four hours, yields a green naphthafluorindine derivative,



which crystallises from dimethylaniline in prisms.

Aminoisorosindone, or isorosinduline, and *o*-naphthylenediamine also yield a green dye. These naphthafluorindine dyes exhibit but little fluorescence except in concentrated sulphuric acid or pyridine solutions (compare Nietzki and Vollenbruck, Abstr., 1904, i, 1062). J. J. S.

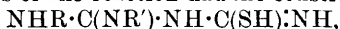
**Disulphides with Neighbouring Double Linkings. Action of Amines and Hydrazines on Thiourets. New Synthesis of Triazoles. II.** EMIL FROMM & EMIL VETTER (*Annalen*, 1907, 356, 178—196. Compare Fromm, Abstr., 1906, i, 656; Fromm and Schneider, *ibid.*, 656, 714; Hantzsch and Wolvekamp, Abstr., 1904, i, 719).—Perthiocyanic acid and thiouret undergo analogous reactions with potassium hydroxide, yielding sulphur and potassium cyanoaminodithiocarbonate and phenyliminocycanoaminodithiocarbonate respectively. The present work was undertaken to determine if thiouret reacts with aniline and phenylhydrazine in a manner analogous to the reaction of perthiocyanic acid with these reagents, which leads to the formation of phenyldithiobiuret and derivatives of triazole respectively.

When heated with aniline on the water-bath in absence of a solvent, phenylthiouret hydrochloride yields thiocarbamilide, but if the reaction



is moderated by dilution of the mixture with alcohol, sulphur and *phenylguanidophenylthiocarbamide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NPh})\cdot\text{NH}_2$ , are formed. This crystallises in white leaflets, m. p.  $197^\circ$ , forms a crystalline *hydrochloride*,  $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}\cdot\text{HCl}$ , m. p.  $179^\circ$ , and on treatment with benzyl chloride and alcoholic sodium hydroxide yields the *benzyl derivative*,  $\text{C}_{21}\text{H}_{20}\text{N}_4\text{S}$ , m. p.  $157^\circ$ .

The constitution of the products of the action of amines on thiouret hydrochlorides is confirmed by the formation of isomeric substances from phenylthiouret hydrochloride and *p*-phenetidine, on the one hand, and from *p*-phenetylthiouret hydrochloride and aniline, on the other, since if the products of the reaction had the constitution



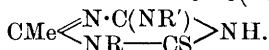
these two combinations would yield the same substance.

*p*-*Phenetylguanidophenylthiocarbamide*,  $\text{C}_{16}\text{H}_{18}\text{ON}_4\text{S}$ , formed from phenylthiouret hydrochloride and *p*-phenetidine, crystallises in leaflets, m. p.  $168^\circ$ , and forms a *benzyl derivative*,  $\text{C}_{23}\text{H}_{24}\text{ON}_4\text{S}$ , m. p.  $230^\circ$ .

The action of *p*-phenetidine on perthiocyanic acid leads to the formation of *p*-phenetyldithiobiuret,  $\text{C}_{10}\text{H}_{13}\text{ON}_3\text{S}_2$ , crystallising in leaflets, m. p.  $178^\circ$ , and *di-p*-phenetylthiocarbamide,  $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2\text{S}$ , crystallising in leaflets, m. p.  $170^\circ$ .

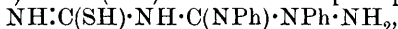
*p*-*Phenetylthiouret hydrochloride*,  $\text{C}_{10}\text{H}_{11}\text{ON}_3\text{S}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , m. p.  $137^\circ$ , reacts with aniline, forming *phenylguanido-p*-phenetylthiocarbamide, m. p.  $170^\circ$ . This yields a *benzyl derivative*,  $\text{C}_{23}\text{H}_{24}\text{ON}_4\text{S}$ , crystallising in leaflets, m. p.  $166^\circ$ .

The arylguanidoarylthiocarbamides form acetyl derivatives,  $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NR}')\cdot\text{NHAc}$ , which are converted by the action of alkalis into anhydro-compounds:  $\text{CMe}\langle\begin{smallmatrix} \text{N}\cdot\text{C}(\text{NR}') \\ \text{S}-\text{C}(\text{NR}) \end{smallmatrix}\rangle\text{NH}$  or

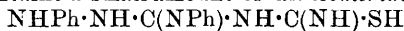


*Acetylphenylguanidophenylthiocarbamide*, R and R' = Ph, m. p.  $240^\circ$ ; the *anhydro*-compound, needles, m. p.  $200^\circ$ ; when heated with benzyl chloride and potassium hydroxide, it forms the benzyl derivative of phenylguanidophenylthiocarbamide. *Acetyl-p*-phenetylguanidophenylthiocarbamide, m. p.  $183^\circ$ ; the *anhydro*-compound, m. p.  $204^\circ$ . *Acetylphenylguanido-p*-phenetylthiocarbamide, needles, m. p.  $172^\circ$ ; the *anhydro*-compound, m. p.  $187^\circ$ .

When heated with phenylhydrazine in alcoholic solution, phenylthiouret hydrochloride forms sulphur and *anilguanidophenylthiocarbamide*,  $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NHPh}$  or perhaps



which separates from alcohol in crystals, m. p.  $167^\circ$ , and if heated with alcoholic sodium hydroxide or dilute hydrochloric acid yields 3-amino-5-anilino-1-phenyltriazole or its hydrochloride (Fromm and Göncz, this vol., i, 872). The filtrate from the preparation of anilguanidophenylthiocarbamide contains a small amount of an *isomeride*,



or  $\text{NH}_2\cdot\text{NPh}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NPh})\cdot\text{SH}$ , which on successive treatment with sodium hydroxide and hydrochloric acid yields 5-amino-3-anilino-1-phenyltriazole hydrochloride (Fromm and Göncz, *loc. cit.*).

*Anilguanido-p*-phenetylthiocarbamide,  $\text{C}_{16}\text{H}_{19}\text{ON}_3\text{S}$ , m. p.  $168^\circ$

(decomp.), when boiled with sodium hydroxide in alcoholic solution, yields 3-amino-5-p-phenetidino-1-phenyltriazole,  $C_{16}H_{17}ON_5$ , m. p.  $134^\circ$ ; the hydrochloride of this,  $C_{16}H_{17}ON_5 \cdot HCl$ , crystallises in thin leaflets, m. p.  $66^\circ$ . The acetyl derivative,  $C_{20}H_{23}O_3N_5 \cdot H_2O$ , crystallises in needles, m. p.  $145-148^\circ$ .

Aminophenylguanido-p-phenetylthiocarbamide,  $C_{16}H_{19}ON_5S$ , obtained from the mother-liquor from the preparation of its isomeride, crystallises in white leaflets, m. p.  $236^\circ$ , and when treated successively with sodium hydroxide and hydrochloric acid yields 5-amino-3-p-phenetidino-1-phenyltriazole hydrochloride, m. p.  $175^\circ$ , which is sparingly soluble. The free triazole forms a gelatinous mass and is readily soluble in alcohol.

G. Y.

*iso*Purone. JULIUS TAFEL and PERCY ALFRED HOUSEMAN (*Ber.*, 1907, 40, 3743—3751. Compare Tafel, *Abstr.*, 1901, i, 236).—The products obtained by the electrolytic reduction of uric acid are treated with concentrated ammonium hydroxide to separate the tetrahydrouric acid, with sodium hydroxide to remove *isopurone*, and the residue yields purone by crystallisation from hot water. *iso*Purone is an unsaturated substance which can be estimated by iodine and thiosulphate. The molecular weights of purone and of *isopurone* determined in aqueous solution by the ebullioscopic method correspond with the formula  $C_5H_8O_2N_4$ .

*iso*Tetrahydrouric acid,  $C_5H_8O_3N_4$ , prepared by the action of bromine on an aqueous solution of *isopurone* at  $0^\circ$ , crystallises in colourless needles, decomposes at  $200^\circ$ , has a neutral reaction, and dissolves readily in alkalis. A boiling solution of barium hydroxide converts it into the yellow barium salt of  $\alpha$ -isouracil,  $C_4H_6O_4N_2Ba$ , from which careful treatment with 2*N*-hydrochloric acid at  $-10^\circ$  liberates  $\alpha$ -isouracil,  $C_4H_4O_2N_2$ . This substance crystallises in needles, decomposes at  $350^\circ$ , has an acid reaction, dissolves in dilute alkalis, decolorises bromine water, and gives a violet-brown coloration with ferric chloride.

The mother-liquor from which the barium salt of  $\alpha$ -isouracil has been precipitated contains  $\beta$ -isouracil,  $C_4H_4O_2N_2$ , which crystallises in slender needles, has a neutral reaction, dissolves in dilute alkalis, and forms a crystalline substance with phenylhydrazine which seems to be a hydrazone.

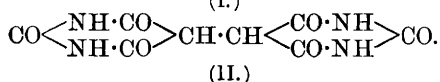
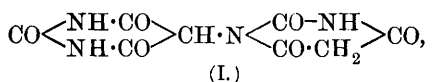
C. S.

**Reduction of Theophylline and Paraxanthine.** JULIUS TAFEL and JULIUS DORT (*Ber.*, 1907, 40, 3752—3757. Compare *Abstr.*, 1900, i, 121).—The electrolytic reduction of theophylline in 30% sulphuric acid at the ordinary temperature, with prepared lead cathodes and a current density of 12 amperes per sq. dcm., results in the formation of deoxytheophylline,  $C_7H_{10}ON_4$ , which separates from hot water in crystals containing  $3H_2O$ , darkens at  $200^\circ$  and has m. p.  $215-225^\circ$ , has a faintly alkaline reaction, and is soluble in dilute acids or alkalis; the hydrochloride and the picrate are mentioned. By the action of bromine in cold glacial acetic acid, the substance yields bromodeoxytheophylline,  $C_7H_9ON_4Br$ , which is converted by sodium hydroxide into 6-hydroxydeoxytheophylline,  $C_7H_{10}O_2N_4 \cdot 2H_2O$ .

Analogous compounds are obtained from paraxanthine by similar treatment. *Deoxyparaxanthine*,  $C_7H_{10}ON_4$ , crystallises from water with  $\cdot 1H_2O$ , decomposes at  $250^\circ$ , has a neutral reaction, and is not more soluble in dilute alkalis than in water. *Bromodeoxyparaxanthine*,  $C_7H_9ON_4Br$ , dissolves in water to a strongly acid solution, and is converted by sodium hydroxide into 6-hydroxydeoxyparaxanthine,  $C_7H_{10}O_2N_4 \cdot 2H_2O$ , which darkens at  $230^\circ$ . C. S.

**Acidity of Deoxyxanthines.** JULIUS TAFEL and JULIUS DODT (*Ber.*, 1907, 40, 3757—3759. Compare preceding abstract).—It has been shown that deoxyxanthine, 3-methyldeoxyxanthine, and deoxytheophylline, unlike deoxyheteroxanthine, deoxyparaxanthine, and deoxytheobromine, are more soluble in dilute alkalis than in water. The authors have measured the strengths of these compounds by Wood's method (*Trans.*, 1906, 89, 1839) and arrive at the conclusions that the deoxyxanthines are weaker acids than the xanthines, and that in the deoxyxanthines the acid properties are conferred solely by the glyoxaline ring. C. S.

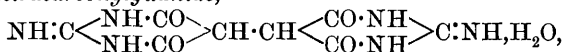
**Hydurilic Acid.** MAX CONRAD (*Annalen*, 1907, 356, 24—31).—Two constitutions have been ascribed to hydurilic acid (I and II).



The author shows that the constitution II is the correct one. Since barbituric acid when heated with concentrated hydrochloric acid is hydrolysed forming carbon dioxide, ammonia, and acetic acid, an acid of the constitution II must under the same conditions yield carbon dioxide, ammonia, and succinic acid. It is found that when heated with concentrated hydrochloric acid at  $200$ — $230^\circ$ , hydurilic acid yields succinic acid in almost quantitative amount.

The constitution II is supported also by the formation of hydurilic acid by condensation of ethyl ethanetetra-carboxylate with carbamide by means of alcoholic sodium ethoxide at  $60$ — $70^\circ$ , and together with small amounts of succinic acid by hydrolysis of ethanetetra-carbonyl-guanide by means of dilute hydrochloric acid at  $150^\circ$ .

*Ethanetetra-carbonyl-guanide*,

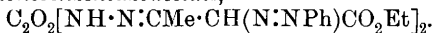


is prepared in a 63% yield by heating ethyl ethanetetra-carboxylate with guanidine hydrochloride and sodium ethoxide in alcoholic solution at  $70^\circ$ ; it crystallises in needles, decomp. when heated, is readily soluble in alkali hydroxides or carbonates, separates in prisms on prolonged heating of its ammoniacal solution, and dissolves in cold nitric acid. The silver salt,  $C_8H_6O_4N_6Ag_2 \cdot \frac{1}{2}H_2O$ , was analysed; the hydrochloride crystallises in white needles. Ammonium hydurilate gives a green coloration with ferric chloride, becoming colourless on addition of hydrochloric acid or on heating, and forms a red solution with potassium nitrite in acetic acid. G. Y.

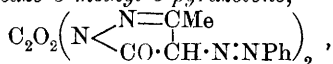
**Azo-derivatives of Esters of Bis- $\beta$ -ketonic Acid Oxalyldihydrazones.** CARL BÜLOW [and, in part, MARTIN LOBECK] (*Ber.*, 1907, 40, 3787—3798).—The two methylene groups in ethyl oxalylbishydrazoneacetoacetate (Bülow and Lobeck, this vol., i, 301) are capable of reacting, like the methylene group in compounds of the type  $\text{COR}''\cdot\text{NH}\cdot\text{N}\cdot\text{CR}'\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$ , with diazobenzene chloride with the formation of *o*-azoacylhydrazones. These azo-derivatives are, generally speaking, far more stable than the parent substances.

*Ethyl oxalyldihydrazone-benzeneazobisacetoacetate,*

$\text{CO}_2\text{Et}\cdot\text{CH}(\text{N}\cdot\text{NPh})\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained by the action of diazobenzene chloride on ethyl oxalylbishydrazoneacetoacetate in alcoholic solution in the presence of sodium acetate at low temperatures, crystallises in yellow, felted needles, m. p.  $155^\circ$  (unsharp); at the same time, is formed a small quantity of *ethyl oxalylbishydrazonebenzeneazoacetate*,



The latter compound alone is produced by using very dilute solutions, but is better prepared by the interaction of oxalyldihydrazide and ethyl benzeneazoacetoacetate in alcoholic or acetic acid solution. It forms colourless crystals, swells and froths up at  $211$ — $212^\circ$  or  $217$ — $218^\circ$ , and decomposes slightly above this temperature into alcohol and 1:1-oxalylbis-4-benzeneazo-3-methyl-5-pyrazolone,



obtained as a yellowish-red, crystalline powder, m. p.  $256$ — $257^\circ$ . This compound is decomposed by hot potassium hydroxide solution or pyridine into oxalic acid and 4-benzeneazo-3-methyl-5-pyrazolone (compare von Rothenburg, *Abstr.*, 1895, i, 686).

Ethyl oxalylbishydrazonebenzeneazoacetoacetate is decomposed on boiling with phenylhydrazine in acetic acid solution with the formation of alcohol, oxalyldihydrazide, and 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone.

The author replies to the criticisms of Curtius, Darapsky, and Müller (this vol., i, 451). W. H. G.

**Action of Diazobenzene Chloride on *p*-Hydroxybenzoic Acid.** EUGEN GRANDMOUGIN and H. FREIMANN (*Ber.*, 1907, 40, 3453—3454. Compare Limpricht, *Abstr.*, 1891, 1036).—Diazobenzene chloride reacts with a solution of *p*-hydroxybenzoic acid in the presence of sodium carbonate, yielding bisbenzeneazophenol together with a small amount of benzeneazo-*p*-hydroxybenzoic acid (Auwers and Röhrig, *Abstr.*, 1897, i, 341). In the presence of sodium hydroxide, the chief product is trisbenzeneazophenol (this vol., i, 664).

J. J. S.

**Preparation of 1-Diazo- $\beta$ -naphtholdi- and tri-sulphonic Acids.** KALLE & Co. (D.R.-P. 184477).—The 1-amino- $\beta$ -naphthol-monosulphonic acids are diazotised normally with sodium nitrite in the presence of organic acids (*Abstr.*, 1905, i, 161); the corresponding di- and tri-sulphonic acids are readily converted into diazo-derivatives in the presence of sulphuric acid, provided that dilute solutions are

employed at 0° to 5°. The diazo-derivatives may be partially salted out from the yellowish-brown solution in the form of a brown mass.

G. T. M.

[The Diazotisation of 1-Amino- $\beta$ -naphtholsulphonic Acids.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 181714).—The interaction of nitrous acid and the 1-amino- $\beta$ -naphtholsulphonic acids leads to the production of quinonoid substances, so that the reaction is largely one of oxidation. If, however, the sodium salts of these 1-amino- $\beta$ -naphtholsulphonic acids are acetylated in the hydroxyl group with acetic anhydride, then the acetyl derivatives thus obtained furnish yellow, crystalline diazo-compounds, such as 2-acetoxy-1-diazonaphthalene-4-sulphonic acid, which, on treatment with dilute aqueous alkalis, lose their acetyl group and give rise to the corresponding 2-hydroxy-1-diazonaphthalenesulphonic acids. This elimination of acetyl may be effected similarly after combining the 2-acetoxy-1-diazonaphthalenesulphonic acid with phenol and aromatic amines, and in this way 2-hydroxyazonaphthalene colouring matters are produced which may be employed as mordant dyes. G. T. M.

**Bisazo-derivatives of Salicylic Acid.** EUGEN GRANDMOUGIN, J. R. GUIBAN, and H. FREIMANN (*Ber.*, 1907, 40, 3450—3453. Compare Limpricht, *Abstr.*, 1891, 1036).—A mixture of bisbenzeneazosalicylic acid, benzeneazosalicylic acid, and the trisazo-derivative of phenol (this vol., i, 664) is formed when a solution of diazobenzene chloride and salicylic acid dissolved in sodium hydroxide is kept at 0° for some five days. The monoazo-compound remains dissolved in the alkaline solution, and may be precipitated by the addition of acid. The *bisbenzeneazosalicylic acid*,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{N}_2\text{Ph})_2\cdot\text{CO}_2\text{H}$ , may be extracted with hot dilute sodium hydroxide solution, and crystallises from chloroform in reddish-brown, felted needles, m. p. 218°. With sulphuric acid, it gives the colorations characteristic of bisazo-compounds, and when reduced with stannous chloride yields 3:5-diaminosalicylic acid.

The *acetyl* derivative of the bisazo-compound has m. p. 196°. *Bis-o-tolueneazosalicylic acid*,  $\text{C}_{21}\text{H}_{18}\text{O}_3\text{N}_4$ , forms dark violet crystals with a metallic lustre, m. p. 170°, and yields an *acetyl* derivative, m. p. 173°. *o-Tolueneazosalicylic acid*,  $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$ , forms yellowish-brown needles, m. p. 191°, and yields an *acetyl* derivative, m. p. 145°.

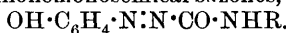
*Tris-o-tolueneazophenol*,  $\text{C}_{27}\text{H}_{22}\text{ON}_6$ , forms bronze-coloured needles, m. p. 198°, and its *acetyl* derivative orange-coloured needles, m. p. 195°. Diazotised nitroanilines yield monoazo-derivatives together with bisazo-derivatives of phenol.

*Bis-p-nitrobenzeneazophenol*,  $\text{C}_{18}\text{H}_{12}\text{O}_5\text{N}_6$ , crystallises from nitrobenzene or tetrachloroethane in brown, felted needles, and its *acetyl* derivative has m. p. 208°.

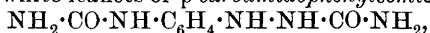
J. J. S.

**Aromatic - aliphatic - *p* - aminoazo - compounds.** WALTHER BORSCHÉ and A. RECLAIRE (*Ber.*, 1907, 40, 3806—3815).—The

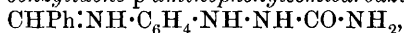
condensation products of quinoneoximes and semicarbazides (compare Borsche, Abstr., 1906, i, 319) are converted on reduction with tin and hydrochloric acid and subsequent oxidation, into aromatic-aliphatic-*p*-aminoazo-compounds of the type  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NHR}$ , corresponding with the quinonemonosemicarbazones,



The reduction of either *p*-nitrophenylsemicarbazide (Hyde, Abstr., 1899, i, 688) or benzoquinone oximesemicarbazone (Thiele and Barlow, Abstr., 1899, i, 47) with tin and hydrochloric acid results in the formation of *p*-aminophenylsemicarbazide (*p*-aminobenzenehydrazoformamide) hydrochloride, colourless leaflets, decomposing at 195–196°; ammonia liberates the free base,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , as small, colourless needles, which rapidly oxidise in the air. A solution of the hydrochloride on treatment with potassium cyanate and sodium acetate deposits pearly, white leaflets of *p*-carbamidophenylsemicarbazide,



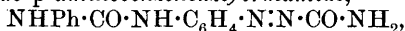
m. p. 201–202° (decomp.). Benzaldehyde reacts with the base with the formation of benzylidene-*p*-aminophenylsemicarbazide,



yellowish-white leaflets, m. p. 204° (decomp.).

*p*-Aminobenzeneazofornamide, obtained only in the form of a hydrate,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$ , is prepared by the oxidation of the hydrazo-compound; it crystallises in dark red needles with a blue reflex, m. p. 125–126° (decomp.). The molecule of water is not removed by keeping the compound some days in a vacuum desiccator. It is converted by strong hydrochloric acid into a greenish-yellow hydrochloride, and is decomposed on heating with potassium hydroxide solution according to the equation:  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CO} \cdot \text{NH}_2 + 2\text{KOH} = \text{NH}_2\text{Ph} + \text{N}_2 + \text{NH}_3 + \text{K}_2\text{CO}_3$ ; at the same time, a small quantity of a substance is formed, which crystallises in brown needles. *p*-Carbamidobenzeneazofornamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$ , prepared by acting on a solution of the hydrazo-compound with ammonia and hydrogen peroxide, crystallises in small, brick-red needles, m. p. 178° (decomp.).

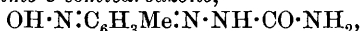
*Phenylcarbamido-p*-aminobenzeneazofornamide,



which results from the interaction of phenylcarbimide and the azo-compound, crystallises in yellowish-red needles, decomposing at 202°.

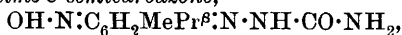
*Benzoyl-p*-aminobenzeneazofornamide,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NH}_2$ , forms small, orange needles, m. p. 218° (decomp.). Bromine acts on the parent azo-compound yielding 3:5(?)-dibromo-4-aminobenzeneazofornamide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{N}_2 \cdot \text{CO} \cdot \text{NH}_2$ , small, yellow needles, m. p. 183°.

*2-Toluquinoneoxime-5-semicarbazone*,



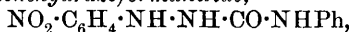
prepared by the interaction of 2-toluquinoneoxime and semicarbazide hydrochloride, is a brown, crystalline powder, decomposing at 220°. It yields, on reduction with tin and hydrochloric acid and subsequent oxidation of the hydrazo-compound, 2-aminotoluene-5-azofornamide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$ , small, reddish-brown needles, m. p. 85–86° (decomp.). In the same way, are obtained 3-toluquinone-

*oxime-6-semicarbazone*, small, brown needles, decomposing at  $243^{\circ}$ , and *2-thymoquinoneoxime-5-semicarbazone*,

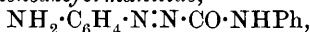


small, yellow needles, m. p.  $221-222^{\circ}$ , which also give rise to amino-azo-compounds.

Phenylcarbimide combines with the three nitrophenylhydrazines, forming *o-nitrobenzenehydrazoformanilide*,



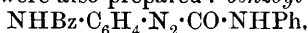
small, slender, yellow needles, m. p.  $220^{\circ}$ ; *m-nitrobenzenehydrazoformanilide*, yellow leaflets, m. p.  $220^{\circ}$ , and *p-nitrobenzenehydrazoformanilide*, small, yellowish-white needles, m. p.  $220^{\circ}$ . Both the latter compound and benzoquinoneoximephenylsemicarbazone (Borsche and Kühl, Abstr., 1906, i, 320) yield on reduction with tin and hydrochloric acid *p-aminobenzenehydrazoformanilide hydrochloride*, small, colourless, slender needles, which decompose and turn violet above  $190^{\circ}$ ; sodium carbonate liberates the free base,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , long, colourless needles, m. p.  $187^{\circ}$  (decomp.), which is converted on oxidation into *p-aminobenzenediazoformanilide*,



large, blood-red leaflets, m. p.  $160-161^{\circ}$  (decomp.). The salts of the latter compound with acids are stable only in the presence of the free acid; *hydrochloride*, small, orange-yellow needles; *oxalate*,



dark brown, crystalline powder, decomposing at  $186-187^{\circ}$ . The following compounds were also prepared: *benzoyl* derivative,



small, yellow needles, m. p.  $219-220^{\circ}$ ; *phenylcarbamido-derivative*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CO}\cdot\text{NHPh}$ , reddish-yellow needles, decomposing at  $210^{\circ}$ ; *dibromo-derivative*,  $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{N}_2\cdot\text{CO}\cdot\text{NHPh}$ , small, yellow needles, m. p.  $155-156^{\circ}$ .

By the same methods as described above are obtained: *2-aminotoluene-5-azoformanilide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$ , reddish-brown, leafy crystals, decomposing at  $150-151^{\circ}$ , and *3-aminotoluene-6-azoformanilide*, dark red needles with green reflex, m. p.  $137^{\circ}$ .

W. H. G.

**Action of Dilute Sulphuric Acid on Proteins.** LEO LANGSTEIN (*Biochem. Zeitsch.*, 1907, 5, 410-412).—Recent authors have stated that the digestion of protein with 0.5% hydrochloric acid leads to the formation of the same end products as are found in gastric digestion, but more slowly. The present experiments confirm earlier views of the author that protein is very resistant to dilute sulphuric acid. After eight months' digestion in 1% acid at  $37^{\circ}$ , only 18% of dried egg-albumin goes into solution; rather more of the other proteins investigated (serum-albumin, &c.) were dissolved. The dissolved nitrogenous substances were completely precipitable by phosphotungstic acid.

W. D. H.

**Influence of Solutions of Pigments on the Heat Coagulation of Proteins.** HANS ARON (*Biochem. Zeitsch.*, 1907, 5, 413-418).—Acid pigments (eosin and aurantia) or their free acids,

when added to protein solutions (dilute serum), destroy the heat-coagulability of the latter. The explanation advanced is that complex colloid is formed, in which the pigment acts towards the protein as a "protective colloid."

W. D. H.

**Dissociation of Serum-Globulin at Varying Hydrogen Ion Concentrations.** T. BRAILSFORD ROBERTSON (*J. Physical-Chem.*, 1907, 11, 437—460. Compare Abstr., 1906, ii, 828; Hardy, Abstr., 1906, i, 121).—Equations are deduced by means of which an expression containing the ratio of the acid and basic constants,  $k_a$  and  $k_b$ , of such an amphoteric electrolyte as serum-globulin can be calculated from two experimental observations. The hydrogen ion concentrations of globulin solutions containing varying proportions of acid were measured by means of concentration cells and the conductivities of globulin solutions to which varying proportions of acid had been added were also measured; from these data, by an indirect method, the value  $68.3 \times 10^{-8}$  was obtained for the expression  $Kk_a/k_b$ , where  $K$  is the dissociation constant for water. By another and probably less accurate method, the value  $265 \times 10^{-8}$  was obtained for the same expression. For the velocity of the serum-globulin ion, the value  $7 \times 10^{-5}$  cm./sec. under a potential gradient of 1 volt/cm. was deduced, whilst Hardy (*loc. cit.*) by a direct method obtained  $10 \times 10^{-5}$  cm./sec.

Serum-globulin is a fairly strong acid, but its basic properties are so slight that it behaves to alkalis as a non-amphoteric acid.

Some evidence has been obtained that solutions of proteins contain more or less complex polymerides of the type  $HXOH$ , and that the equilibrium is displaced by the addition of acids, salts, &c. In the case of serum-globulin, therefore, there is no definite molecular concentration in acid solution, but in alkaline solution, owing to its slightly basic character, the degree of polymerisation and therefore the molecular weight is constant. The molecular weight of serum-globulin in alkaline solution is given as 1967, and the average molecular weight in acid solution as 1684, but the latter value is very uncertain.

G. S.

**Formation of Polypeptides by the Hydrolysis of Proteins.** EMIL FISCHER and EMIL ALDERHALDEN (*Ber.*, 1907, 40, 3544—2562). In part already published (this vol., i, 737. Compare also 1906, i, 718).—When treated with 70% sulphuric acid at  $36^\circ$ , gliadin gives rise to *L*-leucyl-*D*-glutamic acid,  $[\alpha]_D^{20} + 10.2$ , m. p.  $232^\circ$  (corr.), identical with the synthetical product. Levene's claim to have first isolated a dipeptide from the decomposition products of proteins is shown to be inaccurate.

E. F. A.

**Hydrolysis of Glycinin, the Globulin of the Soy Bean, and of the Crystalline Globulin of the Squash Seed (*Cucurbita maxima*).** THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, 19, 468—474, 475—481).—Acid hydrolysis led to the following percentage results calculated on a moisture and ash-free basis for the two proteins mentioned:



	Soy bean.	Squash seed.		Soy bean.	Squash seed.
Glycine.....	0.97	0.57	Serine.....	notisolated	notisolated
Alanine.....	notisolated	1.92	Tyrosine ...	1.86	3.07
Valine .....	0.68	0.26	Arginine....	5.12	14.44
Proline .....	3.78	2.82	Histidine ...	1.39	2.63
Phenylalanine	3.86	3.32	Lysine.....	2.71	1.99
Aspartic acid	3.89	3.30	Ammonia ...	2.56	1.55
Glutamic acid	19.46	12.35	Tryptophan	present	present
Leucine .....	8.45	7.32	Cystine .....	—	0.23

W. D. H.

**The Formation of Acetone from Acetoacetates by means of Organ-extracts and Proteins.** LEO POLLAK (*Beitr. chem. Physiol. Path.*, 1907, 10, 232—250).—By digestion of sodium acetoacetate with blood-serum or organ-extracts, there is a rapid decomposition of the salt, with the formation of carbon dioxide and acetone. The agent in the serum responsible for this is protein. Serum - globulin, crystalline serum-albumin, caseinogen, Witte's peptone, amino-acids (leucine, alanine, &c.) all have the same action. All these substances contain the amino-group.

W. D. H.

**Combining Power of Casein with Certain Acids.** JOHN H. LONG (*J. Amer. Chem. Soc.*, 1907, 29, 1334—1342).—In previous papers (Abstr., 1905, i, 498; 1906, i, 391), it has been shown that casein unites with alkalis to form salts. It has now been found that casein also combines with acids, and the behaviour of various acids has been investigated. At the ordinary temperature, 1 gram of dry casein unites with nearly 7 c.c. of *N*/10 hydrochloric, hydrobromic, hydriodic, sulphuric, and acetic acids. It also combines with tartaric, phosphoric, and oxalic acids, but not with boric acid. If the casein solution is evaporated in presence of dilute acid, a larger quantity of the latter, in the case of hydrochloric acid, four times as much, enters into combination. This is due, to some extent at least, to the partial hydrolysis of the casein and the union of the acid with the products of such hydrolysis.

E. G.

**Action of Dilute Acids on Casein when Soluble Compounds are not Formed.** LUCIUS L. VAN SLYKE and DONALD D. VAN SLYKE (*Amer. Chem. J.*, 1907, 38, 383—456).—In a previous paper (Abstr., 1905, i, 499), it has been shown that casein unites with acids to form insoluble products. A study has now been made of the behaviour of casein with hydrochloric, sulphuric, lactic, and acetic acids of concentrations from *N*/125 to *N*/2000, at temperatures of 0°, 25°, and 45°, and during periods varying from five minutes to forty-eight hours. The results indicate that the insoluble substances formed are not salts, but are produced by adsorption of the acid by the casein. The precipitate produced when milk turns sour is casein containing adsorbed lactic acid.

In carrying out the investigation, casein was shaken with dilute

acids of known strength, and, after filtration, the quantity of acid removed from the solution was calculated from the decrease in conductivity. Experiments were made to ascertain the conditions in which casein is soluble in dilute acids in order that such conditions might be avoided. It was found that the protein does not dissolve to an appreciable extent when left for several hours at  $0^{\circ}$  in contact with acids of concentration of  $N/1000$  or less, but that the solubility increases with the concentration, the temperature, and the time of contact. The rate at which casein dissolves in different acids of equivalent strength is not proportional to the concentration of the hydrogen ions or to the degree of dissociation, but is disproportionately great for the weak organic acids. From dilute acids of equal concentration, the dissolved protein takes up a larger proportion of acid than the undissolved. The solubility of casein in dilute acids is probably due to decomposition of the protein. Casein neither dissolves in  $N/125$  magnesium sulphate or  $N/50$  potassium chloride nor adsorbs either of these salts.

The amount of acid withdrawn by casein from dilute solutions in which it does not dissolve varies with the concentration of the acid, the duration of contact until equilibrium is reached, the degree of agitation until equilibrium is reached, the temperature, and the particular acid employed. The acid is never entirely removed from the solution.

Determinations have been made of the amount of each of the acids adsorbed by 1 gram of casein at the equilibrium point and of the rate at which equilibrium is produced under different conditions. The acid can be removed from the casein by shaking it with water.

E. G.

**Sulphohæmoglobin.** T. WOOD CLARKE and W. H. HARTLEY (*J. Physiol.*, 1907, 36, 62—67).—Sulphohæmoglobin is regarded as a definite compound in aqueous solution. It could not be obtained in crystalline form. The action of carbon monoxide on sulphohæmoglobin, or of hydrogen sulphide on carboxyhæmoglobin, is to form a new compound, carboxysulphohæmoglobin. Reduction of oxyhæmoglobin is a necessary preliminary for the formation of sulphohæmoglobin. Selenohæmoglobin closely resembles sulphohæmoglobin.

W. D. H.

**Hair Pigment, Choroid Pigment, and other Melanins.** EDUARD SPIEGLER (*Beitr. chem. Physiol. Path.*, 1907, 10, 253—264).—The pigment of melanotic livers is different from that of the hair, but both resemble the choroid pigment (from pigs' eyes) in not yielding hæmopyrrole, and so their origin from the blood is impossible. On decomposition of the pigments, acetone derivatives or condensation products of acetone residues are found; the differences between these products in the various pigments, accounts for the differences of the pigments. The parent substances of the pigments are tryptophan and acetone; possibly other aromatic groups of the protein molecule, such as phenylalanine and tyrosine, participate in their formation.

W. D. H.

**The Chemical Nature of the Fundamental Colouring Matter of Urine.** S. DOMBROWSKI (*Compt. rend.*, 1907, 145, 575—577).—The yellow urinary colouring matter, *urochrome*, has been prepared and examined. It may be separated from fresh urine which has been freed from most of its salts by the addition of cupric acetate in a cold faintly acid medium. The analytical data are: C, 43.09; H, 5.14; N, 11.15; S, 5.09; O, 35.53%. The free acid and its *calcium* and *silver* salts are soluble in water. It is readily decomposed by alkalis and reduces ferric salts or iodic acid. The acid contains a pyrrole group which reacts with diazo-salts in much the same manner as pyrrole itself, but quite differently from hemipyrrole.

The pyrrole group, when exposed to the air, in an acidified alcoholic solution, polymerises, and the product gives an absorption band identical with that observed in the spectrum of polymerised pyrrole. When heated with hydrochloric acid, urochrome is decomposed, yielding a *black pigment*: C, 59.16; H, 4.91; N, 9.69; S, 3.55; O, 22.69%.

The normal amount of urochrome eliminated by the human organism in twenty-four hours varies between 0.4 and 0.7 gram, but in cases of infectious diseases, such as typhoid fever, increases considerably.

J. J. S.

**Nucleic Acid from the Pancreas (Guanylic Acid).** OTTO VON FÜRTH and ERNST JERUSALEM (*Beitr. chem. Physiol. Path.*, 1907, 10, 174—187).—Bang states that guanylic acid, the nucleic acid obtained from the pancreas, differs from other nucleic acids, inasmuch as it yields a derivative of glycerol-phosphoric acid, yields one-third of its weight on hydrolysis in the form of a reducing sugar, and contains only one basic substance, guanine. All these assertions are now alleged to be incorrect, and there is no necessity to distinguish between guanylic and other nucleic acids of animal origin.

W. D. H.

**Gelatin Forms Produced by Precipitates of Salts and Crystals.** RAPHAEL E. LIESEGANG (*Chem. Zentr.*, 1907, ii, 415; from *Zeitsch. Chem. Ind. Kolloide*, 1, 364—367. Compare this vol., ii, 337).—The formation of a precipitate, or of crystals of salt or water, may induce gelatin to take certain forms or shapes which are retained after the cause has been removed. Experiments on the crystallisation of potassium dichromate have shown that, contrary to Molisch's theory (*Unters. über das Erfrieren der Pflanzen*, Jena, 1897), the gelatin accumulates at the places where the crystals form. Experiments on freezing gelatin films which had been dyed with methylene-blue proved, however, that both accumulation and dispersion of the gelatin may be caused by the formation of crystals even in the same preparation.

E. W. W.

**The Amounts of Cystin in Various Horny Materials.** HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1907, 52, 474—481. Compare Möerner, *Abstr.*, 1900, i, 128; 1902, i, 331).—The following percentages of cystine have been obtained from the materials mentioned: human hair, 13—14.5; human nails, 5.15; horse hair, 7.98; horses' hoofs, 3.20; ox hair, 7.27; hoofs of oxen, 5.37; pigs' bristles, 7.22; pigs' hoofs, 2.17.

J. J. S.

**Nitrochitins.** OTTO VON FÜRTH and EMIL SCHOLL (*Beitr. chem. Physiol. Path.*, 1907, 10, 188--198).—Chitin is attacked by warm or cold fuming nitric acid alone, or in the presence of sulphuric acid, yielding a mixture of nitrates corresponding in properties with the nitro-celluloses. The chitin dissolves in the acid, and the nitro-products are precipitated by pouring the solution into water. Two products are formed, one of which is insoluble in all the ordinary organic solvents, whereas the other dissolves readily in alcohol, acetone, ethyl acetate, and glacial acetic acid. They are true nitrates, as when hydrolysed with acids or alkalis they yield nitric acid.

Chitosan reacts with nitrous acid, yielding a product with reducing properties soluble in water, acids, and alkalis, but precipitated by alcohol.  
J. J. S.

**Diamino-acids from Koilin.** ERICH VON KNAFFL-LENZ (*Zeitsch. physiol. Chem.*, 1907, 52, 472—473).—The following diamino-acids have been obtained by hydrolysing koilin (compare this vol., i, 884) with sulphuric acid: histidine 0.034, arginine 3.596, lysine 1.640. The numbers are parts per 100 of air-dried and ash-free koilin.

J. J. S.

**A New Solvent for Some Proteins.** IWAN OSTROMYSSLENSKY (*J. pr. Chem.*, 1907, [ii], 76, 267—268).—As Fischer has shown that proteins are complicated amides, it was to be expected (this vol., ii, 847) that they would prove to be soluble in simple amides. It is found that the albumoses and peptones dissolve in formamide and fused acetamide. The latter dissolves over 30% of the peptone of egg-albumin, whereas the albumins, such as egg- and serum-albumins, do not dissolve in this solvent. The concentrated solutions in formamide are viscid at the ordinary temperature, gradually become reddish-brown, and can be filtered. The solubility in formamide may be used in the separation of proteins from each other and from inorganic material. The solutions in acetamide are suitable for use in cryoscopic investigations.  
G. Y.

**Hydrolysis of the Albumoses Occurring in Meat Extract.** KARL MICKO (*Zeitsch. Nahr. Genussm.*, 1907, 14, 253—298).—The experiments described were undertaken for the purpose of ascertaining the origin of the amino-acids obtained in the hydrolysis of meat extract (*Abstr.*, 1906, i, 778). The portion of meat extract precipitated by zinc or ammonium sulphate is not identical with either gelatin or gelatines, and unaltered gelatin cannot be detected in true meat extract itself. During the manufacture of meat extract, gelatin may pass into solution, but it is converted by the lactic acid present into gelatines or acid glutin. The greater part of the portion precipitated by ammonium sulphate consists of a mixture of proteins having the general properties of albumoses and showing no indications of having been derived from gelatin. A small proportion of these albumoses, however, gives reactions very similar to those obtained with gelatines, &c. Hydrolysis of the constituents of meat extract which are soluble in saturated ammonium sulphate solution yields monoamino-acids.

W. P. S.

**Coaguloses.** D. LAWROFF (*Zeitsch. physiol. Chem.*, 1907, 53, 1—7).—In the peptic digestion of proteins, as well as in their digestion by dilute mineral acids, at least two types of coagulose-yielding substances are recognisable. The first are of the type of proteoses, and the coaguloses which arise from them yield on hydrolysis monoamino-acids and basic nitrogenous cleavage products. The second type of coagulose-yielding substances are of the type of polypeptides, and the coaguloses which arise from them yield on hydrolysis only mono-amino-acids.

W. D. H.

**Racemic Tryptophan.** RUDOLF A. ALLERS (*Biochem. Zeitsch.*, 1907, 6, 272—275).—Racemic tryptophan, prepared according to Neuberg's method, and the synthetic preparation of Ellinger and Flamand (this vol., i, 737) both begin to melt at 256°. Optically active tryptophan is stated to melt at 273° by Hopkins and Cole and by Neuberg and Popowsky; at 289° by Abderhalden and Kempe. Racemisation is probably due to the ammonia added at 60° in the process of preparation (compare following abstract).

G. B.

**Tryptophan.** CARL NEUBERG (*Biochem. Zeitsch.*, 1907, 6, 276—282).—An iodine solution, when added to tryptophan dissolved in alkali hydroxide, produces a pale brown, amorphous precipitate having the composition of a mixture of mono- and di-iodotryptophan (compare Neuberg and Popowsky, this vol., i, 253; Nürnberg, this vol., i, 805).

Silver nitrate added to tryptophan dissolved in slightly less than 1 mol. of sodium hydroxide produces a silver salt,  $C_{11}H_{11}O_2N_2Ag$ .

Tryptophan is racemised by concentrated hydrochloric acid at 170°, and then melts at 254—255°. An optically inactive specimen was also obtained by Neuberg's method of preparation, which involves boiling with lead carbonate and ammonia (compare preceding abstract).

G. B.

**The Non-existence of Protagon as a Definite Chemical Compound.** OTTO ROSENHEIM and M. CHRISTINE TEBB (*J. Physiol.*, 1907, 36, 1—16).—Liebreich's, Gamgee and Blankenhorn's, and Cramer's protagons represent the same substance as *cérébrote* prepared by Couerbe in 1834. A similar substance is obtained by extracting brain with boiling acetone after the cholesterol has been removed by cold acetone. All these substances may be split into substances of widely varying phosphorus and nitrogen percentage by simple fractional crystallisation at different temperatures, or with different solvents. They also show great difference in optical activity and in the amount of galactose split off by acid hydrolysis. The base sphingosine as well as choline is found amongst the products of protagon hydrolysis. Protagon is not a definite chemical compound, but a mixture of substances, some of which (such as phrenosin) are phosphorus-free and others (such as sphingomyelin) rich in phosphorus.

W. D. H.

**Protagon.** WILLIAM J. GIES (*J. Biol. Chem.*, 1907, 3, 339—358).—The non-identity of protagon as a chemical individual is maintained,

and Cramer's attempt to rehabilitate it (see preceding abstract) is shown to rest on obviously fallacious reasoning. W. D. H.

**Effect of Colouring Matters on some of the Digestive Enzymes.** H. W. HOUGHTON (*J. Amer. Chem. Soc.*, 1907, 29, 1351—1357).—A study of the effect of various colouring matters on the activity of pepsin has led to the following conclusions. Annatto does not affect the activity of the enzyme towards fibrin, but when present in certain proportions diminishes the activity towards egg-albumin and casein. Saffron lessens the activity towards fibrin, casein, and egg-albumin when it is used in the proportion of 1 : 400, but smaller quantities have no effect. Turmeric reduces the activity towards casein and egg-albumin, but, when present in as small a proportion as 1 : 800, does not affect the digestion of fibrin. Cochineal and Bismarck-brown, when used in a smaller proportion than 1 : 400, do not decrease the activity of the enzyme towards fibrin, but a proportion of 1 : 1600 lessens the activity towards egg-albumin. Crocein-scarlet 1B (1 : 1600) inhibits entirely the action of the enzyme on fibrin, and, when present in the proportion of 1 : 200, it diminishes the activity towards casein and egg-albumin.

Annatto and oil-yellow are found to assist the hydrolysis of butter-fat by lipase, and it is therefore assumed that these colouring matters contain some lipolytically active substance. E. G.

**Behaviour of Hippuric Acid to Erepsin.** OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1907, 52, 526. Compare Abstr., 1906, ii, 294).—Hippuric acid dissolved in sodium hydrogen carbonate solution is not hydrolysed by erepsin. J. J. S.

**Action of the Proteolytic Ferment of *Bacillus pyocyaneus*.** EMIL ZAK (*Beitr. chem. Physiol. Path.*, 1907, 10, 287—298).—The ferment not only cleaves proteoses into simpler products, but evidence is adduced that it also has a synthetic action both in bouillon cultures and in the filtrate freed from organisms. Taylor (this vol., i, 665) has described previously a reversible action in the case of trypsin. W. D. H.

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## Organic Chemistry.

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**Synthetical Production of Optically Active Petroleum from Glycerides.** JULIUS LEWKOWITSCH [and HANS PICK] (*Ber.*, 1907, 40, 4161—4162).—Distillation of chaulmoogra oil with zinc dust leads to the formation of gaseous products and a crude petroleum which has the characteristic odour of the higher fractions of the natural oils, and in addition is dextrorotatory. The conclusion is drawn that optically active glycerides, the activity of which is due to the configuration of the fatty acid, yield optically active hydrocarbons (compare C. Neuberg, this vol., i, 577). W. R.

**Synthesis of Optically Active Petroleum.** CARL NEUBERG (*Ber.*, 1907, 40, 4477—4478).—A claim for priority as against Lewkowitsch and Pick (preceding abstract). G. Y.

**Dimagnesium Compounds of  $\alpha$ -Dibromopentane.** JULIUS VON BRAUN (*Ber.*, 1907, 40, 4065—4066).—The author claims a prior right to the study of the action of the Grignard reagent on  $\alpha$ -dibromopentane (Braun and Steindorff, *Abstr.*, 1905, i, 341; Grignard and Vignon, this vol., i, 689). C. S.

**Behaviour of Various Aldehydes, Ketones, and Alcohols towards Oxidising Agents.** WILLEY DENIS (*Amer. Chem. J.*, 1907, 38, 561—594).—Evans (*Abstr.*, 1906, i, 269) has shown that the oxidation of benzoylcarbinol takes place in definite stages in accordance with the scheme put forward by Nef (*Abstr.*, 1905, i, 7). A study has now been made of the oxidation of ethyl alcohol, ethyl ether, acetaldehyde, and acetic acid under various conditions.

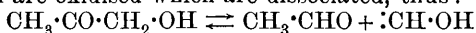
When cold aqueous solutions of ethyl alcohol, ether, and acetaldehyde are treated with *N* potassium permanganate, acetic acid only is produced. In presence of excess of potassium hydroxide, however, acetic acid is the main product, but carbonic and oxalic acids also are formed in quantities varying with the strength of the alkali. In all these cases, the first product of the oxidation is acetaldehyde, which in presence of alkali hydroxide of greater concentration than 0.1% (compare McLeod, this vol., i, 172) is partially converted into vinyl alcohol,  $\text{:C(OH)·CH}_2\text{·H} \rightarrow \text{OH·CH:CH}_2$ . In presence of the permanganate, the vinyl alcohol is oxidised to glycollaldehyde, which suffers dissociation, thus: (a)  $\text{OH·CH}_2\text{·CHO} \rightleftharpoons \text{:CH·OH} + \text{CH}_2\text{O}$  and (b)  $\text{OH·CH}_2\text{·CHO} \rightleftharpoons \text{:CH·CHO} + \text{H}_2\text{O}$ . The portion dissociated in accordance with (a) is converted into carbonic acid with intermediate formation of formic acid, and that dissociated in accordance with (b) is converted into glyoxal with oxalic acid as the final product.

When acetone is oxidised in neutral or acid solution, molecular proportions of acetic and carbonic acids are produced, and it is evident therefore that aqueous solutions of acetone do not contain any of the

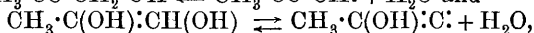
compound in the enolic form. On the addition of potassium hydroxide, however, the presence of *iso*acetone can be proved (1) by its quantitative conversion into mercuric *iso*acetone; (2) by its conversion into diacetone alcohol, and (3) by its oxidation to carbonic and oxalic acids with intermediate formation of acetol.

When acetic acid is treated with alkali hydroxide, it is evident that *iso*acetic acid is not formed, since such a substance would undergo oxidation to oxalic acid with intermediate formation of orthoglycollic acid,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{OH})_2$ .

Acetol, in absence of alkali hydroxide, is oxidised to acetic and carbonic acids, whilst, in presence of alkali, it is converted into oxalic and carbonic acids. Experiments have been made which show that pyruvic, hydroxypyruvic, and mesoxalic acids are successive intermediate products of the oxidation of acetol in presence of alkali. Observations have also been made with reference to the oxidation of lactic acid. When acetol is treated with silver oxide, either alone or in presence of potassium hydroxide, molecular quantities of acetic and formic acids are produced, whence it is concluded that only those molecules of acetol are oxidised which are dissociated, thus:



and  $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{C}\cdot + \cdot\text{CH}\cdot\text{OH}$ . With mercuric oxide, however, acetol is not oxidised in neutral solution, but, on addition of alkali hydroxide, *r*-lactic acid is produced together with small quantities of formic and acetic acids. In this case, therefore, only those molecules undergo oxidation which are dissociated as follows:  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot + \text{H}_2\text{O}$  and



whence it is evident that pyruvaldehyde is the primary oxidation product and undergoes rearrangement into *r*-lactic acid.

When a concentrated aqueous solution of mesoxalic acid is heated at  $100^\circ$ , the acid is converted quantitatively into glyoxylic and carbonic acids. If the acid is heated at  $150^\circ$  with concentrated potassium hydroxide, theoretical quantities of formic and oxalic acids are produced.

Ethyl diketobutyrate is rapidly converted by solutions of sodium carbonate or hydroxide into methyltartronic acid. When a concentrated solution of methyltartronic acid is heated at  $100^\circ$ , it is decomposed into carbonic and *r*-lactic acids. On heating ethyl diketobutyrate with water at  $63\text{--}65^\circ$ , carbon dioxide is slowly evolved and pyruvaldehyde and lactic and oxalic acids are formed. The lactic acid is produced by a rearrangement of the pyruvaldehyde, the latter being formed, thus:  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{H}_2\text{O} \rightarrow \text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{EtOH} \rightarrow \text{CH}_3\cdot\text{CO}\cdot\text{CHO} + \text{CO}_2 + \text{EtOH} + \text{H}_2\text{O}$ . When ethyl diketobutyrate is treated with water and silver oxide, molecular quantities of acetic and oxalic acids are obtained. In presence of sodium hydroxide, methyltartronic, oxalic, and acetic acids are produced together with small quantities of carbonic and formic acids. E. G.

**Preparation of Monochlorohydrin.** DEUTSCHE SPRENGSTOFF AKTIEN-GESELLSCHAFT (D.R.-P. 180668).—Glycerol (100 parts) is mixed with 150 parts of hydrochloric acid (sp. gr. 1.180 to 1.190) and the



mixture heated in an autoclave for fifteen hours at  $120^{\circ}$  under a pressure of one atmosphere. The mixture, on fractionation under 12—15 mm. pressure, yields first water and excess of acid, then monochlorohydrin at  $130$ — $150^{\circ}$ , and, finally, the unchanged glycerol at  $165$ — $180^{\circ}$ . The yield of monochlorohydrin is about 75%, and in these conditions there is no tendency for the formation of the dichlorohydrin. G. T. M.

**$\psi$ -Butylene Chlorohydrin**,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{Cl}$ . K. KRASSUSKY (*Compt. rend.*, 1907, 145, 762—763).—The  $\psi$ -butylene chlorohydrin described by Henry (this vol., i, 887) was obtained by the author in 1902 (*Abstr.*, 1902, i, 425). It can be obtained by addition of hydrochlorous acid to  $\psi$ -butylene, prepared either by the action of alcoholic potash on *sec.*-butyl iodide or by withdrawal of bromine from butylene bromide,  $\text{CHMeBr}\cdot\text{CHMeBr}$ , by means of zinc dust in aqueous alcoholic solution.  $\psi$ -Butylene chlorohydrin, when heated in a sealed tube with aniline, gives methyl ethyl ketone. By prolonged shaking of the chlorohydrin with lead oxide and water, *s*-dimethylethylene oxide is formed, but by heating with lead oxide and water in a sealed tube at  $140^{\circ}$  methyl ethyl ketone is produced. When prepared according to the first method, the chlorohydrin contains a small quantity of the *n*-butylene chlorohydrin, revealed in the reaction with lead oxide by production of a small quantity of aldehyde. E. H.

**By-products of the Hydrolysis of Tetramethylethylene [ $\beta\gamma$ -Dimethyl- $\Delta^{\beta}$ -butylene] Bromohydrin.** MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 978—987. Compare this vol., i, 578).—When  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene bromohydrin is hydrolysed by aqueous potassium hydroxide, the chief product is the hydrocarbon,  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene. The residue contains no appreciable quantity of alcohol, but probably consists of a mixture of isomeric bromides. The latter consist of (1) the bromide of a primary alcohol, not attacked by silver acetate, but forming an acetin when heated at  $200^{\circ}$  with potassium acetate, probably of the constitution  $\text{CHMe}_2\cdot\text{CHMe}\cdot\text{CH}_2\text{Br}$ , and (2) a bromide which, when treated with silver acetate, gives a tertiary alcohol. No asymmetric compounds were identified, possibly owing to the ease with which the change,  $\text{CMe}_3\cdot\text{CHMeBr} \rightarrow \text{CHMe}_2\cdot\text{CMe}_2\text{Br}$ , would be effected. E. H.

**Facts and Hypotheses concerning Isomeric Changes in Derivatives of Pinacone.** MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 987—995. Compare preceding abstract).—Chiefly theoretical. By saturating crude  $\beta\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene with hydrogen bromide, and acting on the bromide formed with potassium acetate at  $200^{\circ}$ , a large proportion of an acetin, b. p.  $155^{\circ}$  (approx.), is formed, which, on hydrolysis, gives an alcohol, b. p.  $141^{\circ}$ , but is probably different from the acetin boiling at the same temperature obtained by similar treatment of  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene. Whilst  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene readily combines with the haloid acids,  $\beta\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene does not do so in the cold, and, in order to transform it completely into the chlorohydrin, the hydrocarbon must be heated at  $100^{\circ}$  with hydrochloric acid for fifteen days. The same chlorohydrin is formed in each case. E. H.

**Dimethylketol.** I. OTTO DIELS and ERICH STEPHAN (*Ber.*, 1907, 40, 4336—4340).—Pechmann has already described the preparation of dimethylketol,  $\text{OH}\cdot\text{CHMe}\cdot\text{COMe}$ , by the reduction of diacetyl. The authors describe a convenient method of preparing diacetyl.

von Pechmann and Dahl (*Abstr.*, 1890, i, 1234) have described two solid modifications of dimethylketol, one with m. p.  $126\text{--}128^\circ$ , and the other with m. p.  $94\text{--}98^\circ$ . The authors are unable to confirm this, but find that two modifications, with the melting points  $95\cdot5^\circ$  and  $85\cdot5^\circ$  respectively, exist. These modifications are very similar in appearance; they can be crystallised without difficulty, and are dimolecular forms of dimethylketol. The difference between the results obtained by the authors and those obtained by von Pechmann and Dahl is ascribed to the latter authors having used ether in crystallising their compounds; it is found that the polymerides in question cannot be crystallised when ether is present.

Dimethylketol, obtained by the reduction of diacetyl with zinc and dilute sulphuric acid, was allowed to remain in a closed vessel for three and a-half months, when it was transformed into a crystalline compound,  $\text{C}_8\text{H}_{16}\text{O}_4$ , with m. p.  $95\cdot5^\circ$ ; that it is a dimolecular form of dimethylketol was shown by a determination of its molecular weight in acetone by the ebullioscopic method.

When a little granulated zinc was added to dimethylketol and the whole immersed in a freezing mixture, the compound,  $\text{C}_8\text{H}_{16}\text{O}_4$ , separated as a crystalline mass, m. p.  $85\cdot5^\circ$ .

Each of these modifications crystallises in rhombic leaflets; their solubilities are of the same order. That they are distinct is shown by the depression of the melting point, which occurs with a mixture of the two.

The *benzoyl* derivative,  $\text{C}_{11}\text{H}_{12}\text{O}_3$ , obtained by benzoylating dimethylketol in pyridine solution, has b. p.  $140\text{--}141^\circ/8$  mm. and  $D^{18} 1\cdot104$ .

A. McK.

**Chloromethyl Sulphate.** JOSEF HOUBEN and HANS R. ARNOLD (*Ber.*, 1907, 40, 4306—4310).—Chloromethyl ether, prepared from hydrogen chloride and a paste of trioxymethylene and methyl alcohol at  $0^\circ$  (compare Litterschied, *Abstr.*, 1904, i, 962), reacts with sulphur trioxide in a freezing mixture to form *chloromethyl sulphate*,  $\text{CH}_2\text{Cl}\cdot\text{SO}_4\text{Me}$ , b. p.  $92^\circ/18$  mm.,  $D^{18} 1\cdot473$ , which is extraordinarily reactive, and is decomposed by water, forming methylsulphuric acid, formaldehyde, and hydrogen chloride.

*s*-Dichloromethyl ether reacts with sulphur trioxide to form a liquid, b. p.  $79^\circ/18\text{--}19$  mm., which reacts explosively with water, alcohol, acetone, acetic acid, benzene, or light petroleum; the analytical data do not correspond with the formula  $(\text{CH}_2\text{Cl})_2\text{SO}_4$ .

C. S.

**The Alkaline Hydrolysis of Alkyl Nitrates; a Contribution to the Constitution of Nitric Acid.** PETER KLASON and TOR CARLSON (*Ber.*, 1907, 40, 4183—4191. Compare *Abstr.*, 1906, i, 787).—The presence of phenyl hydrosulphide during the hydrolysis of alkyl nitrates prevents the formation of resin; in the absence of hydro-

sulphide, the peroxide formed is converted into aldehyde, and this gives rise to the resin. With glyceryl trinitrate, the reaction is normal, but with the nitrates derived from monohydric alcohols in addition the hydrosulphide is alkylated. It might be assumed that during the change the nitrate was first reduced to nitrite, the hydrosulphide being oxidised to disulphide, and then that hydrolysis of the nitrite occurred, so that a quantitative examination was necessary to decide between (I)  $R \cdot NO_3 + KSR^1 = R \cdot S \cdot R^1 + KNO_3$  and (IIa)  $R \cdot NO_3 + KSR^1 + HSR^1 = R \cdot NO_2 + KOH + R^1S \cdot SR^1$ , (b)  $R \cdot NO_2 + KOH = KNO_2 + R \cdot OH$ .

It was found that the velocity of hydrolysis with sodium phenylsulphide was 100 to 200 times that with alkali alone. The first step was the determination of  $\chi$ , the ratio of  $x:y$ , where  $x$  and  $y$  are the decrease in the concentration of nitrate due to reactions I and IIa. The value of  $\chi$  was found to be independent of the time, and consequently the two reactions proceed simultaneously.

By determining the concentration of the alkali, it was found that the hydrolysis is a reaction of the second order in both cases, and the constant obtained is the sum of those due to the two reactions. The proportion of nitrate hydrolysis,  $k_x$ , to nitrite hydrolysis,  $k_y$ , for various alkyl nitrates is appended :

	$K_x$ .	$K_y$ .
Ethyl nitrate .....	0.0243	0.0082
<i>n</i> -Propyl nitrate .....	0.0160	0.0082
<i>iso</i> Butyl nitrate.....	0.0013	0.0078
<i>iso</i> Amyl nitrate .....	0.0081	0.0083

With methyl nitrate, the hydrolysis to nitrate and phenyl methyl sulphide is almost quantitative, only 0.7% of nitrite being formed. The velocity of nitrate hydrolysis decreases rapidly as the series is ascended, and that of nitrite is practically constant. W. R.

**The Alkaline Hydrolysis of Alkyl Nitrates in the Presence of Hydrogen Peroxide.** TOR CARLSON (*Ber.*, 1907, 40, 4191—4194. Compare preceding abstract).—In the hydrolysis of alkyl nitrates, the proportion of nitrate and nitrite may be determined by evaporation of the solvent and unchanged alkyl nitrate in a vacuum, the residue being treated with potassium iodide and hydrochloric acid, and the nitric acid decomposed by iron chloride. The values obtained at 70° with 95% alcohol, concentration 0.5*N*, are:  $CH_3NO_3$ , nitrite, trace;  $EtNO_3$ , 7% nitrite;  $Pr^aNO_3$ , 17% nitrite; *i*- $BuNO_3$ , 35% nitrite; *i*- $C_5H_{11}NO_3$ , 20% nitrite. The results are not particularly accurate in consequence of the reducing action of aldehyde. With nitrates of polyatomic alcohols, the reaction velocity is greater and more nitrite is formed; glyceryl trinitrate giving 67%, glycyl dinitrate 87%, and nitrocellulose (12.5% *N*) 82%. In these reactions, the alkyl complex is destroyed and glycol, glycerol, and cellulose are not regenerated.

Now if peroxide is formed during hydrolysis, oxygen should be liberated when hydrogen peroxide is present,  $R \cdot CH_2O \cdot OH + HO \cdot OH = R \cdot CH_2 \cdot OH + H_2O + O_2$ , and this is proved to be the case; nitrocellulose, evolving oxygen and hydrated cellulose, being generated. Experiments should give according to theory 1 mol. of  $O_2$  for every mol. of nitrite;

this is not realised, due, perhaps, to catalytic decomposition of peroxide by alkali, and also the alcohol behaving as an "acceptor."

Benzyl nitrate and alkali phenyl sulphide give almost no nitrite, but phenyl benzyl sulphide and nitrate. W. R.

### Relative Volatility of Various Groups of Acetic Esters.

LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 742—764).—This paper is supplementary to two already published (*Abstr.*, 1903, ii, 8; this vol., i, 674). The replacement of a hydrogen atom by an acetyl group should lower the volatility in proportion to the increase in molecular weight, but this effect is liable to be obscured by other influences. For example, (1) the position of the hydrogen atom substituted; (2) when the hydrogen atom is attached to a carbon atom, the nature of the other groups or elements connected with the latter, and (3) the relative extents to which the molecules of the parent substance and of its acetyl derivative are associated. The coefficients of association have different values, not only for compounds possessing different chemical functions, but also for substances of the same function but containing different numbers of carbon atoms in the molecule.

A large number of tables are given in the original, showing the volatility relations between substances of the same types and their acetyl derivatives, and exemplifying the effects of the several influences, and especially of the third, referred to above. The following examples may be quoted. Ethyl acetate boils  $1^{\circ}$  below ethyl alcohol, whilst difluoroethyl acetate boils  $11^{\circ}$  higher than the corresponding alcohol. The reason of this difference is found in Swarts' observation (*Abstr.*, 1903, i, 222) that difluoroethyl alcohol is much less associated than ethyl alcohol. Similarly, the effect of a lower association value is shown by the replacement of hydrogen by acetyl in the SH group of ethyl mercaptan, which leads to an increase of  $80^{\circ}$  in the boiling point, whereas the analogous substitution in the case of ethyl alcohol lowers the boiling point by  $1^{\circ}$ . T. A. H.

### [Preparation of Salts of the Iodated Higher Fatty Acids.]

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 180622).—*Calcium iodobehenate*,  $\text{Ca}(\text{C}_{22}\text{H}_{42}\text{O}_2\text{I})_2$ , is most conveniently prepared in a stable condition by slowly adding an alcoholic solution of behenic acid to the filtered solution produced by dissolving hydrated calcium chloride in alcohol and precipitating ammonium chloride by passing in an excess of ammonia. The organic calcium salt separates as a colourless powder, insoluble in water or alcohol. This compound may also be prepared either by double decomposition from an alkali iodobehenate and calcium chloride or by mixing equivalent amounts of the acid and calcium hydroxide dissolved in water. *Strontium* and *magnesium iodobehenates*, *calcium* and *strontium iodostearates*, and *calcium iodopalmitate* were also prepared by the foregoing methods, and similarly obtained as colourless, insoluble powders.

G. T. M.

**Preparation of Iodobehenic Acid.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186214).—Although the chlorine in

chlorobehenic acid is not replaced by iodine on treating this substance with metallic iodides, nevertheless the corresponding bromo-compound readily undergoes this substitution. Bromobehenic acid, obtained by adding hydrogen bromide to erucic acid, when warmed with sodium iodide and glacial acetic acid furnishes iodobehenic acid. Other metallic iodides may be employed instead of sodium iodide, and the solvent or diluent may also be varied. G. T. M.

**Preparation of Bromo-Aliphatic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186740).—It has been found that the unsaturated aliphatic acids readily combine with nascent hydrogen bromide, and become thus converted into bromo-aliphatic acids. A mixture of erucic acid, potassium bromide, and concentrated sulphuric and glacial acetic acids when shaken at a high temperature give rise to bromobehenic acid. Bromostearic acid was obtained by warming and shaking a mixture of oleic acid, sodium bromide, and an acetic acid solution of hydrogen chloride. G. T. M.

**Mono- and Di-alkylcyanovinylacetic [Mono- and Di-alkyl-cyano- $\Delta^3$ -butenoic] Acids.** II. ICILIO GUARESCHI (*Mem. Accad. Sci. Torino*, 1907, [ii], 57, 287—307. Compare *Abstr.*, 1901, i, 630).—The author has prepared a number of substituted  $\beta$ -butenoic acids of the types: (1)  $\text{CN}\cdot\text{CH}:\text{CR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ; (2)  $\text{CN}\cdot\text{CH}:\text{CR}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ ; (3)  $\text{CN}\cdot\text{CH}:\text{CR}\cdot\text{CHR}'\cdot\text{CO}_2\text{H}$ , and (4)  $\text{CN}\cdot\text{CH}:\text{CR}'\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ , R representing an alkyl and R' an aromatic radicle. These acids are energetic reducing agents, absorb bromine, and give colorations with alkali or, better, ammonium carbonate, or with potassium nitrite. When they are stored in glass vessels, the latter become coloured, owing to the alkalinity of the glass. With ferric chloride, acids of type (1) give a coloration, whilst those of types (2), (3) and (4) undergo condensation, yielding hexa-substituted derivatives of dihydrophthalic acid of the form:

$$\begin{array}{c} \text{CN}\cdot\text{C}:\text{CR}\cdot\text{CR}\cdot\text{CO}_2\text{H} \\ \text{CN}\cdot\text{C}:\text{CR}\cdot\text{CR}\cdot\text{CO}_2\text{H} \end{array}$$

The above  $\Delta^3$ -butenoic acids are prepared by the action of 60% sulphuric acid on (1) 3:5-dicyano-2:6-diketo-4-alkyl- $\Delta^3$ -tetrahydropyridines, which are converted, by way of unstable tricarboxylic acids, into  $\gamma$ -cyano- $\beta$ -alkyl- $\Delta^3$ -butenoic acids; (2) 3-cyano-2:6-diketo-4-alkyl- $\Delta^3$ -tetrahydropyridines or 3-cyano-2:6-diketo-4:5-dialkyl- $\Delta^3$ -tetrahydropyridines; in no case was the intermediate di- or tri-carboxylic acid isolated.

$\gamma$ -Cyano- $\alpha\beta$ -dimethyl- $\Delta^3$ -butenoic acid,  $\text{CN}\cdot\text{CH}:\text{CMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , prepared from 3-cyano-2:6-diketo-4:5-dimethyl- $\Delta^3$ -tetrahydropyridine, crystallises from water in colourless or faintly yellow, acicular prisms, m.p. 191.5—192°, forms a yellowish-brown copper salt,  $(\text{C}_7\text{H}_8\text{O}_2\text{N})_2\text{Cu}$ , rapidly reduces potassium permanganate or auric chloride, but does not reduce Fehling's solution.

$\gamma$ -Cyano- $\beta$ -methyl- $\alpha$ -ethyl- $\Delta^3$ -butenoic acid,  
 $\text{CN}\cdot\text{CH}:\text{CMe}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$ ,  
 prepared from 3-cyano-2:6-diketo-4-methyl-5-ethyl- $\Delta^3$ -tetrahydro-

pyridine, crystallises from water in colourless, prismatic needles or short prisms, m. p. 175—176°.

*γ-Cyano-α-methyl-β-ethyl-Δ<sup>β</sup>-butenoic acid*,  
 $\text{CN}\cdot\text{CH}\cdot\text{CET}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ ,

prepared from 3-cyano-2 : 6-diketo-5-methyl-4-ethyl-Δ<sup>3</sup>-tetrahydropyridine, has m. p. about 200°.

*γ-Cyano-β-propyl-Δ<sup>β</sup>-butenoic acid*,  $\text{CN}\cdot\text{CH}\cdot\text{CP}_{1^a}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3 : 5-dicyano-2 : 6-diketo-4-propyl-Δ<sup>3</sup>-tetrahydropyridine, or the ammonium derivative of its enolic form, crystallises from alcohol in prisms or needles, m. p. 225—227° (decomp.).

*γ-Cyano-β-isopropyl-Δ<sup>β</sup>-butenoic acid*,  $\text{CN}\cdot\text{CH}\cdot\text{CPr}^{\beta}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3 : 5-dicyano-2 : 6-diketo-4-isopropyl-Δ<sup>3</sup>-tetrahydropyridine, forms crystals, m. p. 177—178°.

*γ-Cyano-β-methyl-α-propyl-Δ<sup>β</sup>-butenoic acid*,  
 $\text{CN}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHPr}\cdot\text{CO}_2\text{H}$ ,

prepared from 3-cyano-2 : 6-diketo-4-methyl-5-propyl-Δ<sup>3</sup>-tetrahydropyridine, crystallises from water in colourless or faintly yellow, acicular prisms, m. p. 154—155°, and forms a crystalline dibromide,  $\text{C}_9\text{H}_{13}\text{O}_2\text{NBr}_2$ .

*γ-Cyano-β-hexyl-Δ<sup>β</sup>-butenoic acid*,  $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_{13})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3 : 5-dicyano-2 : 6-diketo-4-hexyl-Δ<sup>3</sup>-tetrahydropyridine, has m. p. 175—180°.

*γ-Cyano-β-phenyl-Δ<sup>β</sup>-butenoic acid*,  $\text{CN}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3-cyano-2 : 6-diketo-4-phenyl-Δ<sup>3</sup>-tetrahydropyridine or from the ammonium salt of 3 : 5-dicyano-2 : 6-diketo-4-phenyl-Δ<sup>3</sup>-tetrahydropyridine, crystallises from alcohol in colourless or faintly yellow plates, m. p. 256—257°.

*γ-Cyano-β-m-tolyl-Δ<sup>β</sup>-butenoic acid*,  $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from the ammonium salt of 3 : 5-dicyano-2 : 6-diketo-4-m-tolyl-Δ<sup>3</sup>-tetrahydropyridine, crystallises from acetic acid in short, heavy, colourless or faintly yellow prisms, m. p. 255—257°.

*γ-Cyano-β-cumyl-Δ<sup>β</sup>-butenoic acid*,  $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Pr}^a)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3 : 5-dicyano-2 : 6-diketo-4-cumyl-Δ<sup>3</sup>-tetrahydropyridine, separates from alcohol in crystals, m. p. 240°.

*γ-Cyano-α-benzyl-β-methyl-Δ<sup>β</sup>-butenoic acid*,  
 $\text{CN}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ ,

prepared from 3-cyano-2 : 6-diketo-4-methyl-5-benzyl-Δ<sup>3</sup>-tetrahydropyridine, forms colourless crystals, m. p. 156—157°.

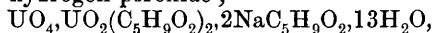
*γ-Cyano-β-ethyl-Δ<sup>β</sup>-butenoic*, *γ-cyano-β-isobutyl-Δ<sup>β</sup>-butenoic*, *γ-cyano-α-methyl-β-isopropyl-Δ<sup>β</sup>-butenoic*, and *γ-cyano-β-methyl-α-allyl-Δ<sup>β</sup>-butenoic* acids have also been obtained in small quantities, but have not been analysed.

T. H. P.

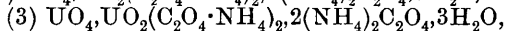
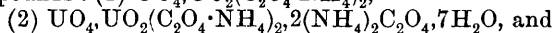
**Complex Salts of Uranium Peroxide.** ARRIGO MAZZUCHELLI and FERRUCCIO BIMBI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 576—584. Compare this vol., ii, 54).—The following derivatives of uranium peroxide, prepared by the authors, are yellow or orange-yellow in colour, and are decomposed by water with precipitation of uranium peroxide.

$\text{UO}_4$ ,  $\text{UO}_2(\text{OAc})_2\cdot 2\text{NH}_4\cdot\text{OAc}$  was obtained by the interaction of uranium nitrate, ammonium acetate, and hydrogen peroxide ;

$\text{UO}_4, \text{Ba}(\text{OAc})_2, 6\text{H}_2\text{O}$ , by the interaction of uranyl and barium acetates, acetic acid, and hydrogen peroxide ;

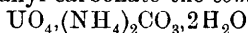


from uranyl nitrate, sodium valerate, and hydrogen peroxide ; the three compounds : (1)  $\text{UO}_4, \text{UO}_2(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_2$ ,



from ammonium uranyl oxalate, ammonium oxalate, and hydrogen peroxide ;  $\text{NaO}_2 \cdot \text{UO}_2 \cdot \text{C}_8\text{H}_4\text{O}_4\text{Na}, 5\text{H}_2\text{O}$ , from sodium uranyl phthalate and hydrogen peroxide. The compound formed by sodium uranyl succinate and hydrogen peroxide is obtained as a yellow precipitate, but was not purified or analysed.

With uranyl nitrate, chloride, sulphate, &c., hydrogen peroxide gives orange-coloured liquids, but the compounds formed could not be isolated. With sodium uranyl pyrophosphate, the compound  $2\text{UO}_4, \text{Na}_4\text{P}_2\text{O}_7, 18\text{H}_2\text{O}$  or  $[\text{NaO}_2 \cdot \text{UO}_2 \cdot \text{O} \cdot \text{PO}(\text{ONa})]_2\text{O}$  (?) is obtained, and with ammonium uranyl carbonate the compound



or  $\text{NH}_4 \cdot \text{O}_2 \cdot \text{UO}_2 \cdot \text{CO}_3 \cdot \text{NH}_4$ .

T. H. P.

**Complex Salts of Iridium. Irido-oxalates.** CESARE GIALDINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 551—561).—When a solution of iridic chloride or an alkaline iridichloride is treated with excess of potassium or sodium hydroxide, the principal reaction, represented by :  $\text{IrCl}_4 + 4\text{KOH} = \text{IrO}_2 + 4\text{KCl} + 2\text{H}_2\text{O}$ , is accompanied by secondary reactions, expressed by the equations :  $2\text{IrCl}_4 + 7\text{KOH} = \text{Ir}_2\text{O}_3 + 7\text{KCl} + 3\text{H}_2\text{O} + \text{HClO}$  ;  $\text{HClO} + \text{KOH} = \text{KCl} + \text{H}_2\text{O} + \text{O}$  ;  $\text{Ir}_2\text{O}_3 \cdot \text{Aq} + \text{O} = 2\text{IrO}_2 \cdot \text{Aq}$ . Hence, in order to prevent the ready decomposition of the hydroxide,  $\text{Ir}(\text{OH})_4$ , it is necessary to limit as far as possible the reaction :  $\text{Ir}(\text{OH})_4 + \text{Cl}^- \rightleftharpoons \text{Ir}(\text{OH})_3 + \text{HClO}$ . By adding hypochlorous acid, it is found possible to displace the equilibrium of this reaction from right to left, and so facilitate the precipitation of iridium dioxide, the preparation and separation of which usually occupy several days.

The action of oxalic acid on iridium dioxide takes place in two stages :  $2\text{IrO}_2 + \text{H}_2\text{C}_2\text{O}_4 = \text{Ir}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{CO}_2$  and  $\text{Ir}_2\text{O}_3 + 6\text{H}_2\text{C}_2\text{O}_4 = 2\text{H}_3\text{Ir}(\text{C}_2\text{O}_4)_3 + 3\text{H}_2\text{O}$ , for the completion of which it is necessary to boil the solution for thirty to thirty-five hours. *Potassium sesqui-irido-oxalate*,  $\text{K}_3\text{Ir}(\text{C}_2\text{O}_4)_3, 4\text{H}_2\text{O}$ , prepared by neutralising the acid with potassium carbonate, separates from water in pale orange-yellow, triclinic crystals [Zambonini,  $a:b:c = 0.7319 : 1 : 0.9565$  ;  $\alpha = 88^\circ 34' 37''$ ,  $\beta = 94^\circ 30' 12''$ , and  $\gamma = 57^\circ 1' 18''$ ].

T. H. P.

**Oxymethylenecamphor and Mesityloxidoxalic Esters.** WILHELM FEDERLIN (*Annalen*, 1907, 356, 251—280).—Wislicenus's studies of tautomeric compounds (Abstr., 1896, i, 552 ; 1900, i, 9) led to the conclusion that solvents with slight dissociating powers and non-dissociating solvents favour the formation of the enolic form of desmotropic compounds, whilst the ketonic form is stable in strongly dissociating solvents. This rule, however, does not hold good for all tautomeric substances. Two exceptions, oxymethylenecamphor and

mesityloxidoxalic ester, have been studied spectrometrically by Brühl (Abstr., 1899, ii, 735). The present author has investigated the behaviour of the same substances by Wislicenus's ferric chloride colorimetric method (Abstr., 1900, i, 9). The results obtained with oxymethylenecamphor confirm Brühl's statement (*loc. cit.*) that this substance has the ketonic constitution and that enolic transformation does not take place either in feebly or strongly dissociating solvents.

$\beta$ -Mesityloxidoxalic esters do not give a coloration with ferric chloride in ether, benzene, or chloroform solution, but after some time give a slight coloration in ethyl- or methyl-alcoholic solution. On the other hand, the enolic or  $\alpha$ -esters undergo the ketonic transformation rapidly in methyl- or ethyl-alcoholic, but only slowly in ethereal or benzene, and most slowly in chloroform, solution. In these solvents, the  $\beta$ -esters slowly polymerise, the polymerisation being accelerated by exposure of the solution to light. In consequence of preceding ketonic transformation, the  $\alpha$ -esters yield the same polymerides in the above solvents with the exception of chloroform. The ketonic transformation of the  $\alpha$ -esters and the polymerisation of the  $\beta$ -esters do not take place completely even on prolonged action of the solvent. A converse transformation from the polymeride could not be observed. The propyl and amyl esters polymerise more slowly than do methyl and ethyl mesityloxidoxalates.

The *polymeride* of ethyl mesityloxidoxalate,  $(C_{10}H_{14}O_4)_2$ , formed in eight days, separates in monoclinic crystals [ $a:b:c=1.9825:1:1.7810$ ;  $\beta=143^\circ 16'$ ], m. p.  $175^\circ$ , sublimes unchanged, is less soluble than the  $\beta$ -ester, and does not give a coloration with ferric chloride.

The *polymeride* of methyl mesityloxidoxalate,  $(C_9H_{12}O_4)_2$ , formed in ten to twelve days, separates in monoclinic crystals [ $a:b:c=1.0319:1:1.1761$ ;  $\beta=91^\circ 54'$ ], m. p.  $225^\circ$ , and has properties similar to those of the polymeride of the ethyl ester. A *polymeride*,  $(C_9H_{12}O_4)_2$ , m. p.  $236-237^\circ$  (partial decomp.), which resembles, but is slightly less stable than, the preceding substance, is obtained when the solid  $\beta$ -methyl ester is exposed to diffused light for eight days.

*Propyl mesityloxidoxalate*, prepared by the action of sodium on mesityl oxide and propyl oxalate in ethereal solution, is obtained as a yellow oil, b. p.  $120-150^\circ/20$  mm., which gives a strong coloration with ferric chloride. The  $\alpha$ -ester forms a green, crystalline *copper* salt,  $(C_{11}H_{15}O_4)_2Cu, H_2O$ , from which it is liberated by treatment with chloroform and dilute sulphuric acid. The *polymeride*,  $(C_{11}H_{16}O_4)_2$ , m. p.  $111^\circ$ , forms in ninety days, sublimes with partial decomposition, and does not give a ferric chloride reaction.

*Amly mesityloxidoxalate*, prepared from amyl oxalate, is obtained as a yellow oil, b. p.  $100-130^\circ/20$  mm., gives a strong ferric chloride reaction, and forms a green, crystalline *copper* salt,  $(C_{13}H_{19}O_4)_2Cu, H_2O$ , which loses  $H_2O$  at  $115^\circ$ ; m. p.  $129-130^\circ$ . The  $\alpha$ -ester is obtained from the copper salt as a viscid, yellow oil. The *polymeride*,  $(C_{13}H_{20}O_4)_2$ , formed in one hundred and twenty days, separates from light petroleum in crystals, m. p.  $113-114^\circ$ .  
G. Y.

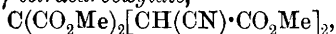
**Preparation of Methylenecitryl Halides.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186659).—Methylenecitric acid is



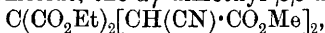
a somewhat unstable substance, which cannot be converted into its chloride or bromide by means of either phosphorus trichloride or tribromide, or the corresponding oxyhalide. It has now been found that this reaction may be readily effected by means of phosphorus pentachloride or pentabromide. Methylenecitric acid (1 part) is mixed with 2 parts of phosphorus pentachloride, hydrogen chloride is evolved, and the oxychloride produced is distilled off, whilst the *methylenecitryl chloride*,  $\text{CH}_2\text{C}(\text{CO}_2)\text{C}(\text{CH}_2\cdot\text{COCl})_2$ , colourless prisms, m. p. 74—75°, is crystallised from benzene or chloroform with the addition of light petroleum. *Methylenecitryl bromide*, a viscid oil, is obtained when the phosphorus pentachloride is replaced in the foregoing experiment by 4 parts of phosphorus pentabromide. The alkali methylenecitrates may be employed in these reactions in place of the free acid.

G. T. M.

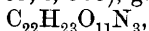
**Condensation of the Esters of Mesoxalic or Oxalacetic Acid with the Esters of Cyanoacetic Acid.** CH. SCHMITT (*Ann. Chim. Phys.*, 1907, [viii], 12, 406—432).—Mainly a résumé of work already published (compare Abstr., 1905, i, 508; 1907, i, 112), but the following compounds are described for the first time. *Methyl  $\alpha$ -dicyanopropene- $\alpha\beta\beta\gamma$ -tetracarboxylate*,



m. p. 120°, prepared by the action of methyl mesoxalate on excess of methyl cyanoacetate, yields the compound,  $\text{C}_{20}\text{H}_{21}\text{O}_{11}\text{N}_3$ , m. p. 115°, on treatment with alcoholic hydrogen chloride;  *$\beta\beta$ -dimethyl  $\alpha$ -diethyl  $\alpha$ -dicyanopropene- $\alpha\beta\beta\gamma$ -tetracarboxylate*,  $\text{C}(\text{CO}_2\text{Me})_2[\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}]_2$ , m. p. 73°, is similarly obtained from methyl mesoxalate and ethyl cyanoacetate; its isomeride, the  $\alpha$ -dimethyl  $\beta\beta$ -diethyl ester,

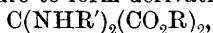


already described (Abstr., 1905, i, 508), gives the compound,

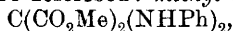


m. p. 116°, when treated with alcoholic potassium hydroxide.

The esters of mesoxalic acid condense with certain aromatic amines at the ordinary temperature to form derivatives of the type:



of which the following are described: *methyl bisanilinomesoxalate*,



m. p. 113.5°, *ethyl bisanilinomesoxalate*,  $\text{C}(\text{CO}_2\text{Et})_2(\text{NHPh})_2$ , m. p. 103°, and *methyl bis-*o*-toluidinomesoxalate*,  $\text{C}(\text{CO}_2\text{Me})_2(\text{NH}\cdot\text{C}_7\text{H}_7)_2$ , m. p. 172°.

M. A. W.

**Additive Compound of Two Dicarboxyglutaconic Ester Radicles.** MAX GUTHZEIT [and ERNST HARTMANN] (*Ber.*, 1907, 40, 4043).—In the course of a study of the halogen derivatives of ethyl dicarboxyglutaconate, a crystalline compound,  $\text{C}_{30}\text{H}_{42}\text{O}_{16}$ , m. p. 86°, has been obtained by heating ethyl bromodicarboxyglutaconate with ethyl sodiodicarboxyglutaconate in xylene solution. This compound, which is formed also in a 90% yield by the action of iodine on ethyl sodiocarboxyglutaconate in toluene solution, or by prolonged boiling of the copper derivative of the ester with finely-divided sulphur in

benzene, reacts readily with alcoholic sodium ethoxide in the cold. Its behaviour towards bromine, alkaline permanganate, and tin and glacial acetic acid shows that it does not contain an ethylene linking.  
G. Y.

**Preparation of Thioglycollic Acid from Chloroacetic Acid.** KALLE & Co. (D.R.-P. 180875).—When chloroacetic acid is treated in alkaline solution with sodium sulphide and sulphur, a dithioglycollic acid is produced, and this substance on reduction either with zinc dust or hydrogen sulphide furnishes thioglycollic acid,  $\text{HS}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .  
G. T. M.

**Deaminocystine and Aminoethyl Disulphide.** CARL NEUBERG and ERICH ASCHER (*Biochem. Zeitsch.*, 1907, 5, 451—455).—By the gentle action of nitrous acid on cystine,  $\alpha$ -hydroxypropionic acid  $\beta$ -disulphide,  $\text{S}_2[\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}]_2$ , can be obtained as the barium salt;  $[\alpha]_D^{22} - 19\cdot08^\circ$ . By precipitation of the latter with sulphuric acid, the disulphide is obtained in solution;  $[\alpha]_D - 10\cdot6^\circ$ . On dry distillation, cystine loses carbon dioxide and yields a small quantity of aminoethyl disulphide,  $\text{S}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$ , which can be isolated as the picrate, m. p.  $197^\circ$ .  
G. B.

**Conversion of Methyl Alcohol into Formaldehyde and the Preparation of Formalin.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1023—1044. Compare this vol., i, 892).—The experiments were performed either in the apparatus described previously or in a slightly simplified form of it. The following catalysts are very energetic, but produce chiefly carbon dioxide and monoxide, hydrogen and oxygen, the quantity of formaldehyde in the product being very slight: asbestos containing (1) freshly-reduced powdered copper; (2) a mixture of cerium sulphate and thorium oxide; (3) platinum-black. With coke coated with reduced copper, 39·78% of alcohol was changed directly into formaldehyde, whilst, with metallic platinum, 41% was so changed. Contrary to the statement of Sabatier and Senderens, the former substance hardly acts as a catalyst at all, even at  $300^\circ$ , when methyl alcohol is passed over it without admixture of air.

The reaction is exothermic, 31·1 Cal. being evolved for every gram-molecule of methyl alcohol converted into formaldehyde; consequently if the reaction is once started, it should, under certain conditions, proceed without any further application of external energy. A method, which can also be applied technically, has been devised, and 49% of methyl alcohol can thus be transformed when freshly-reduced copper gauze is employed as catalyst; the alcohol must not contain more than 1% of acetone. With platinum or iron filings as catalysts, the yields are unsatisfactory. When methyl alcohol without admixture of air is passed over heated iron filings, the products obtained are carbon monoxide and dioxide, hydrogen, oxygen and methane, carbon, very small quantities of formaldehyde, and a gas, possibly  $(\text{CH})_2\text{O}$ , the constitution of which has not yet been finally determined; with iron it may form  $\text{Fe}\langle\text{C}\rangle\text{O}$ , which on heating decomposes forming  $\text{Fe} + \text{CO} + \text{C}$ .

The percentage composition of the gases depends on the strength of alcohol employed and the rate of passage of the alcohol vapours over the catalyst. Z. K.

**Metacetaldehyde.** ARTHUR HANTZSCH and J. OECHSLIN (*Ber.*, 1907, 40, 4341—4344).—Metacetaldehyde has hitherto been considered by the majority of those who have investigated it as stereoisomeric with paracetaldehyde, and accordingly to be a termolecular form of acetaldehyde. The authors are led to the following conclusions. Metacetaldehyde exists in one form only; when pure, it is quite stable; it is not changed when dissolved in phenol, that is, acetaldehyde is not formed. Metacetaldehyde is not termolecular, but is quadrimolecular in phenol solution; in thymol solution, it is probably sexamolecular. From these results, it is certain that metacetaldehyde is not isomeric with paracetaldehyde. A. McK.

**Action of Magnesium Hydroxide on Chloral Hydrate.** LEOPOLD ROSENTHALER and R. REIS (*Chem. Zentr.*, 1907, ii, 891; from *Apoth. Zeit.*, 1907, 22, 678—679).—Chloroform is not decomposed when heated with magnesium hydroxide on a water-bath. Chloral hydrate when similarly treated is decomposed chiefly into chloroform and formic acid, but at the same time a secondary reaction takes place whereby a greater proportion of magnesium hydroxide is neutralised, carbon monoxide and magnesium chloride also being formed. The action of magnesium hydroxide on chloral hydrate cannot therefore be employed in the quantitative estimation of the latter compound. W. H. G.

**Solubility of Bisulphite Compounds of Aldehydes and Ketones.** JOHN B. CORPOCK (*Chem. News*, 1907, 96, 225).—It has been observed that when aldehydes or ketones are treated with the deep yellow solution prepared by saturating sodium carbonate solution with sulphur dioxide, the bisulphite compounds do not separate. Experiments have been carried out which show that this is due to the solubility of the compounds in sulphurous acid, and it has been found that in preparing the bisulphite solutions from sodium carbonate the sulphur dioxide should only be passed into the solution until a very pale green tint appears. E. G.

**Preparation of Formaldehydesulphoxylates.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 180832. Compare *Abstr.*, 1906, i, 400).—Acetone and its homologues react with alkali hyposulphites to form crystallisable ketonesulphoxylates. A dilute aqueous solution of acetone is saturated with sulphur dioxide and the liquid then treated in the cold with zinc dust, the temperature being finally raised to 50—60°. After cooling, the solution deposits zinc acetonesulphoxylate, which is converted into the sodium salt by treatment with sodium carbonate. The sodium acetonesulphoxylate when treated in water with aqueous formaldehyde is readily changed into sodium formaldehydesulphoxylate, whilst the acetone is eliminated. G. T. M.

**Combined Sulphurous Acids. II.** WILHELM KERP and EMIL BAUR (*Chem. Zentr.*, 1907, ii, 970—971; from *Arb. Kais. Ges.-A.*, 1907, 26, 231—268. Compare Abstr., 1904, i, 713).—It has been shown that formaldehyde-sulphurous acid and acetaldehyde-sulphurous acid are both strong acids, and it is therefore highly probable that the sulphurous acids of benzaldehyde, acetone, and arabinose are also strong acids. This could not be proved, however, by electrical conductivity measurements, because of the high degree of dissociation of the complex in water. As a rule, the degree of dissociation of the complex is greater in an acid solution than in a neutral solution, from which it follows that the dissociation of the non-ionised acid is greater than that of the anion. The rate of dissociation of the complex is, however, diminished by the presence of an acid.

The addition of acetaldehyde to an aqueous solution of acetaldehyde sodium hydrogen sulphite diminishes the degree of dissociation of the complex in agreement with the law of mass action. The dissociation of the complex increases with a rise of temperature.

*Chloral sodium hydrogen sulphite*,  $\text{CCl}_3 \cdot \text{CHO} \cdot \text{HSO}_3\text{Na}$ , obtained in a crystalline form by passing sulphur dioxide into a solution of sodium carbonate to which is added a solution of chloral hydrate, is, unlike the latter compound, decomposed to a high degree in aqueous solution.

W. H. G.

**The Ammonia Reaction for Distinguishing between Enolic and Ketonic Derivatives.** ARTHUR MICHAEL and HAROLD HIBBERT (*Ber.*, 1907, 40, 4380—4388. Compare Hantzsch and Dollfus, Abstr., 1902, i, 223, 675; Hantzsch, this vol., i, 927).—The authors tested this reaction by inquiring (1) how far the assumption is correct that the reaction  $\cdot\text{CH}_2 \cdot \text{CO} \cdot + \text{NH}_3 \rightarrow \cdot\text{CH}_2 \cdot \text{C}(\text{OH}) \cdot \text{NH}_2$  is slower than the salt formation  $\cdot\text{CH} : \text{C}(\text{OH}) \cdot + \text{NH}_3 \rightarrow \cdot\text{CH} : \text{C}(\text{ONH}_4) \cdot$ , and, also, if the intramolecular change  $\cdot\text{CH}_2 \cdot \text{CO} \rightarrow \cdot\text{CH} : \text{C}(\text{OH})$  takes place with measureable velocity; (2) if there really exists a sharp difference between the solvents, chloroform, benzene, and toluene, on the one hand, and ether, on the other; (3) whether all real acids and enolic compounds gives instantaneously stable insoluble ammonium salts, as does benzoic acid.

It is found that, in general, enols react more easily than ketones, but there are exceptions, for instance, acetylacetone and the ketonic ethyl diacetoacetate, the former gives the *ammonia* compound,  $\text{CH}_3\text{Ac}_2\text{NH}_3$ , stable at 5°, m. p. 65—67°, at once on mixing a toluene solution with *N*/4 ammonia in toluene, or at -10° with ether, carbon tetrachloride, or toluene solutions. The reaction velocity does not depend solely on the structure, but also on the "chemical potential" of the interacting compounds.

Triethylamine when mixed with either the ketonic or enolic modification of dibenzoylacetylmethane in acetonitrile or ethyl bromide solution at -10° gives instantaneously the yellow colour of the salt with the same intensity in either case. Inasmuch as the ketonic isomeride is fairly stable in these media, the conclusion is drawn that the ketonic  $\rightarrow$  enolic change takes place practically instantaneously.

The authors cannot confirm the alleged difference between ether and

other solvents; sometimes precipitation occurs more quickly in toluene solution, sometimes in ether: the speed of precipitation depends, not only on the stability and insolubility of the ammonium salt, but also on the phenomena of supersaturation, as, when experiments are carried out at  $-10^{\circ}$  with acetylacetone, the additive product is at once precipitated, whereas at  $-5^{\circ}$  there is a decrease in the velocity with increasing dilution.

The use of benzoic acid ( $k$  0.0060) as a typical acid is criticised. When phenylacetic acid ( $k$  0.0055) of approximately the same strength as benzoic acid is treated with ammonia in benzene, precipitation of the salt is not instantaneous; 0.0025 of acid in 5 c.c. dry benzene with 4 c.c.  $N/480$  ammoniacal benzene takes four minutes at  $15^{\circ}$  before crystals appear, although the solubility of salt is 1 in 15,000.

In the case of acetic acid, ammonia does not at once produce a precipitate when the acid is in excess, although ammonium acetate is insoluble; this is explained by assuming the formation of a soluble hydrogen salt.

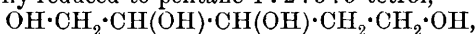
The "ammonia reaction" cannot therefore be used to distinguish between enolic and ketonic compounds.

The additive compounds with phloroglucinol, dimethyldihydroresorcin, and methyldihydroresorcin have m. p.'s  $88-91^{\circ}$ ,  $130^{\circ}$ , and  $137-140^{\circ}$  respectively. W. R.

**Decomposition of Pentaerythritol Tetraformate on Heating.** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 10, 166-168).—The ease with which  $\Delta^{4\gamma\epsilon}$ -hexatriene is obtained (van Romburgh and van Dorssen, *Abstr.*, 1906, i, 722) by heating *s*-divinylglycol formate has led to a study of the decomposition of the formates of polyhydric alcohols.

Pentaerythritol tetraformate, m. p.  $57^{\circ}$ , does not decompose in the same manner as *s*-divinylglycol formate, but, on heating at  $220-230^{\circ}$ , carbon monoxide is evolved and pentaerythritol regenerated. E. G.

**Derivatives of the  $C_5$  Sugars from Meta- and Para-Saccharin.** HEINRICH KILIÁNI and A. SAUTERMEISTER (*Ber.*, 1907, 40, 4294-4296. Compare *Abstr.*, 1904, i, 373).—Although meta- and para-saccharinic acids are entirely different in constitution, their barium salts crystallise together, and the quinine salts show almost identical melting points and solubility. The corresponding C sugars obtained on reduction are different, but their oximes have almost identical properties. The *oxime* of pentane-3 : 4 : 5-triolal (metasaccharopentose) forms thin, prismatic crystals, less soluble than sodium chloride, m. p.  $135-136^{\circ}$ ,  $[\alpha]_D + 10.6^{\circ}$ ; the *oxime* of pentane-1 : 4 : 5-triol-3-one (parasaccharopentose) has m. p.  $136-137^{\circ}$ ,  $[\alpha]_D + 11.8^{\circ}$ . The pentane-triolal is readily reduced to pentane-1 : 2 : 3 : 5-tetrol,



by means of sodium amalgam; the use of calcium (Neuberg and Marx, this vol., i, 387) for this purpose being unsuccessful. The tetrol is a syrup, but its *tetrabenzoate* forms glistening needles, m. p.  $85-86^{\circ}$ , which, like benzoyldextrose, is resistant towards acids or alkali hydroxides, but readily hydrolysed by sodium ethoxide. The tetrol so regenerated is a hygroscopic syrup;  $[\alpha]_D + 29^{\circ}$ . E. F. A.

**Combined Sulphurous Acids. III. Dextrose-sulphurous Acid.** WILHELM KERP and EMIL BAUR (*Chem. Zentr.*, 1907, ii, 971; from *Arb. Kais. Ges.-A.*, 1907, 26, 269—296. Compare this vol., i, 1010).—Two optically active stereoisomeric compounds, which are not mirror images of one another, are obtained by the interaction of sodium hydrogen sulphite and dextrose. The compound investigated up to the present is the less soluble salt; it is levorotatory, and gradually changes in solution into the other isomeride until equilibrium is established, the solution then being dextrorotatory. From electrical conductivity measurements, it follows that the free acid belongs to the strong acids. The dissociation of the complex anion is but slightly decreased by the addition of dextrose, whereas the effect produced by an increase in the number of hydrogen sulphite ions is normal. The degree of dissociation of the complex in an acid solution is not much greater than in a neutral solution, neither does it increase to any great extent with a rise of temperature. The diminution in the rate of dissociation of the complex produced by the addition of acids is very great. The addition of acetaldehyde to an aqueous solution of dextrose-sulphurous acid results in the formation of acetaldehyde-sulphurous acid and the liberation of dextrose. W. H. G.

**The Hydrolysis of Sugars.** ROBERT J. CALDWELL (*Brit. Assoc. Report*, 1906, 76, 267—292).—The report contains an historical section and summary of the different conditions under which sugar is hydrolysed. The various theories put forward to account for the inverting action of acids are discussed, and the facts in favour of the addition theory are set forth in some detail. The report also contains a complete bibliography, and the matter which is arranged in chronological sequence in each section is dated systematically throughout. G. T. M.

**Diastasic Liquefaction of Starch.** AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1907, 145, 261—263).—The diastasic liquefaction of starch is subject to the same influences as liquefaction under pressure (Abstr., 1906, i, 803, 804). N. H. J. M.

**The Present Position of the Chemistry of the Gums.** HENRY H. ROBINSON (*Brit. Assoc. Report*, 1906, 76, 227—232).—A summary of the investigations made on the nature of different gums. G. T. M.

**Complex Metal Ammonias. IV. Tetraethylenediamine-diquotelecobaltodibaltic Salts.** ALFRED WERNER [and, in part, GUSTAV JANTSCH] (*Ber.*, 1907, 40, 4426—4434. Compare this vol., i, 482).—The salts obtained by the atmospheric oxidation of aqueous solutions of cobaltous salts in the presence of ethylenediamine are found on investigation, excluding water and oxygen, to have the composition  $[\text{Co}_3\text{En}_4]\text{X}_4$ , where En = ethylenediamine and X a univalent acid radicle. When treated with cold hydrochloric acid, no halogen is evolved, but 1 mol. of the salt yields 1 mol. of a cobaltous salt and 2 mols. of a *cis*-diaquodiethylenediaminecobaltic

salt,  $[(\text{H}_2\text{O})_2\text{CoEn}_2]\text{X}_3$ . The  $\text{H}_2\text{O}$  mols. in the 2 mols. of the diaquo-salt are not present as such in the parent substance, since these compounds do not react like diaquo-salts; however, the complex of the parent compound contains 4 atoms of oxygen, which must be present in four OH groups; consequently two  $[(\text{OH})_2\text{CoEn}_2]\text{X}$  residues must be employed in the building up of the molecule. Since the molecule is decomposed by hydrochloric acid as stated above, it follows that these compounds are formed by the combination of 1 mol. of a cobaltous salt with 2 mols. of a dihydroxodiethylenediaminecobalt salt,  $\text{CoX}_2 + 2[(\text{HO})_2\text{CoEn}_2]\text{X}$ . They, however, contain, in addition, 2 mols. of water retained by them in the dried state (the function of which is not yet known), and, as in solution the whole of the acid radicle is ionised, the following constitutional formula is assigned to these salts, which are consequently named *tetraethylenediamine-diaquotetrolcobaltodicobaltic salts*,  $\left\{ \text{Co}'' \left[ \begin{smallmatrix} (\text{H}_2\text{O})_2 \\ [(\text{HO})_2\text{CoEn}_2]_2 \end{smallmatrix} \right] \right\} \text{X}_4$ .

It is pointed out that cobaltous-cobaltic hydroxide,  $\text{Co}_3(\text{OH})_8$ , probably has a similar constitution.

A solution of cobalt chloride containing ethylenediamine yields, on exposure to the air and subsequent treatment with common salt, a precipitate containing the *chloride* of the series and triethylenediaminecobalt chloride. The latter compound is removed by treating the precipitate with water, leaving the former as a bright red, slightly blue powder. This is converted by sodium sulphate into the *sulphate*,  $\left\{ \text{Co} \left[ \begin{smallmatrix} (\text{H}_2\text{O})_2 \\ [(\text{HO})_2\text{CoEn}_2]_2 \end{smallmatrix} \right] \right\} (\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ , crystallising in bright red, microscopic needles. A solution of cobalt sulphate containing ethylenediamine deposits, on exposure to the air, the sulphate in the form of red needles. It cannot be recrystallised, being sparingly soluble in water, but, when treated with barium chloride and then with sodium sulphate, a *sulphate* similar to the above, but containing  $7\text{H}_2\text{O}$ , is obtained. The following salts are similarly obtained from the chloride by double decomposition: *dithionate*,  $\text{Co}_3\text{C}_8\text{H}_{38}\text{O}_{18}\text{N}_8\text{S}_4 \cdot 2\text{H}_2\text{O}$ , a bluish-red powder; *platinichloride*,  $\text{Co}_3\text{C}_8\text{H}_{38}\text{O}_6\text{Cl}_8\text{Pt}_2 \cdot 2\text{H}_2\text{O}$ , a light brownish-red, crystalline powder; *iodide*,  $\text{Co}_3\text{C}_8\text{H}_{38}\text{O}_6\text{N}_8\text{I}_4 \cdot 2\text{H}_2\text{O}$ , a brownish-red, crystalline powder.

W. H. G.

**Action of Ammonia on the Oxides and Chlorohydrins of Hexylene and Tetramethylethylene [ $\beta$ -Dimethyl- $\Delta^{\beta}$ -butylene].** K. KRASSUSKY and L. DUDA (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1061—1076).—The tendency of  $\alpha$ -olefine oxides to combine with ammonia does not depend so markedly on the structure of the oxide as is the case with its tendency to combine with water, and in so far as the former tendency does depend on the structure of the oxide it is the reverse of that of its combination with water. The first products obtained by the action of ammonia on the chlorohydrins of hexylene and  $\beta$ -dimethyl- $\Delta^{\beta}$ -butylene are the corresponding oxides, which are formed at quite low temperatures; consequently, in the formation of  $\alpha$ -hydroxy-amines, the oxides are probably always intermediate products, and probably the whole of

the  $\alpha$ -hydroxy-amine formed from  $\alpha$ -monochlorohydrin is identical with the amine obtained from the corresponding  $\alpha$ -oxide.

$\alpha$ -Hexylene oxide is formed by heating hexylene with bleaching powder, and is best purified with 1% aqueous potassium permanganate. With aqueous ammonia in a sealed tube at  $100^\circ$ , the hexylene oxide yields: (1) a secondary hydroxy-amine,  $(C_6H_{13}O)_2NH$ ; (2)  $\alpha$ -hydroxy-hexylamine,  $NH_2 \cdot C_6H_{12} \cdot OH$ , b. p.  $189.5-190.5/750$  mm.,  $D_4^{20}$  0.9283,  $D_4^{20}$  0.9141, which behaves as an alkali towards many reagents, and is also formed under similar conditions by hexylene chlorohydrin. The *platinichloride*, *hydrochloride*, and *carbonate* have been obtained in an impure form. With nitrous acid, the  $\alpha$ -amine yields the same ketone as hexylene glycol.

$\beta\gamma$ -Dimethyl- $\Delta^8$ -butylene oxide was obtained by distilling the corresponding chlorohydrin over potassium hydroxide. To form the  $\alpha$ -amine, the oxide or chlorohydrin must be heated with a large excess of aqueous ammonia at  $100^\circ$ . The amine,  $NH_2 \cdot C_6H_{12} \cdot OH$ , has b. p.  $162-164/756$  mm., solidifies below  $0^\circ$ , and melts at  $0-2^\circ$  (Demjanoff: solid,  $10^\circ$ ), readily absorbs carbon dioxide, forming a *carbonate*, and water, forming a crystalline *hydrate*, probably  $NH_2 \cdot C_6H_{12} \cdot OH \cdot 6H_2O$ , m. p.  $30-32^\circ$ , which is also formed when the moist amine is distilled or mixed with water. On desiccation, the hydrate is transformed into the liquid amine. With the dry amine, nitrous acid produces pinacolone, but chiefly pinacone. Z. K.

**Choline Cadmium Chloride.** FRIEDRICH W. SCHMIDT (*Zeitsch. physiol. Chem.*, 1907, 53, 428).—*Choline cadmium chloride*,  $C_5H_{14}ONCl, CdCl_2$ ,

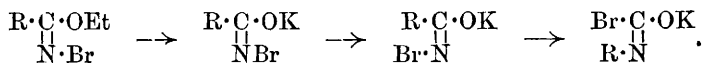
is recommended as a substitute for the platinichloride in the preparation and purification of choline. It is thrown down as a crystalline precipitate on the addition of an alcoholic solution of cadmium chloride to an aqueous solution of choline chloride. J. J. S.

**The Chemistry of Bile. II. Affinity Constant of Glycocholic Acid.** SAMUEL BONDI (*Zeitsch. physiol. Chem.*, 1907, 53, 8-13).—Pure glycocholic acid (Abstr., 1906, i, 633) is a comparatively strong acid. The dissociation constant, calculated from the results of electrical conductivity determinations with concentrations varying from 750-3000, is 0.0132. The value of  $\mu_\infty$  calculated from the sodium salt is 363. The conclusion is drawn that in cholic acid the  $\cdot CH \cdot OH$  group is not in the  $\alpha$ -position with respect to the carboxyl group. J. J. S.

**Formation of isoSerine from  $\alpha\beta$ -Dibromopropionic Acid.** CARL NEUBERG and ERICH ASCHER (*Biochem. Zeitsch.*, 1907, 6, 559-562).—In the preparation of  $\alpha\beta$ -diaminopropionic acid from  $\alpha\beta$ -dibromopropionic acid, a secondary reaction takes place, resulting in the formation of about 10% of *isoserine*,  $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CO_2H$ . This reaction is analogous to the formation of methylisoserine from  $\alpha\beta$ -dibromobutyric acid, described by Neuberg and Federer (Abstr., 1906, i, 805). G. B.



**Formation of Amines from Halogen Imino-Ethers.** MITSURU KUHARA and MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōto*, 1907, 1, 187—194. Compare Stieglitz, *Abstr.*, 1903, i, 235; 1904, i, 39).—Stieglitz (*loc. cit.*) has shown that such compounds as chloro- and bromo-benzimino-ethyl ethers,  $C_6H_5 \cdot C(OEt) : N\dot{X}$ , do not undergo the Beckmann rearrangement, but yield with hydrochloric acid, ethyl benzoate and the corresponding halogen hypo-acid. The authors now find, however, that bromo- acetimino-, -propimino-, and benzimino-ethyl ethers on heating gently with potassium hydroxide and subsequently distilling, yield considerable amounts of the corresponding amines. As Stieglitz has shown that these esters probably have the *anti*-configuration, it is suggested that on saponification the potassium salts of the same form are obtained, which change to the more stable *syn*-form, undergo the Beckmann transformation, and then decompose under the influence of alkali, yielding amines as follows :

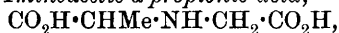


*Aceto bromoimino-ethyl ether*,  $CH_3 \cdot C(OEt) : NBr$ , was obtained as an oily liquid by the action of potassium hypobromite on acetimino-ethyl ether. Besides the decomposition referred to above with concentrated alkali, it is split up on heating with water or hydrochloric acid, ethyl acetate and bromine distilling over. The corresponding *propionimino-ether* was obtained by an analogous method, and behaves like the acetate.

Benzobromoimino-ethyl ether,  $C_6H_5 \cdot C(OEt) : NBr$ , already described by Stieglitz (*loc. cit.*), decomposes when in contact with water for some time, cyaphenine crystallising out, and bromine and ethyl benzoate being liberated. G. S.

**Iminoacetic- $\alpha$ -propionic Acid.** GEORGE STADNIKOFF (*Ber.*, 1907, 40, 4350—4353. Compare this vol., i, 393).—With the view of supporting the explanation previously given regarding the mode of formation of  $\alpha$ -iminonitriles, the author has studied the synthesis of unsymmetrical imino-acids with the idea that these can be formed by the action of an oxynitrile on an aminonitrile or an ester of an amino-acid.

A concentrated aqueous solution of potassium cyanide was gradually added to a mixture of an aqueous solution of ethyl glycine hydrochloride and acetaldehyde. The mixture was subsequently saponified by hydrochloric acid, evaporated, and the salt of the imino-acid extracted with alcohol. After successive treatment with lead hydroxide and hydrogen sulphide, the aqueous solution of the imino-acid was concentrated. *Iminoacetic- $\alpha$ -propionic acid*,



separates from aqueous alcohol in large crystals, m. p. 222—223°. Its *copper* salt was prepared. Its *ethyl* ester is a colourless, viscid liquid, with b. p. 122.5°/12 mm., and  $D_4^{20}$  1.0457; the ester forms a *nitroso*-derivative,  $C_9H_{16}O_5N_2$ , with b. p. 168—169°/13 mm., and  $D_4^{20}$  1.1398.

A. McK.

**Imino- $\alpha$ -propionicbutyric Acid.** GEORGE STADNIKOFF (*Ber.*, 1907, 40, 4353—4356. Compare preceding abstract).—Two optically inactive compounds of the formula  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$  are theoretically possible. The author has prepared these two isomeric acids, one of which is formed in greater amount than the other; the acids can be separated by means of absolute alcohol.

By the interaction of acetaldehyde, potassium cyanide, and  $\alpha$ -aminobutyronitrile hydrochloride (or ethyl  $\alpha$ -aminobutyrate hydrochloride), the mixture of acids is obtained. The one, *imino- $\alpha$ -propionicbutyric acid*, which is the more sparingly soluble of the two in alcohol, crystallises in needles, m. p. 222—223° (decomp.); its *copper* salt was prepared. The *isomeric acid* could not be obtained crystalline, but was converted into its *copper* and *nickel* salts and its *ethyl ester*,  $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}$ , having b. p. 126°/16 mm., and  $D_4^{21}$  1.0063. A. McK.

**Aminocampholic Acids.** HANS RUPE and J. SPLITTGERBER (*Ber.*, 1907, 40, 4311—4318).—The compound obtained by Oddo and Leonardi (*Abstr.*, 1897, i, 86) by heating the hydrochloride of their so-called  $\beta$ -aminocampholic acid (which really belongs to the  $\alpha$ -series) is identical with Tafel and Eckstein's  $\alpha$ -camphidone (*Abstr.*, 1902, i, 43). The authors find that the hydrochloride of  $\alpha$ -aminocampholic acid has m. p. 247—248°, and is insoluble in light petroleum (Oddo and Leonardi, m. p. 268—270°, soluble in light petroleum); the *platinichloride*,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{PtCl}_6$ , separates from water in reddish-yellow leaflets.

$\beta$ -Camphoramic acid, prepared from camphorimide and sodium hydroxide, contains the  $\alpha$ -isomeride. A separation is readily effected by treating the alkaline solution of the sodium salts with hydrochloric acid; so long as the solution does not contain free mineral acid,  $\beta$ -camphoramic acid alone separates. By treatment with cold acetyl chloride, followed by the addition of the product to 12% ammonium hydroxide, it forms camphoro- $\beta$ -mononitrile, which is reduced by sodium in dilute alcoholic solution to  $\beta$ -aminocampholic acid, of which the *hydrochloride* has m. p. 215—220° and yields  $\beta$ -camphidone above its m. p. or by treating its aqueous solution with solid sodium sulphite. The *carbamide*,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , also yields  $\beta$ -camphidone above its m. p., 203—204°. By careful treatment with sodium nitrite in the cold, the hydrochloride of  $\beta$ -aminocampholic acid yields a yellow oil, which is converted by boiling barium hydroxide into the easily soluble *barium salt*,  $(\text{OH}\cdot\text{CH}_2\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2)_2\text{Ba}$ , which on acidification yields a *lactone*, b. p. 121—122°/12 mm., which is probably  $\beta$ -campholide. C. S.

**Preparation of Acetamide by the Action of Ammonium Hydroxide on Ethyl Acetate.** ISAAC K. PHELPS and M. A. PHELPS (*Amer. J. Sci.*, 1907, [iv], 24, 429—432).—In a previous paper (Phelps and Deming, this vol., i, 832), it has been shown that, under certain conditions, a quantitative yield of formamide can be obtained from ethyl formate and ammonium hydroxide.

It is now shown that nearly theoretical quantities of acetamide can be obtained by leaving mixtures of ethyl acetate and strong solution

of ammonia for about a fortnight. The reaction takes place more rapidly if a large excess of solution of ammonia is used, or if dry ammonia is passed into the mixture at  $-8^{\circ}$  to  $-10^{\circ}$  until it is saturated.

E. G.

**Preparation of  $\alpha$ -Bromoisovalerylcarbamide.** KNOLL & Co. (D.R.-P. 185962).— $\alpha$ -Bromoisovalerylcarbamide, leaflets, m. p.  $149^{\circ}$ , obtained by the action of  $\alpha$ -bromoisovaleryl bromide or chloride on dry powdered carbamide at  $70^{\circ}$ , is a trustworthy hypnotic, which is quite free from the unpleasant secondary effects attending the therapeutic application of valeric and  $\alpha$ -bromoisovaleric acids and their derivatives.

G. T. M.

**Preparation of Aliphatic Thiocyanates, Nitriles, and Nitro-compounds.** PAUL WALDEN (*Ber.*, 1907, 40, 4301. Compare this vol., i, 752).—A correction. The interaction of methyl sulphate with potassium cyanide, potassium nitrite, and potassium thiocyanate has already been studied by Kaufler and Pomeranz (*Abstr.*, 1901, i, 634).

E. F. A.

**Dithiocyanatotetra-amminechromium Salts.** PAUL PFEIFFER and M. TILGNER (*Zeitsch. anorg. Chem.*, 1907, 55, 361—370. Compare this vol., ii, 694).—Complex salts of the type  $[(\text{SCN})_2\text{Cr}(\text{NH}_3)_4]\text{X}$ , in which X represents Cl, Br, SCN,  $\text{NO}_3$ ,  $\frac{1}{2}\text{SO}_4$ , have been prepared. The *thiocyanate* is obtained by warming an aqueous solution of chloro-aquotetra-amminechromium chloride,  $[(\text{OH}_2)\text{ClCr}(\text{NH}_3)_4]\text{Cl}_2$ , with excess of potassium thiocyanate; by the addition of hydrochloric or hydrobromic acid to the solution of this salt, the corresponding *chloride* and *bromide* are obtained. The *nitrate* is prepared from the chloride by precipitation with nitric acid, and the *sulphate* by rubbing the chloride with sulphuric acid.

The salts in question occur in small, brick-red to orange-red crystals, soluble in water with neutral reaction. The saturated solution of the chloride contains 2% of the salt.

On warming the chloride with ethylenediamine and then treating the resulting product in aqueous solution with potassium iodide, *triethylenediaminechromium iodide*,  $\{\text{Cr}[\text{C}_2\text{H}_4(\text{NH}_2)_2]_3\}\text{I}_3 \cdot \text{H}_2\text{O}$ , was obtained in yellow crystals.

Attempts to prepare compounds containing  $\text{Cl}_2$  or  $\text{Br}_2$  instead of  $(\text{SCN})_2$  in the nucleus have so far been unsuccessful.

G. S.

**Preparation of Dialkylbromoacetamides from Dialkylcyanoacetic Acids.** PAUL HOERING (D.R.-P. 186739. Compare *Abstr.*, 1905, i, 638).—The dialkylbromoacetamides, which are valuable hypnotics, are readily obtained from the dialkylcyanoacetic acids by successively converting these into dialkylacetoneitriles, bromodialkylacetoneitriles, and then by hydrolysis into the required amide. Diethylcyanoacetic acid when repeatedly distilled at  $145$ — $200^{\circ}$ , or when heated under pressure, is converted into *diethylacetoneitrile* [*pentane- $\gamma$ -carboxylonitrile*],  $\text{CHEt}_2 \cdot \text{CN}$ , b. p.  $144^{\circ}$ ; *dipropylacetoneitrile* [*heptane- $\delta$ -carboxylonitrile*],  $\text{CHPr}_2 \cdot \text{CN}$ , b. p.  $183$ — $184^{\circ}$ , is a colourless liquid with an agreeable odour.

On bromination, the two preceding compounds yield respectively *bromodiethylacetonitrile*, colourless oil, b. p. 183—185°, and *bromo-dipropylacetonitrile*, b. p. 209—211°.

*Bromodiethylacetamide*,  $\text{CHEt}_2\cdot\text{CONH}_2$ , m. p. 64—65°, is prepared by hydrolysing the corresponding acetonitrile with concentrated sulphuric acid on the water-bath. G. T. M.

**Action of Diazo-derivatives of Aliphatic Compounds on Cyanogen and its Derivatives. IV. and V. Hydrocyanic Acid.** ALBERTO PERATONER and F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 432—441, 501—513. Compare this vol., i, 979).—According to von Pechmann (*Abstr.*, 1895, i, 328, 493), the action of diazomethane on hydrocyanic acid yields acetonitrile. The authors, who have studied the interaction of these compounds in the gaseous state and in ethereal solution, and also the action of gaseous diazomethane on liquid hydrogen cyanide, find that acetonitrile is only a secondary product of the reaction, and is always accompanied by methylcarbylamine; no trace of a triazole derivative is obtained. The previous results indicate that, with a hydrogen cyanide of normal structure, the synthesis of osotriazole should take place with great readiness.

The literature dealing with the structure and tautomerism of hydrocyanic acid is discussed. T. H. P.

**The Study of Hydro-aromatic Substances.** EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, jun., MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1906, 76, 257—267).—A résumé of recent work on hydroaromatic substances, containing also references to a comparative study of dihydrolaurole, dihydroisolaurole, and 1:1-dimethylcyclohexane, and to the action of phosphorus pentachloride on trimethyldihydroresorcin. G. T. M.

**Reduction of Trimethylene [cycloPropane].** RICHARD WILLSTÄTTER and JAMES BRUCE (*Ber.*, 1907, 40, 4456—4459).—Whilst ethylene is reduced by hydrogen and nickel at 30—45°, cyclobutane is reduced to butane only at 180° (following abstract). It is now found that cyclopropane, which in its constitution lies between ethylene and cyclobutane, is reduced to propane at an intermediate temperature, the reduction commencing at 80° and taking place rapidly at 120°. Contrary to Wolkoff and Menschutkin's statement (*Abstr.*, 1899, i, 196, 321; 1900, i, 423), pure cyclopropane is readily obtained by the action of zinc dust on trimethylene dibromide (Gustavson, *Abstr.*, 1899, i, 421). G. Y.

**Derivatives of cycloButane. II.** RICHARD WILLSTÄTTER and JAMES BRUCE (*Ber.*, 1907, 40, 3979—3999).—*cyclo*Butene, prepared by distillation of trimethylcyclobutylammonium hydroxide, contains up to 10% of  $\Delta\gamma$ -butadiene. As was shown previously (Willstätter and Schmaedel, *Abstr.*, 1905, i, 514), these hydrocarbons yield dibromides which can be separated by treatment with dimethylamine when  $\alpha\delta$ -butadiene dibromide is converted into  $\alpha\delta$ -tetramethyldiamino-

$\Delta^{\beta}$ -butylene, *cyclobutene* dibromide remaining unchanged. Pure *cyclobutene* is now obtained by reduction of its dibromide with zinc dust and alcohol; on reduction by means of finely-divided nickel and hydrogen (Sabatier and Senderens, Abstr., 1905, i, 333, 401) at  $100^{\circ}$ , it yields *cyclobutane*, whilst, when reduced at  $180$ – $200^{\circ}$ , it forms butane. Attempts to prepare *cyclobutene* by distillation of amino-*cyclobutane* phosphate (Harries, Abstr., 1901, i, 194) led to the formation of butadiene. The preparation of *cyclobutane* completes the series *cyclopropane*–*cyclononane*; a table is given showing the rise of the b. p., m. p.,  $D_4^0$ , and mol. vol. at  $0^{\circ}$  throughout the series. The mol. vols. of two neighbouring members of the series differ on the average by 13, except in the case of the last pair, the mol. vol. of *cyclononane* exceeding that of *cyclooctane* by 28.54. The molecular refractions of all members of the series to *cyclooctane*, so far as observed, agree with those calculated, whereas that observed for *cyclononane* (Zelinsky, this vol., i, 780) exceeds the calculated by 0.75.

*cycloButene*, b. p.  $1.5$ – $2^{\circ}/729$  mm.,  $D_4^0$  0.733, has a slight odour, dissolves readily in acetone, is absorbed by caoutchouc, reduces potassium permanganate instantaneously, and forms additive compounds rapidly with chlorine and bromine, but slowly with iodine.

*cycloButylamine phosphate*,  $C_4H_7 \cdot NH_2, H_3PO_4$ , crystallises in prisms, m. p.  $177$ – $179^{\circ}$ . The action of bromine on the product obtained on distilling the phosphate leads to the formation of the two stereoisomeric butadiene tetrabromides, m. p.  $118^{\circ}$  and  $40$ – $41^{\circ}$  (Ciamician and Magnaghi, Abstr., 1886, 521), or of butadiene dibromide.

*cycloButane*,  $C_4H_8$ , b. p.  $11$ – $12^{\circ}/760$  mm. (corr.), remains liquid at  $-80^{\circ}$ ,  $D_4^0$  0.703,  $D_4^{-5}$  0.718,  $n_D^{20}$  1.37520, has a slight odour, burns with a luminous flame, and is stable towards concentrated hydriodic acid or bromine in chloroform solution at the ordinary temperature. Butane, formed by reduction of *cyclobutene*, *cyclobutane*, or  $\psi$ -butylene by means of hydrogen and nickel at  $180$ – $200^{\circ}$ , has b. p.  $-4^{\circ}$  to  $-1.5^{\circ}/722$  mm.

*cycloButene dichloride*,  $C_4H_6Cl_2$ , is a colourless liquid, b. p.  $133.5$ – $134.5^{\circ}/760$  mm. (corr.),  $D_4^0$  1.235,  $D_4^{20}$  1.213, and is not inflammable, but imparts a green colour to a bunsen flame. *cycloButene di-iodide* crystallises in plates, m. p.  $48^{\circ}$ ,  $D_4^{20}$  2.659, has an odour of camphor, and commences to dissociate at  $140^{\circ}$ .

The tendency of the *cyclobutane* derivatives to yield acyclic compounds, especially in reactions at high temperatures, is well known. It is now shown that *cyclobutene* dibromide and dichloride do not react with bromine alone even when heated, but, with bromine in presence of iron, *cyclobutene* dibromide yields  $\alpha\alpha\delta\delta$ -(or  $\alpha\alpha\beta\beta$ )-*tetrabromobutane*, which is obtained as a colourless oil, b. p.  $138$ – $145^{\circ}/10$  mm.,  $D_4^0$  2.562,  $D_4^{20}$  2.529,  $n_D^{20}$  1.60771, and on further bromination in presence of iron loses hydrogen bromide, forming an oily product containing small amounts of hexabromocyclobutane, and when heated with alcoholic potassium hydroxide yields a *product*,  $C_4H_4Br_2$ , b. p.  $47$ – $48^{\circ}/14$  mm.,  $D_4^0$  1.99. This is readily oxidised by potassium permanganate, forms an *additive* compound with 1 mol. of bromine, and is probably a *cyclopropane* derivative.

The action of bromine on *cyclobutene* dichloride in presence of

iron leads to the formation of *dichlorodibromobutane*, b. p. 120—125°/13 mm.,  $D_4^{20}$  2.1, *dichlorotribromobutane*, b. p. 155—157°/18 mm.,  $D_4^0$  2.47, which is the chief product, and *dichlorotetrabromobutane*, b. p. 176—185°/21 mm.,  $D_4^0$  2.69.

Whilst *cyclobutene* dibromide does not react with bromine in presence of iodine, *cyclobutene* di-iodide reacts with bromine alone, yielding tetrabromobutane.

*α-Bromobutadiene*,  $\text{CHBr}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ , formed together with a small amount of *hydrocarbon*, which gives a white precipitate with silver nitrate by the action of potassium hydroxide on *αδ*-butadiene dibromide, is obtained as a mobile liquid, b. p. 92—94°/760 mm. (corr.),  $D_4^0$  1.416, has an odour of vinyl bromide, and gradually changes into a sparingly soluble, dark brown mass, probably a polymerisation product. *α*-Bromobutadiene combines slowly with 2 mols. of bromine, forming *ααβγδ-pentabromobutane*,  $\text{C}_4\text{H}_5\text{Br}_5$ , which is a colourless oil, b. p. 165—170°/10 mm.  $D_4^0$  2.78, and consists of a mixture of two crystalline *isomerides*, which form prisms, m. p. 108°, and plates, m. p. 57—58°, respectively.

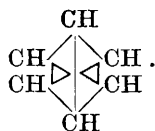
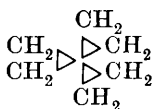
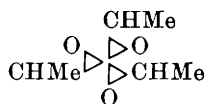
1:1-Dibromocyclobutane,  $\text{C}_4\text{H}_6\text{Br}_2$ , b. p. 157—158.5°/760 mm. (corr.),  $D_4^0$  1.960,  $D_4^{20}$  1.933,  $n_D^{20}$  1.53618 (Kijner, Abstr., 1905, i, 355), is prepared by the action of hydrogen bromide on bromo- $\Delta^1$ -cyclobutene in glacial acetic acid solution. 1:1:2-Tribromocyclobutane,  $\text{C}_4\text{H}_5\text{Br}_3$ , formed by the action of bromine on bromo- $\Delta^1$ -cyclobutene in chloroform solution, is a colourless oil, b. p. 109—110°/19—20 mm.,  $D_4^0$  2.374, has an odour of camphor, is volatile in a current of steam, and when treated with methyl-alcoholic potassium hydroxide yields 1:2-dibromo- $\Delta^1$ -cyclobutene,  $\begin{array}{c} \text{CBr}\cdot\text{CBr} \\ | \quad | \\ \text{CH}_2\cdot\text{CH}_2 \end{array}$ , which is obtained as an oil, b. p. 155—156°,  $D_4^0$  2.036, has an odour of vinyl bromide, gradually polymerises, and on oxidation with permanganate in neutral solution yields succinic acid.

1:1:2:2-Tetrabromocyclobutane,  $\text{C}_4\text{H}_4\text{Br}_4$ , formed by the action of bromine on 1:2-dibromo- $\Delta^1$ -cyclobutene in chloroform solution, crystallises in hexagonal plates, m. p. 126°, distils unchanged in a vacuum, and yields 1:2-dibromo- $\Delta^1$ -cyclobutene when heated with methyl-alcoholic potassium hydroxide. A mixture of this tetrabromocyclobutane with the somewhat similar *α*-butadiene tetrabromide has m. p. about 50°.

1:1:2:2:3-Pentabromocyclobutane,  $\text{C}_4\text{H}_3\text{Br}_5$ , formed by the action of bromine and iron powder on tetrabromocyclobutane, is a colourless oil, b. p. 175—185°/19 mm.,  $D_4^{20}$  2.88, has a terpene odour, and on treatment with bromine and iron powder at 50—80° yields 1:1:2:2:3:4-hexabromocyclobutane,  $\text{C}_4\text{H}_2\text{Br}_6$ , which crystallises from benzene in plates, m. p. 186.5° (corr.), and decomposes, evolving bromine, when heated in a tube. This hexabromo-compound closely resembles Sabanéff's hexabromotetramethylene, m. p. 183.3° (corr.) (Noyes and Tucker, Abstr., 1897, i, 261). G. Y.

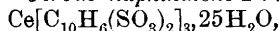
**Improbability of Kekulé's Hypothesis.** RAYMOND VIDAL (*Chem. Zentr.*, 1907, i, 1787; from *Mon. sci.*, 1907, [iv], 21, i, 244—249).—The author discusses the known objections to Kekulé's

benzene formula, and maintains that the formation of aromatic from aliphatic compounds, for example, paraldehyde from acetaldehyde and hexahydrobenzene and benzene from ethylene, is better understood by the use of such formulæ as the following :



W. H. G.

**Cerium Salts of Certain Organic Acids.** GILBERT T. MORGAN and EDWARD CAHEN (*Pharm. J.*, 1907, 78, 428—430. Compare *Trans.*, 1907, 91, 475).—*Cerous naphthalene-2 : 7-disulphonate*,



crystallises in small, nacreous leaflets having a pink colour; the water of crystallisation is only removed completely at 160°. *Cerous 4-nitrotoluene-2-sulphonate*,  $\text{Ce}[\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)\text{SO}_3]_6, 10\text{H}_2\text{O}$ , crystallises in yellow plates and intumesces on heating, leaving a bulky residue of ceric oxide. *Cerous isovalerate*,  $\text{Ce}_2(\text{C}_5\text{H}_9\text{O}_2)_6, 5\text{H}_2\text{O}$ ; *benzoate*,  $\text{Ce}_2(\text{C}_7\text{H}_5\text{O}_2)_6$ ; *cinnamate*; *o-coumarate*; *succinate*,  $\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_4)_3, 5\text{H}_2\text{O}$ , and *camphorate*,  $\text{Ce}_2(\text{C}_{10}\text{H}_{14}\text{O}_4)_3, 9\text{H}_2\text{O}$ , are white, amorphous or micro-crystalline powders, very sparingly soluble in water. *Cerous salicylate*,  $\text{Ce}_2(\text{C}_7\text{H}_5\text{O}_3)_6, 3\text{H}_2\text{O}$ , is soluble in water, and crystallises from a hot solution in stellate groups of small, light needles having a pale mauve tinge. *Cerous lactate* is very soluble; when its aqueous solution is dehydrated over sulphuric acid, it solidifies to a crystalline mass, the composition of which corresponds with a salt containing 7H<sub>2</sub>O. *Cerous oleate*, prepared by stirring precipitated cerous hydroxide and oleic acid together, is a buff-coloured substance having the consistence of lard.

H. M. D.

**Preparation of Aromatic Fluoro-compounds by Decomposing Diazo- and Bisdiazo-compounds with Concentrated Hydrofluoric Acid.** VALENTINER and SCHWARZ (D.R.-P. 186005).—The methods for obtaining fluoro-derivatives of the aromatic hydrocarbons have hitherto only furnished small yields of the products. It is now found that the diazo-fluoride produced by adding hydrofluoric acid to a solution of the diazo- or bisdiazo-chloride is readily decomposed catalytically by ferric chloride, yielding the aromatic fluoro-derivative. 4 : 4'-Difluorodiphenyl is produced on adding successively concentrated hydrofluoric acid and 10% ferric chloride solution to a solution of bisdiazodiphenyl chloride. The fluoro-derivatives of benzene, cumene, and naphthalene may be obtained similarly.

G. T. M.

**Derivatives of Diphenyleneiodonium Hydroxide: New Class of Heterocyclic Compounds containing Iodine in the Closed-Chain.** LUIGI MASCARELLI (*Atti R. Accad. Lincei.*, 1907, [v], 16, ii, 562—567).—By treating di-iodoxydiphenyl or di-iodosodiphenyl with moist silver oxide (compare Hartmann and Meyer, *Abstr.*, 1894, i, 242), the author has obtained diphenylene-

iodonium hydroxide,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{I} \cdot \text{OH}$ , closure of the ring being effected by the iodine atom becoming trivalent.

*o*-Di-iododiphenyl,  $\text{C}_6\text{H}_4\text{I} \cdot \text{C}_6\text{H}_4\text{I}$ , prepared by diazotising *o*-diaminodiphenyl and decomposing the diazo-compound with potassium iodide, separates from water as a pale yellow, microcrystalline powder, m. p. 210—211°. Its tetrachloride,  $\text{C}_6\text{H}_4\text{Cl}_2\text{I} \cdot \text{C}_6\text{H}_4\text{Cl}_2\text{I}$ , separates from chloroform in yellow, acicular crystals, m. p. 130—135° (decomp.).

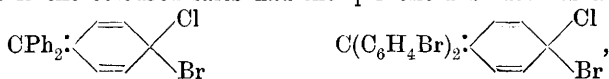
*o*-Di-iodosodiphenyl,  $\text{OI} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{OI}$ , obtained by the action of dilute potassium hydroxide solution on *o*-di-iododiphenyl tetrachloride, is a yellow, amorphous powder, m. p. 109—110°.

*o*-Di-iodoxydiphenyl,  $\text{IO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$ , obtained on boiling *o*-di-iodosodiphenyl with water, forms slender, white crystals, m. p. 280°.

Diphenyleneiodonium hydroxide, crystallising in slender, white filaments, m. p. 145—148° (decomp.), was not analysed. The *acetyl* derivative,  $\text{I}(\text{C}_6\text{H}_4)_2\text{Ac}$ , crystallises in hard, white prisms, m. p. 195.5° (decomp.), and has the normal molecular weight in freezing ethylurethane. The *oxalate*,  $\text{C}_2\text{O}_4[\text{I}(\text{C}_6\text{H}_4)_2]_2$ , crystallises from water in colourless prisms, m. p. 191—192°. T. H. P.

#### Problem of the Structural Formula of "Triphenylmethyl."

ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1907, 40, 3965—3970).—The author criticises Gomberg's quinonoid theory of the coloured salts derived from triphenylcarbinol (this vol., i, 504) from the same point of view as does Baeyer (this vol., i, 691). When treated with water, the strongly coloured double salts of stannic chloride and *p*-bromo- and tri-*p*-bromo-triphenylmethyl chlorides yield hydrogen chloride, but not even traces of hydrogen bromide. In the same manner, no trace of alkali bromide is obtained together with the alkali chloride when *p*-bromo- and tri-*p*-bromo-triphenylmethyl chlorides are heated with sulphur dioxide at 50° and subsequently with an aqueous alkali, whereas if the coloured salts had the quinonoid structures annexed:



the isomerisation would lead to the formation of mixtures of carbonyl chlorides and bromides and hence of alkali chlorides and bromides.

Schmidlin's supposed isomeric magnesium triphenylmethyl chlorides (this vol., i, 26) are criticised. Both the  $\alpha$ - and  $\beta$ -modifications react with benzoyl chloride and ethyl benzoate, forming benzopinacolin in an 80% yield. Contrary to Schmidlin's statement, the  $\alpha$ -modification on treatment with carbon dioxide in ethereal solution yields triphenylacetic acid in a 90% yield; the action of water on the reaction product leads to the formation of triphenylmethane in good yields. The *p*-benzoyltriphenylmethane obtained by Schmidlin is formed most probably by condensation of triphenylmethane with benzaldehyde.

G. Y.

**Phenanthrene Series. XXI. Hydrophenanthrenes.** JULIUS SCHMIDT and ROBERT MEZGER (*Ber.*, 1907, 40, 4240—4257).—Only two hydrophenanthrenes have been referred to previously, namely,



$\alpha$ -tetrahydrophenanthrene (Bamberger and Lodter, Abstr., 1888, 292) and octohydrophenanthrene (Graebe, Abstr., 1873, 894). By using different methods and conditions of reduction, the authors have succeeded in preparing a number of hydrogenated derivatives comprised between the limiting di- and dodeca-hydrophenanthrenes. The lower members of this series are obtained by means of sodium and amyl alcohol, and the higher ones by means of phosphorus and hydriodic acid. In order to obtain pure products and not mixtures of various hydro-derivatives difficult to resolve into their constituents, it is necessary to adhere closely to the conditions laid down by the authors. The experiments of Liebermann and Spiegel (Abstr., 1889, 719) have been repeated, the results indicating that the perhydrophenanthrene described by these authors does not exist.

9 : 10-Dihydrophenanthrene,  $C_{14}H_{12}$ , prepared either by the action of sodium and amyl alcohol on phenanthrene or by passing a mixture of hydrogen and phenanthrene vapour over reduced nickel at  $200^\circ$ , crystallises from alcohol in shining, snow-white leaflets, m. p.  $94-95^\circ$ , b. p.  $312-314^\circ/739$  mm., and closely resembles phenanthrene in its solubility and other properties. It is not acted on by bromine, but yields a *picrate*,  $C_{14}H_{12} \cdot C_6H_3O_7N_3$ , forming brick-red needles, m. p.  $135-137^\circ$ . On oxidation, it yields phenanthraquinone in almost theoretical proportion.

$\alpha$ -Tetrahydrophenanthrene [2 : 7 : 9 : 10- or 4 : 5 : 9 : 10-tetrahydrophenanthrene],  $C_{14}H_{14}$  (compare Graebe, *loc. cit.* and Bamberger, *loc. cit.*), is a colourless oil, b. p.  $307^\circ/317$  mm., m. p.  $-4^\circ$  to  $-5^\circ$ ,  $D_4^{20}$  1.080,  $n_D^{20}$  1.5820. It gives a *picrate*,  $C_{14}H_{14} \cdot C_6H_3O_7N_3$ , forming orange-red needles, m. p.  $105-106^\circ$ .

$\beta$ -Tetrahydrophenanthrene [2 : 7 : 9 : 10- or 4 : 5 : 9 : 10-tetrahydrophenanthrene],  $C_{14}H_{14}$ , is a yellow oil, b. p.  $302-303^\circ/737$  mm., m. p.  $-3^\circ$  to  $-4^\circ$ ,  $D_4^{20}$  1.085,  $n_D^{20}$  1.5820, more stable to the action of air and light than the  $\alpha$ -derivative, and yields no *picrate*.

Hexahydrophenanthrene,  $C_{14}H_{16}$ , is a colourless oil, b. p.  $289-290^\circ/737$  mm., m. p.  $-7^\circ$  to  $-8^\circ$ ,  $D_4^{20}$  1.045,  $n_D^{20}$  1.5704, and yields no *picrate*.

Octohydrophenanthrene (compare Graebe, *loc. cit.*),  $C_{14}H_{18}$ , is a colourless oil, b. p.  $282^\circ/737$  mm., m. p.  $-11^\circ$  to  $-12^\circ$ ,  $D_4^{20}$  1.012,  $n_D^{20}$  1.5599; it does not form a *picrate*.

Decahydrophenanthrene,  $C_{14}H_{20}$ , is a colourless oil, b. p.  $274-275^\circ/737$  mm., m. p.  $-18^\circ$  to  $-20^\circ$ ,  $D_4^{20}$  0.993,  $n_D^{20}$  1.5335; it does not yield a *picrate*.

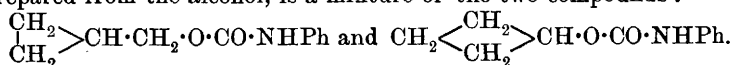
Dodecahydrophenanthrene,  $C_{14}H_{22}$ , is obtained as a colourless oil, b. p.  $268-269^\circ/737$  mm.,  $D_4^{20}$  0.964,  $n_D^{20}$  1.5119, remaining liquid at  $-20^\circ$ ; it gives no *picrate*.

No more highly hydrogenated derivative than the dodecahydro-compound could be prepared.

T. H. P.

Isomerisation of Cyclic Amines containing the Side-chain  $CH_2 \cdot NH_2$ . The Nature of the Alcohol obtained from the Amine:  $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} > CH \cdot CH_2 \cdot NH_2$ . NICOLAUS J. DEMJANOFF (*Ber.*, 1907, 40, 4393-4397; *J. Russ. Phys. Chem. Soc.*, 1907, 39, 1077-1085).—The

amine and its corresponding alcohol were prepared as described previously (*ibid.*, 1905, 37, 622), some modifications being introduced in the formation of the nitrile,  $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CN}$ . The phenylurethane, prepared from the alcohol, is a mixture of the two compounds:



When oxidised with chromic acid, the alcohol yields a mixture of aldehydes, which form two semicarbazones, one of which,



m. p. 125—126°, is soluble in ether, the other has m. p. 202.5—203°, is insoluble in ether, and is identical with the one obtained from the alcohol prepared from aminocyclobutane,  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{NH}_2$ , and

probably also with Kijner's semicarbazone of ketocyclobutane. The alcohol is also oxidised readily with nitric acid, forming much succinic acid, whilst the pure cyclopropyl carbinol yields only traces of succinic acid. It is thus evident that, contrary to Dalle's statement (*Abstr.*, 1902, i, 525), the amine,  $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{NH}_2$ , when converted into an alcohol, isomerises partially, forming a cyclobutane derivative.

Z. K.

**Preparation of Derivatives of Formaldehydesulphoxylic Acid containing Nitrogen.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 185689. Compare *Abstr.*, 1906, i, 480).—A mixture of aniline, sodium formaldehydesulphoxylate, and water is heated at 70—80° until the base has dissolved. The solution when concentrated under diminished pressure yields a deposit of acicular crystals of a new compound of aniline and the sulphoxylate. This substance decomposes in the dry state, but is stable in the form of a paste. The homologues of aniline yield similar products, and a corresponding compound of ammonia may be obtained as a white, porcelain-like mass, which differs from the original formaldehydesulphoxylate in being insoluble in methyl alcohol. The aliphatic amines give rise to similar compounds. These formaldehydesulphoxylate derivatives are powerful reducing agents, and may be employed in the printing of textile fabrics. They reduce indigo-carmin on warming, or even in the cold in the presence of mineral acids. When warmed with aqueous sodium hydroxide, these new compounds are reconverted into their generators.

G. T. M.

**Derivatives of *m*-Iodonitrobenzene, *m*-Iodoaniline, and *m*-Iodoacetanilide containing Multivalent Iodine.** CONRAD WILLGERODT and E. HJALMAR WIKANDER (*Ber.*, 1907, 40, 4066—4069).—The following salts of di-*m*-nitrophenyliodinium hydroxide are described. The *chloride*, m. p. 214°, white needles; *bromide*, white powder, decomposing at 183—184°; *iodide*, m. p. 130.5° (decomp.), yellowish-white powder; *periodide*,  $(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2\text{I}_2$ , m. p. 127° (decomp.), dark brown needles, obtained from the preceding salt and

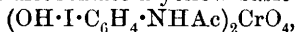
alcoholic iodine; *platinichloride*,  $2(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2\text{I} \cdot \text{PtCl}_6$ , m. p. 196—197° (decomp.), dark brown needles; *nitrate*, m. p. 194°, white needles; *hydrogen sulphate*, m. p. 168·5°; *dichromate*, yellow powder, exploding at 163°.

*m-Nitrodiphenyliodinium chloride*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{I} \cdot \text{PhCl}$ , m. p. 170—172°, is obtained by triturating *m*-nitrophenyl iododichloride and mercury diphenyl under water; the *mercurichloride* has m. p. 152°; the *platinichloride* decomposes at 177°; the *iodide* at 153°, and the *periodide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{I} \cdot \text{Ph}_3\text{I}_3$ , has m. p. 118° (decomp.).

Iodoso-, iodoxy-, and iodinium compounds have not yet been isolated from iodoanilines.

*m-Acetylaminophenyl iododichloride*,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{ICl}_2$ , is obtained in yellow crystals by passing chlorine into a solution of *m*-iodoacetanilide in glacial acetic acid at 0°, but not in chloroform; it decomposes at 66°, and by treatment with a solution of sodium carbonate is converted into *m-iodosoacetanilide*, which decomposes at 72°. C. S.

**Derivatives of *p*-Iodoacetanilide containing Multivalent Iodine, and *p*-Aminodiphenyliodinium Compounds.** CONRAD WILLGERODT and WALTER NÄGELI (*Ber.*, 1907, 40, 4070—4077. Compare preceding abstract).—*p-Acetylaminophenyl iododichloride*,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{ICl}_2$ , m. p. 110° (decomp.), prepared in the usual manner, forms very stable yellow needles. Cold sodium carbonate solution converts it into *p-iodosoacetanilide*, which decomposes at 114°, and forms with potassium dichromate a yellow basic *chromate*,



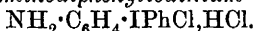
which decomposes at 85—90°. *p-Iodoxyacetanilide*,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$ , prepared from the iodoso-compound and a small excess of sodium hypochlorite solution, the reaction being accelerated by the addition of a few drops of glacial acetic acid, explodes at 163°.

*p-Acetylaminodiphenyliodinium hydroxide*,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{I} \cdot \text{Ph} \cdot \text{OH}$ , is obtained in aqueous solution from iodoxybenzene and *p*-iodosoacetanilide in the usual manner, or by decomposing the iodinium chloride with moist silver oxide. The *chloride*, m. p. 190°, is prepared from the hydroxide, or from mercury diphenyl and *p*-acetylaminophenyl iododichloride. The *bromide* has m. p. 183°; the *iodide*, m. p. 174°; the *periodide*, m. p. 145° (decomp.); *nitrate*, m. p. 180·5°; *dichromate*, decomp. 60°; *platinichloride*, m. p. 166°; *mercurichloride*, decomp. 109°.

*Di-p-acetylaminophenyliodinium hydroxide*,  $(\text{NHAc} \cdot \text{C}_6\text{H}_4)_2\text{I} \cdot \text{OH}$ , forms the following salts. The *chloride* is too soluble to be isolated in the crystalline state. The *bromide*, m. p. 165°; the *iodide*, m. p. 176·5°; *dichromate*, m. p. 176° (decomp.); *platinichloride*, m. p. 162° (decomp.); *mercurichloride*, m. p. 162°. *p-Acetylaminophenyl-p-tolyliodinium hydroxide* forms the salts: *chloride*, m. p. 204·5°; *bromide*, m. p. 185°; *iodide*, m. p. 157°; *dichromate*, m. p. 140° (decomp.); *platinichloride* begins to decompose at 159°, and then has m. p. 178°; *mercurichloride*, m. p. 145°.

Hydrolysis of *p*-acetylaminodiphenyliodinium chloride takes place when the substance is heated with 10% alcoholic hydrogen chloride

for one hour on the water-bath, the products being ethyl acetate and the *hydrochloride* of *p*-aminodiphenyliodinium chloride,



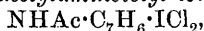
The corresponding *platinichloride*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{I} \cdot \text{Ph} \cdot \text{HPtCl}_6$ , prepared from a strongly acidified solution of the iodinium chloride and excess of platonic chloride, crystallises in small needles, m. p.  $194^\circ$  (decomp.).

The *platinichloride*,  $2\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{I} \cdot \text{Ph} \cdot \text{PtCl}_6$ , is a yellow, crystalline precipitate obtained by adding platonic chloride to an aqueous solution of the iodinium chloride, and decomposes above  $240^\circ$ . The *bromide* has m. p.  $182.5^\circ$ ; the *iodide*, m. p.  $164^\circ$ ; the *dichromate* blackens at  $130^\circ$ , and has m. p.  $143^\circ$  (decomp.).

Azo-compounds are obtained in an impure state from a diazotised solution of *p*-aminodiphenyliodinium bromide and  $\beta$ -naphthol or *R*-salt. C. S.

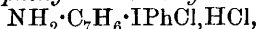
**Derivatives of *p*-Iododiphenyliodinium Chloride and of Iodoaceto-*o*-toluidide containing Multivalent Iodine. Preparation of Chloroacylamines containing Iodine.** CONRAD WILLGERODT and KARL HEUSNER (*Ber.*, 1907, 40, 4077—4085).—Meyer and Hartmann's *p*-iododiphenyliodinium iodide can be prepared by treating the diazotised solution of the hydrochloride of *p*-aminodiphenyliodinium chloride (preceding abstract) with a solution of potassium iodide (2 mols.); it has m. p.  $145^\circ$ ; the *bromide* has m. p.  $166^\circ$ .

*Iodoaceto-*o*-toluidide*,  $\text{NHAc} \cdot \text{C}_7\text{H}_6\text{I}$ , m. p.  $169.5^\circ$ , is obtained from aceto-*o*-toluidide and iodine monochloride in glacial acetic acid. The position of the halogen is not yet determined, but it is probably para to the acetyl-amino-group. The following compounds are prepared by the usual methods: *o*-acetylaminotolyl iododichloride,



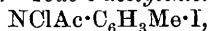
forms stable yellow crystals and decomposes at  $109^\circ$ ; the *iodoso*-compound is very unstable, and the *iodoxy*-compound has not been isolated. *Phenyl-*o*-acetylaminotolyl iodinium hydroxide* forms a *chloride*, m. p.  $179^\circ$ ; *bromide*, m. p.  $173.5^\circ$ ; *iodide*, m. p.  $152^\circ$ ; *dichromate*, decomposing at  $65^\circ$ ; *platinichloride*, beginning to decompose at  $100^\circ$ , and m. p.  $135^\circ$  (decomp.).

The *hydrochloride* of *phenyl-*o*-aminotolyl iodinium chloride*,



is obtained by hydrolysing the preceding iodinium chloride by 10% alcoholic hydrogen chloride; it begins to decompose at  $150^\circ$ , and has m. p.  $255^\circ$  (decomp.). The *bromide*,  $\text{NH}_2 \cdot \text{C}_7\text{H}_6 \cdot \text{I} \cdot \text{PhBr}$ , has m. p.  $175^\circ$ ; the *iodide*, m. p.  $169^\circ$ ; *dichromate*, decomp.  $155^\circ$ ; *platinichloride*, m. p.  $157^\circ$  (decomp., beginning at  $120^\circ$ ).

*Iodoxy-*o*-acetylchloroaminotoluene*,  $\text{NClAc} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{IO}_2$ , is obtained from *o*-acetylaminotolyl iododichloride and sodium hypochlorite in acetic acid solution; the composition is controlled by an estimation of the halogens and of the iodine liberated from potassium iodide. *Acetylchloroamino-*p*-iodoxybenzene*,  $\text{NClAc} \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$ , prepared in a similar manner, explodes at  $158^\circ$ . *Iodo-*o*-acetylchloroaminotoluene*,



m. p.  $92^\circ$  (decomp., beginning at  $85^\circ$ ), is obtained by adding slowly a

solution of sodium hypochlorite to a not too concentrated solution of iodoaceto-*o*-toluidide in glacial acetic acid. *Acetylchloroamino-p*-iodobenzene,  $\text{NClAc} \cdot \text{C}_6\text{H}_4 \cdot \text{I}$ , prepared in a similar manner, has m. p.  $127^\circ$  (decomp., beginning at  $115^\circ$ ).  
C. S.

**The Transformation of Aromatic Nitroamines and Allied Substances and its Relation to Substitution in Benzene Derivatives.** FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Ass. Report*, 1906, 76, 159—161).—A summary of the reactions of *s*-tribromonitroaminobenzene and of changes which lead to the displacement of halogen by hydroxyl in halogenated benzene-diazo-compounds.  
G. T. M.

**Preparation of *p*-Nitrodiphenylamine and its Derivatives.** IRMA GOLDBERG (D.R.-P. 185663).—Although *p*-chloronitrobenzene and aniline do not interact alone, a mixture of the two compounds may be caused to condense by heating with potassium carbonate in the presence of a small proportion of cuprous iodide. Nitrobenzene may be employed as a diluent, and the aniline may be replaced by other aromatic amines. 4-Nitrophenyl-*p*-tolylamine, green crystals, m. p.  $138^\circ$ , was thus obtained from *p*-toluidine; 4 : 4'-dinitrodiphenylamine was produced from *p*-nitroaniline, *p*-chloronitrobenzene, potassium carbonate, and cuprous iodide when the mixture was heated for eighteen hours in boiling nitrobenzene. When the *p*-nitroaniline is replaced by anthranilic acid, 4-nitrophenylanthranilic acid, m. p.  $211^\circ$ , was obtained.  
G. T. M.

**Beckmann's Rearrangement.** MITSURU KUHARA and TADAKA KAINOSHÔ (*Mem. Coll. Sci. Eng. Kyôto*, 1907, 1, 254—264. Compare Beckmann, *Abstr.*, 1894, i, 240).—Varying quantities of diphenylketoxime, dissolved in chloroform, were heated with a constant quantity of acetyl chloride for some hours at  $100$ — $110^\circ$ , and it was found that the amount of benzanilide formed by the Beckmann rearrangement was proportional to the oxime concentration only; it is therefore suggested that the action of the acetyl chloride in the reaction is catalytic. Further, when a fixed amount of acetyldiphenylketoxime is heated for some time with varying proportions of hydrochloric acid in chloroform solution, the amount of benzanilide formed is approximately proportional to the concentration of acid. Chlorobenzylideneaniline,  $\text{NPh} : \text{CPhCl}$ , which may be an intermediate product in the Beckmann rearrangement, reacts immediately with a mixture of acetic anhydride and glacial acetic acid with formation of benzanilide and acetyl chloride.

On the basis of these results and of those of previous observers, it is suggested that the Beckmann rearrangement in the presence of acetyl chloride depends on the formation of an intermediate compound of acetyl chloride and the oxime, which undergoes rearrangement under the catalytic influence of the hydrochloric acid produced, the

latter also taking a direct part in the final stage of the reaction, in which the substituted amide is produced and acetyl chloride regenerated.  
G. S.

***N*-Alkylketoximes.** JOHANNES SCHEIBER and HUBERT WOLF (*Annalen*, 1907, **357**, 25—48. Compare Beckmann and Scheiber, this vol., i, 829).—Aldehydes react with  $\beta$ -substituted hydroxylamines forming additive compounds which undergo intramolecular condensation to *N*-alkylaldoximes. It was to be expected that the products obtained from the action of  $\beta$ -substituted hydroxylamines on acetone and ethyl acetoacetate are formed in the same manner. A comparison of these substances with the *N*-alkylaldoximes leads to the conclusion that the first stage of the reaction is the formation of an additive compound; the further action, however, varies with the ketone and the  $\beta$ -substituted hydroxylamine. The condensation products of acetone and  $\beta$ -substituted hydroxylamines differ from the *N*-alkylaldoximes in that they decompose on fusion, are unstable in solution, have mol. weights double those corresponding with the

formula  $\text{CRR}''\text{<}\begin{smallmatrix} \text{NR}' \\ \text{O} \end{smallmatrix}$ , and are decomposed by phenylcarbimide and acid chlorides or anhydrides. The action of hydrogen chloride on *N*-alkylacetoximes in ethereal solution leads to the formation of an unstable, white *substance*, probably a decomposition product. The action of hydrogen chloride on a mixture of acetone and an arylhydroxylamine leads to the formation of the hydrochloride of the basic transformation product of the latter. When boiled with hydriodic acid, *N*-arylacetoximes are hydrolysed, forming their components, the hydroxylamine being then reduced to the corresponding amine. As mesityl oxide condenses with phenylhydroxylamine, forming a *product*, m. p. 107°, and with benzylhydroxylamine, forming an *additive* compound,  $\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}$ , m. p. 101—102°, the reaction of acetone with arylhydroxylamines cannot be preceded by condensation of the ketone. When heated with hydroxylamine hydrochloride and sodium hydrogen carbonate in alcoholic solution, the condensation product of acetone and phenylhydroxylamine yields a *product*,  $(\text{C}_6\text{H}_{10}\text{ON})_x$ , m. p. 135°; similarly, the condensation product of acetone and *p*-tolylhydroxylamine yields a *substance*, m. p. 112°, having approximately the same composition. It is considered that the condensation products of acetone with arylhydroxylamines may be formed by condensation of 2 mols. of the primary additive compound and be represented by the formula  $\text{O<}\begin{smallmatrix} \text{NR}\cdot\text{CMe}_2 \\ \text{NR}\cdot\text{CMe}_2 \end{smallmatrix}\text{O}$  or  $\text{O<}\begin{smallmatrix} \text{NR}\cdot\text{CMe}_2 \\ \text{CMe}_2\cdot\text{NR} \end{smallmatrix}\text{O}$ .

It is now found that the action of phenylhydroxylamine on ethyl acetoacetate leads to the formation of two isomeric *products*,  $\text{C}_{22}\text{H}_{24}\text{O}_5\text{N}_2$ , crystallising in white prisms, m. p. 120—121° and 136° respectively, which when treated with glacial acetic acid are transformed into a third *isomeride* crystallising in needles, m. p. 137°. A mixture of this with the isomeride, m. p. 136°, has m. p. 110°. When treated with bromine in alcoholic solution, the three isomerides form a mixture of *mono*- and *di*-bromo-derivatives, m. p. 166°. The constitution of the condensation products of phenylhydroxylamine and ethyl

acetoacetate, which may be stereoisomerides, is discussed. It is probable that the three substances are formed by way of an intermediate product,

$\text{OH}\cdot\text{NPh}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{NPh}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which may undergo further condensation in various directions.

The action of *p*-tolylhydroxylamine on ethyl acetoacetate leads to the formation of only the one product, m. p. 172°, which has probably the constitution  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{C}(\text{Me})\cdot\text{CO}_2\text{Et}$ . With bromine in alcoholic solution, it yields a *bromo*-derivative,  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{NBr}$ , m. p. 190°.

Diacetyl and benzylhydroxylamine form a white, crystalline *additive* compound,  $\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}$ , m. p. 107·5°, which gradually decomposes to a brown, viscid oil, and is soluble in hot, but insoluble in cold, solvents; its formation may serve to characterise benzylhydroxylamine. With hydrogen chloride, phenylhydrazine, phenylcarbimide, and hydroxylamine, the additive compound gives the reactions of its components.

Phenylhydroxylamine forms two white, crystalline *additive* compounds with diacetyl:  $\text{C}_4\text{H}_6\text{O}_2\cdot\text{C}_6\text{H}_7\text{ON}$ , m. p. 95°, and  $2\text{C}_4\text{H}_6\text{O}_2\cdot\text{C}_6\text{H}_7\text{ON}$ ,

m. p. 105°; the constitution of the former is represented by the formula  $\text{OH}\cdot\text{NPh}\cdot\text{CMe}(\text{OH})\cdot\text{COMe}$ , but that of the latter, although discussed, remains undecided.

In the absence of a solvent, diacetyl and *p*-tolylhydroxylamine form a white, crystalline *additive* compound,  $2\text{C}_4\text{H}_6\text{O}_2\cdot\text{C}_7\text{H}_9\text{ON}$ , m. p. 106°, but in solution and cooled by ice an *isomeride*, m. p. 132°. Naphthylhydroxylamine and diacetyl combine with slight development of heat, forming a viscid *product*. When heated with dilute mineral acids, the additive compounds of diacetyl and arylhydroxylamines are decomposed quantitatively into their components.

Methyl ethyl diketone reacts with  $\beta$ -substituted hydroxylamines with slight development of heat, forming unstable *products*. Attempts to form additive compounds of benzyl methyl diketone and benzil with  $\beta$ -substituted hydroxylamines were unsuccessful. G. Y.

**Compounds of  $\alpha$ -Naphthylcarbimide with Amino-Acids.** CARL NEUBERG and E. ROSENBERG (*Biochem. Zeitsch.*, 1907, 5, 456—460).—By shaking the alkaline solutions of amino-acids with  $\alpha$ -naphthylcarbimide, the following compounds were obtained. With *l*-alanine,  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_2$ , m. p. 202°; with *d*-isoleucine,  $\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}_2$ , m. p. 178°; with *l*-aspartic acid,  $\text{C}_{15}\text{H}_{14}\text{O}_5\text{N}_2$ , m. p. 115°; with *l*-asparagine,  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3$ , m. p. 199°; with *d*-phenylalanine,  $\text{C}_{20}\text{H}_{18}\text{O}_3\text{N}_2$ , m. p. 155°; with tryptophan,  $\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}_3$ , m. p. 159—160°; with *dl*-serine,  $\text{C}_{14}\text{H}_{14}\text{O}_4\text{N}_2$ , m. p. 192°; with  $\delta$ -aminovaleric acid,  $\text{C}_{16}\text{H}_{18}\text{O}_3\text{N}_2$ , m. p. 195—196°; with *dl*-leucylglycine,  $\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}_3$ , m. p. 186°. The yield is mostly 80—90%;  $\alpha$ -naphthylcarbimide derivatives can be precipitated as the very stable silver or copper salts, and these can be estimated by ignition. G. B.

**Analysis of Pine Tar.** PETER KLASON, JOHN KÖHLER, and F. FRIEDEMANN (*Arkiv. Kem. Min. Geol.*, 1907, 2, No. 36, 1—31).—Methods and results of analysis of pine tars of various origins are given (compare Ström, *Abstr.*, 1900, i, 577). T. H. P.

**Red and White Isomeric Silver Salts of 2:4:6-Tribromophenol.** HENRY A. TORREY and WILLIAM H. HUNTER (*Ber.*, 1907, 40, 4332—4335).—Three methods are described for the preparation of a colourless silver 2:4:6-tribromophenoxide, of which the best is the following. The freshly precipitated red silver salt is dissolved in a small quantity of concentrated ammonium hydroxide, the solution diluted, and nearly neutralised with dilute sulphuric acid. After further dilution, the solution is treated with a concentrated solution of silver nitrate, whereby the pure white silver salt is generally precipitated. The red and the white varieties yield the same ethyl ether, and behave alike towards ethyl or methyl iodide in the absence of a solvent, forming an amorphous substance, m. p. above  $250^{\circ}$  (decomp.), which does not contain iodine.

The authors propose the ordinary benzenoid formula for the white salt, and an ortho-quinonoid formula for the red,  $O:C_6H_2Br_3:BrAg$ .

C. S.

**Aminophenolsulphonic and Aminocresolsulphonic Acids.**  
**II. 3-Nitro- and 3-Amino-o-cresolsulphonic Acids.** GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4319—4322. Compare Abstr., 1906, i, 837).—3-Nitro-o-cresol-5-sulphonic acid, prepared by heating 3-nitro-o-cresol with twice the quantity of concentrated sulphuric acid, crystallises with  $3H_2O$ . The sodium, potassium, barium, strontium, and calcium salts are described; those of the type  $NO_2 \cdot C_7H_7(OH) \cdot SO_3M$  are less coloured than those containing two equivalents of the metal. By reduction with hydrochloric acid and stannous chloride, the acid yields 3-amino-o-cresol-5-sulphonic acid, which crystallises in needles containing  $\frac{1}{2}H_2O$ , and gives a deep red coloration with ferric chloride.

C. S.

**Aminophenolsulphonic and Aminocresolsulphonic Acids.**  
**III. 4-Nitro- and 4-Amino-m-cresol-6-sulphonic Acids.** GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4322—4323).—4-Nitro-m-cresol and concentrated sulphuric acid at  $70^{\circ}$  yield, after four to six hours, 4-nitro-m-cresol-6-sulphonic acid, which crystallises in needles; the disodium salt,  $NO_2 \cdot C_7H_7(ONa) \cdot SO_3Na, 3H_2O$ , forms orange-yellow prisms. By reduction, the acid yields the corresponding amino-acid.

C. S.

**Aminophenolsulphonic and Aminocresolsulphonic Acids.**  
**IV. Sulphonation of 3-Nitro-p-cresol.** GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4324—4325).—3-Nitro-p-cresol is not attacked by concentrated sulphuric acid at the ordinary temperature, and is decomposed at higher temperatures. Fuming sulphuric acid at  $0^{\circ}$  converts it into an acid,  $C_7H_8O_4$ , m. p.  $128^{\circ}$ , which forms an ethyl ester,  $C_6H_7O_2 \cdot CO_2Et$ , b. p.  $205^{\circ}$ , with an odour of melons, of which the yellow phenylhydrazone has m. p.  $96^{\circ}$ , and the colourless semicarbazone, m. p.  $110^{\circ}$ .

C. S.

**2-Amino-1-methylphenylene-4:5-dithiol [2-Amino-4:5-dithioltoluene] and Sulphineazo-dyes.** FRITZ FICHTER, JAROSLAV FRÖHLICH, and MARX JALON (*Ber.*, 1907, 40, 4420—4425. Compare Fröhlich, this vol., i, 632).—In accordance with the views of Fried-



länder and Mauthner (Abstr., 1905, i, 102), the introduction of two mercaptan groups in positions ortho to one another into a simple azo-dye, such as *o*-tolueneazo- $\beta$ -naphthylamine, is found to confer on the compound the characteristic dyeing properties of sulphur dyes.

2-Nitro-*p*-toluidine-5-sulphonic acid is converted by Leuckart's method (Abstr., 1890, 603) into *potassium 4-xantho-2-nitrotoluene-5-sulphonate*,  $C_{10}H_{10}O_6NS_3K, 1\frac{1}{2}H_2O$ , obtained as very small, light brown, prismatic needles, decomposing above  $150^\circ$ . Hydrolysis by potassium hydroxide results in the formation of the *dipotassium salt of 6-nitro-4-thioltoluene-3-sulphonic acid*,  $C_7H_5O_5NS_2K_2, 2H_2O$ , crystallising in brilliant, dark red prisms; a solution of the salt gives a light yellow precipitate with lead acetate. Both the solid salt and its aqueous solutions are oxidised by atmospheric oxygen to the *potassium salt of the corresponding disulphide*,  $S_2[C_6H_2Me(NO_2) \cdot SO_3K]_2, 5H_2O$ , obtained as long, yellow needles, which is reduced by stannous chloride and hydrochloric acid to the corresponding *amine*,  $S_2[C_6H_2Me(NH_2) \cdot SO_3H]_2$ , forming small, colourless crystals. The potassium salt of the nitro-compound yields with phosphorus pentachloride the *sulphochloride*,  $S_2[C_6H_2Me(NO_2) \cdot SO_2Cl]_2$ , crystallising in light brown prisms, m. p.  $208^\circ$ , which on reduction is converted into 2-amino-4:5-dithioltoluene, the *hydrochloride* of which,  $C_7H_9NS_2, HCl$ , is obtained as a white, crystalline powder; the *lead salt* is orange-red; the *diethyl ether*,  $C_{11}H_{17}NS_2$ , is a thick oil, b. p.  $225-227^\circ/25$  mm.; its *sulphate*,  $(C_{11}H_{17}NS_2)_2, H_2SO_4$ , crystallises in long, colourless, silky needles. 2-Amino-4:5-dithioltoluene is oxidised by the air with the formation of a *substance*,  $(C_7H_7NS_2)_x$ , obtained as an amorphous, yellow powder insoluble in the common solvents.

*Toluene-2-azo- $\beta$ -naphthylamine 4:5-disulphide*,  $C_{17}H_{13}N_3S_2$ , obtained by the addition of  $\beta$ -naphthylamine to a diazotised solution of 2-amino-4:5-dithioltoluene as a dark red, amorphous powder, is insoluble in the common solvents, but dissolves in an aqueous alkali sulphide solution, forming a dark red solution which dyes unmordanted wool red. The precipitate obtained on acidifying this solution is partially soluble in alcohol, from which solution after a time, or on the addition of hydrogen peroxide, the disulphide separates; it is therefore probable that the disulphide is reduced to the dithiol before it dissolves.

W. H. G.

**Condensation of Aldehydes with Phenols. Condensation of Quinol with Benzaldehyde and Formaldehyde.** PAWEŁ SHORYGIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1094-1109).—A short summary of the work done so far on the subject is given, and it is pointed out that one criterion for judging the mode of reaction of aldehydes and phenols in the cases which do not comply with the general rule has never been applied, namely, the determination of the molecular weights of the substances formed.

Quinol reacts with benzaldehyde, forming 3:6:3':6'-*tetrahydroxy-triphenylmethane*,  $CHPh[C_6H_3(OH)_2]_2$ , readily soluble in, but decomposed by, alkalis, dissolves in concentrated sulphuric acid, forming a dense, dark red liquid, reduces Fehling's solution, and when heated at ordinary or reduced pressure does not melt, but loses water and decom-

poses. Oxidising agents, such as chromic acid or hydrogen peroxide, also decompose it. When kept over phosphoric oxide, the *anhydride*,  $\text{CHPh} \langle \text{C}_6\text{H}_3(\text{OH}) \rangle \text{O}$ , is formed, which, when exposed to air, is reconverted to the original compound.

The *triacetyl* derivative, possibly  $\text{CPhAc} \langle \text{C}_6\text{H}_3(\text{OAc}) \rangle \text{O}$ , is hydrolysed readily, forming a brown, powdery *substance*,  $\text{C}_{21}\text{H}_{16}\text{O}_4$ , which decomposes on heating. The *tribenzoyl* derivative,  $\text{C}_{40}\text{H}_{26}\text{O}_6$ , is a light amorphous, pink powder, which turns dark red on heating and has m. p. 220—240° (decomp.).

With formaldehyde, quinol forms 3:6:3':6'-*tetrahydroxydiphenylmethane*,  $\text{CH}_2[\text{C}_6\text{H}_3(\text{OH})_2]_2$ , a light amorphous, brown powder, which decomposes on distillation at ordinary or reduced pressure, forming a small quantity of a colourless *substance*, m. p. 100—115°.

The diphenyl compound is very similar in properties to the triphenyl compound, but does not dissolve in sulphuric acid; with acetic anhydride, it forms a *diacetyl* derivative,  $\text{C}_{17}\text{H}_{16}\text{O}_6$ , a bright yellow, amorphous substance similar in properties to the corresponding triphenyl derivative. Z. K.

**Main Constituent of Japanese Lac.** RIKO MAJIMA and S. CHŌ (*Ber.*, 1907, 40, 4390—4393. Compare Yoshida, *Trans.*, 1883, 43, 472; Tschirch and Stevan, *Abstr.*, 1906, i, 31; Miyama, *japanische Amtsber.*, 1906, No. 1000).—Urushic acid has the composition C 79.65 and H 9.75 after careful purification by alcohol and petroleum; the "nitrogen" previously found in the acid was really carbon monoxide (Miyama, *loc. cit.*). Dry distillation of urushic acid gives methane, hexane, hexylene, heptane, heptylene, octane, octylene,  $\text{C}_{14}\text{H}_{28}$ ,  $\text{C}_{14}\text{H}_{26}$ , and catechol, with small quantities of fatty acids and carbon dioxide. Oxidation with nitric acid gives a mixture from which oxalic, succinic, and suberic acids were isolated. Methylation of urushic acid gives a substance which has no longer phenolic reactions, is not hydrolysed by alcoholic potassium hydroxide, and not oxidised by nitric acid. Methoxyl determinations appear to show that about one-sixth of the oxygen is not methylated.

Urushic acid is readily acetylated and benzoylated, and these results show that urushic acid is a polyhydroxyphenol containing a large hydrocarbon grouping. W. R.

**Preparation and Properties of Trimethylenecarbinol [*cyclo*-Propylcarbinol] and some of its Derivatives.** NICOLAUS J. DEMJANOFF and K. FORTUNATOFF (*Ber.*, 1907, 40, 4397—4399; *J. Russ. Phys. Chem. Soc.*, 1907, 39, 1085—1094. Compare this vol., i, 1023).—Pure *cyclopropylcarbinol* was prepared by reducing ethyl *cyclopropionate* according to Bouveault and Blanc's method (*Abstr.*, 1904, i, 642), and has b. p. 123.2—123.4°/738 mm.,  $D_0^{20}$  0.9154,  $D_0^{17.5}$  0.8995,  $n_D^{15.1}$  1.4313; the *urethane* forms needle-shaped crystals, m. p. 100—104°. With chromic acid, the alcohol yields the corresponding *aldehyde*,  $\text{CH}_2 \rangle \text{CH} \cdot \text{COH}$ , b. p. 98°/734 mm.,  $D_0^{20}$  0.9473,

$D_0^{17.6}$  0.9294,  $n_D^{15.2}$  1.4286, which yields a *semicarbazone*, m. p. 126°, soluble in ether.

Prolonged heating with hydrobromic acid causes the ring to break, and most of the alcohol is converted into a mixture of dibromides, mostly  $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , together with  $\text{CH}_2\text{Me}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$  and  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_2\cdot\text{CH}_2\text{Br}$ . A small quantity of a *monobromide*,

probably  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CH}\cdot\text{CH}_2\text{Br}$ , is also formed, and has b. p. 103°,  $n_D^{15}$  1.4633,  $D_0^{6.3}$  1.3740,  $D_0^{15}$  1.3600. Z. K.

### Fission of Substituted Phenyl Benzyl Ethers by Alkalis.

KARL AUWERS [and, in part, OTTO MAHLER] (*Annalen*, 1907, 357, 85—94. Compare Auwers and Rietz, this vol., i, 919).—Certain halogen substituted phenyl benzyl ethers (Auwers, Traun, and Welde, *Abstr.*, 1900, i, 168) are hydrolysed, not only by strong acids, but also when gently heated with alcoholic alkalis, or even when boiled with acetic anhydride. As Kumpf (*Abstr.*, 1884, 1005) and Frische (*Abstr.*, 1884, 1337) found that di- and tri-nitro-derivatives of phenyl and *p*-tolyl benzyl ethers are hydrolysed by alcoholic potassium hydroxide, whereas the mono-nitro-derivatives and parent ethers remain unchanged, it seemed probable that the ease with which the halogen substituted ethers in question are hydrolysed depends on the accumulation of the negative substituting groups. The authors have now found that, when boiled with alcoholic potassium hydroxide for three days, mono- and di-bromo-, dichloro-, and bromonitro-derivatives of phenyl benzyl ether, as also tribromo-derivatives having the bromine atoms distributed between the two benzene nuclei, remain unchanged, whereas under the same conditions 2:4:6-tribromo-, pentabromo-, and 2:4:6-trichloro-phenyl, and 2:4:6-tri-iodo-*m*-tolyl benzyl ethers, as also 2:4-dichlorophenyl 4-nitrobenzyl ether, are completely hydrolysed to the phenol and benzyl alcohol in one day or less. Since  $\psi$ -cumyl and dibromo- $\psi$ -cumyl benzyl ethers remain unchanged, the stability of phenyl benzyl ether is not diminished by the introduction of methyl groups.

The following substituted phenyl benzyl ethers are prepared by boiling the corresponding phenol with the benzyl chloride or bromide and sodium ethoxide in alcoholic solution.

*o*-Bromophenyl benzyl ether,  $\text{C}_{13}\text{H}_{11}\text{OBr}$ , slightly yellow oil, decomp. on distillation. *p*-Bromophenyl benzyl ether,  $\text{C}_{13}\text{H}_{11}\text{OBr}$ , rose-coloured needles, m. p. 64—65°. *o*-Bromophenyl *o*-bromobenzyl ether,  $\text{C}_{13}\text{H}_{10}\text{OBr}_2$ , viscid oil, which slowly crystallises, m. p. slightly above the ordinary temperature. *p*-Bromophenyl *p*-bromobenzyl ether, small, white needles, m. p. 111°. *p*-Bromophenyl *o*-bromobenzyl ether, oil, decomp. partially on distillation. *o*-Bromophenyl *p*-bromobenzyl ether, small, white needles, m. p. 72—74°. 2:4-Dibromophenyl benzyl ether, small needles, m. p. 68°. 2:4-Dibromophenyl *o*-bromobenzyl ether,  $\text{C}_{13}\text{H}_9\text{OBr}_3$ , long, white needles, m. p. 79°. 2:4-Dibromophenyl *p*-bromobenzyl ether, long, white needles, m. p. 93°. 2:4-Dichlorophenyl benzyl ether,  $\text{C}_{13}\text{H}_{10}\text{OCl}_2$ , crystallises in cubes, m. p. 61—62°. *p*-Bromo-*o*-nitrophenyl benzyl ether,  $\text{C}_{13}\text{H}_{10}\text{O}_3\text{NBr}$ , yellow needles, m. p. 84—85°. 2:4:6-Tribromophenyl benzyl ether,  $\text{C}_{13}\text{H}_9\text{OBr}_3$ , needles, m. p. 85°.

*Pentabromophenyl benzyl ether*,  $C_{13}H_7OBr_5$ , white needles, m. p. 203—204°. *2:4:6-Trichlorophenyl benzyl ether*,  $C_{13}H_9OCl_3$ , long, white needles, m. p. 64—65°. *Tri-iodo-m-tolyl benzyl ether*,  $C_{14}H_{11}OI_3$ , white needles, m. p. 131°. *2:4-Dichlorophenyl p-nitrobenzyl ether*,  $C_{13}H_9O_3NCl_2$ , yellow needles, m. p. 148—150°. *Benzyl  $\psi$ -cumyl ether*,  $C_{16}H_{18}O$ , prisms, m. p. 45°. *Benzyl dibromo- $\psi$ -cumyl ether*,  $C_{16}H_{16}OBr_2$ , white needles, m. p. 110—111°. These ethers are readily or moderately soluble in organic solvents. G. Y.

**Base-forming Property of Carbon.** JAMES F. NORRIS (*Amer. Chem. J.*, 1907, **38**, 627—642).—Norris and Franklin (Abstr., 1903, i, 341) in discussing the properties of triphenylcarbinol suggested that by a change in the nature of the radicles, the basic property of the compound could be increased to such a degree that a true carbon base would be produced. The present investigation was undertaken with the object of studying this point.

When triphenylcarbinol is treated with cold hydrochloric acid (D 1.20), hydrobromic acid (D 1.49), or hydriodic acid (D 1.7), it is converted quantitatively into the corresponding triphenylmethyl halide.

Tri-*p*-tolylcarbinol has a greater basicity than the triphenyl-compound, and is converted into the chloride by hydrochloric acid of D 1.12. It reacts with nitric acid (D 1.42) with formation of the *nitrate*,  $C(C_6H_4Me)_3 \cdot NO_3 \cdot 2HNO_3$ , whilst triphenylcarbinol is not affected by this treatment. Triphenylcarbinol dissolves in concentrated sulphuric acid, and is reprecipitated on the addition of a small quantity of water. The tritolyl-compound, however, dissolves in a mixture of equal volumes of sulphuric acid and water, and yields a *sulphate*,  $C(C_6H_4Me)_3 \cdot HSO_4 \cdot H_2SO_4$ , which forms deep orange-coloured, silky needles.

The compounds obtained from triphenylcarbinol behave as true salts. A solution of the chloride in acetone has electrical conductivity, and, when a direct current is passed through the solution, a red substance, probably analogous to triphenylmethyl, is deposited on the cathode. On adding silver nitrate to a solution of the chloride in acetone, silver chloride is precipitated. The chloride is decomposed by strong sulphuric acid with formation of the sulphate and liberation of hydrogen chloride. It reacts with alcohol, thus:  $C(C_6H_4Me)_3Cl + EtOH \rightleftharpoons C(C_6H_4Me)_3 \cdot OEt + HCl$ .

Benzyl alcohol can be converted into the chloride, bromide, and iodide by concentrated solutions of the halogen acids.

The behaviour of alcohols of the paraffin series under the same conditions has been studied. *tert*-Butyl alcohol, when treated with concentrated hydrochloric acid, gives a quantitative yield of the chloride at the ordinary temperature. Usually, however, it is necessary to employ heat to bring about the reaction between alcohols and acids, and for this reason the mixtures of acids and water of constant boiling point have been used. In this way, yields of 91% and 89% were obtained of *tert*-butyl bromide and iodide respectively, and 95% of *sec*-butyl iodide.

When *sec*-butyl alcohol was distilled with concentrated hydro-

chloric acid, the chloride was not produced, but, on using the acid of constant boiling point, a yield of 50% was obtained. The primary alcohols are not converted into the chlorides when distilled with hydrochloric acid.

This method is recommended for the preparation of alkyl bromides and iodides. On slowly distilling a mixture of the alcohol with a large excess of the acid of constant b. p., the halide passes over and collects in the early fractions. The product is shaken with concentrated hydrochloric acid to remove unchanged alcohol, and is afterwards dried and distilled. Excellent yields of methyl, ethyl, *n*- and *iso*-propyl, *iso*-, *sec*-, and *tert*-butyl, *iso*amyl, and allyl bromides and iodides have been obtained in this way. E. G.

**A Vinyl Alcohol of the Type  $C_6H_5 \cdot CH \cdot OH$ .** MARC TIFFENEAU and DAUFRESNE (*Compt. rend.*, 1907, 145, 628—631).—The alcohol obtained from estragole dibromide by the successive action of alcoholic potassium acetate and potassium hydroxide is  $\beta$ -anisyl- $\beta$ -methylvinyl alcohol,  $OMe \cdot C_6H_4 \cdot CMe \cdot CH \cdot OH$ , and not anisylcyclopropanol as previously described (this vol., i, 515). This alcohol, b. p. 154—155°/14 mm., is stable in neutral or alkaline medium, and is converted into *p*-methoxyhydratropaldehyde by distillation under ordinary pressure, by the action of dilute acids, or when preserved in a vacuum over sulphuric acid. The methyl ether,  $OMe \cdot C_6H_4 \cdot CMe \cdot CH \cdot OMe$ , b. p. 262—264°,  $D_{15}^{20}$  1.073,  $D_4^{15.7}$  1.0615, is identical with the ether obtained by the action of yellow mercuric oxide on the methyl iodohydrin of anethole (Tiffeneau, this vol., i, 922); the acetyl derivative has b. p. 164—165°/13 mm., or 288° under ordinary pressure,  $D_{15}^{20}$  1.123,  $D_4^{15.8}$  1.111,  $n_D^{15}$  1.5409. M. A. W.

**The Solubility of Castor Oil in Lipoids.** WILHELM FILEHNE (*Beitr. Chem. Physiol. Path.*, 1907, 10, 299—311).—The solubility of the lipid, cholesteryl stearate, in olive oil, oleic acid, castor oil, ricinoleic acid,  $\psi$ -ricinoleic and crotonoleic acids has been determined by the methods of (1) melting point, (2) specific gravity, and (3) iodine value. Similarly, the solubilities of the oils and acids in the lipid have been determined. J. J. S.

**A Phytosterol from *Echinophora spinosa*.** J. TARBOURIECH and J. HARDY (*Chem. Zentr.*, 1907, ii, 969—970; from *Bull. Sci. Pharm.*, 1907, 14, 387—392).—The fatty substances obtained from the roots of *Echinophora spinosa* yield on hydrolysis a phytosterol crystallising in small, white, orthorhombic plates, m. p. 148°. The following derivatives were prepared: benzoate, m. p. 145°; acetate, pearly-white leaflets, m. p. 124—125°; propionate, crystallising from alcohol in leaflets, m. p. 109—110°, but when precipitated by alcohol from a carbon tetrachloride solution, m. p. 105°. W. H. G.

**Production of Phenolic Acids by Oxidation of Ammonium Salts of Benzoic Acid.** HENRY D. DAKIN and MARY DOWS HERTER (*J. Biol. Chem.*, 1907, 3, 419—434).—Hydrogen peroxide, acting on the ammonium salts of benzoic acid or its chloro-, bromo-, nitro-, and amino-

derivatives, can introduce hydroxyl groups into the nucleus, but the yield of phenolic acid is small. Hippuric acid undergoes nuclear oxidation with difficulty. Benzoic acid yields *o*-, *m*-, and *p*-hydroxybenzoic acids in about equal amount; on further oxidation, the last two yield protocatechuic (3:4-dihydroxybenzoic) acid, whilst salicylic acid yields 2:3-dihydroxybenzoic acid. Thus the second hydroxy-group takes up a position ortho to that already in the ring. A part of the benzoic acid is oxidised to carbon dioxide, and probably other products are also formed. The reaction occurs in approximately neutral solutions, and to some extent at the ordinary temperature. The possible origin of phenolic substances in animal and vegetable tissues is considered, and, although there is ample proof of their origin by the oxidation of pre-formed aromatic substances, there is little evidence at present that they originate directly from the condensation or rearrangement of aliphatic substances.

W. D. H.

***m*-Toluic Acid.** VICTOR JÜRGENS (*Ber.*, 1907, 40, 4409—4415).—It has been shown by Findelee (Abstr., 1906, i, 42) and Kusel (Abstr., 1904, i, 619) that phthalylglycine esters containing a methyl or ethoxy-radicle in position 4, undergo the same transformation as phthalylglycine ester, being converted by sodium methoxide into isoquinoline derivatives (compare Gabriel and Colman, Abstr., 1905, i, 944). In order to see if phthalylglycine esters substituted in position 3 undergo a similar change, 3-methylphthalylglycine ethyl ester has been prepared and its behaviour towards sodium methoxide investigated; it is found to undergo no such transformation.

Several of the following new compounds were obtained in unsuccessful attempts to prepare 3-methylphthalic acid (compare Young, Abstr., 1892, 1221); the acid was finally obtained from methyl 2-nitro-*m*-toluate (compare Findelee, Abstr., 1906, i, 21) by reduction to the amine, replacement of the amino-group by the cyano-group, and subsequent hydrolysis of the cyano-derivative.

2-Nitro-*m*-toluic acid, when treated with phosphorus pentachloride and subsequently with ammonia, is converted into the *amide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{NH}_2$  [2:1:3], m. p. 192°; this compound when heated with phosphoric oxide yields 2-nitro-*m*-toluonitrile,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CN}$ , crystallising in needles, m. p. 84°. The action of alcoholic ammonium sulphide on the latter compound leads to the formation of 2-amino-*m*-toluamide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 149°.

*Methyl 2-nitro-*m*-toluate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{Me}$ , m. p. 74°, yields, on reduction with tin and hydrochloric acid, the crystalline *hydrochloride* of *methyl 2-amino-*m*-toluate*,  $\text{C}_9\text{H}_{11}\text{O}_2\text{N} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ; the free *base* is a viscid oil with an odour like orange-peel. It is converted on diazotisation and treatment with cuprous cyanide into *methyl 2-cyano-*m*-toluate*,  $\text{CN} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{Me}$ , crystallising in long, white, pointed needles, m. p. 68—70°. This compound is hydrolysed by hydrochloric acid to 3-methylphthalic acid; the *imide*, m. p. 187°, and anhydride, m. p. 114—115° (Young gives m. p. 109—110°), were prepared. 3-Methylphthalylglycine,  $\text{C}_8\text{H}_5\text{MeO}_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , resulting from the interaction of glycine and 3-methylphthalic anhydride, crystallises in white, felted needles, m. p. 195°; the *methyl ester*, m. p. 105°, as

stated already, undergoes no transformation when treated with sodium methoxide.

*2-Amino-m-toluic acid*, m. p. 172°, the methyl ester of which is described above, reacts with potassium cyanate, forming 2:4-dihydroxy-8-methylquinazoline,  $\begin{array}{c} \text{CH} \cdot \text{CMe} : \text{C} \cdot \text{N} \equiv \text{C} \cdot \text{OH} \\ | \quad | \\ \text{CH} \cdot \text{CH} = \text{C} \cdot \text{C}(\text{OH}) : \text{N} \end{array}$ , a crystalline substance, m. p. 283°. It is converted by phosphorus pentachloride into 2:4-dichloro-8-methylquinazoline,  $\text{C}_9\text{H}_6\text{N}_2\text{Cl}_2$ , crystallising in fine, white, felted flakes, m. p. 140°. The latter compound is reduced by hydriodic acid to 8-methyldihydroquinazoline,  $\begin{array}{c} \text{CH} \cdot \text{CMe} : \text{CN} = \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{CH} = \text{C} \cdot \text{CH}_2 \cdot \text{NH} \end{array}$ , short, pointed, prismatic crystals, m. p. 112°. The *chromate*, *aurochloride*, and *platinichloride*,  $(\text{C}_9\text{H}_9\text{N}_2)_2, \text{H}_2\text{PtCl}_6$ , are well-defined, crystalline substances. W. H. G.

**Synthesis of Polypeptides. XXII. Derivatives of *l*-Phenylalanine.** EMIL FISCHER and WALTER SCHOELLER (*Annalen*, 1907, 357, 1—24).—Polypeptides derived from optically active phenylalanine have not been prepared previously because of the difficulty of obtaining the active amino-acids. *r*-Phenylalanine has now been resolved into its active components by means of the formyl derivative (compare Fischer and Warburg, *Abstr.*, 1906, i, 72). Whilst glycyl-*l*-phenylalanine is obtained by the action of chloroacetyl chloride on *l*-phenylalanine, *l*-phenylalanylglycine is prepared by the action of ammonia on *d*- $\alpha$ -bromohydrocinnamoylglycine, which is formed from *d*-phenylalanine by way of *d*- $\alpha$ -bromohydrocinnamic acid (Fischer and Carl, this vol., i, 9) and *d*- $\alpha$ -bromohydrocinnamoyl chloride. These two dipeptides yield the same anhydride.

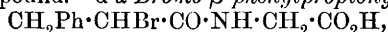
*Formyl-r-phenylalanine*,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$ , prepared by heating *r*-phenylalanine with formic acid on the water-bath, crystallises from water in microscopic plates, softening at 165.5° (corr.), m. p. 168.8—169.8° (corr.); when heated with brucine and methyl alcohol, it dissolves and the solution on cooling deposits the *brucine* salt of the *d*-compound, which, on hydrolysis, yields *formyl-d-phenylalanine*,  $[\alpha]_D^{20} - 75.43^\circ$  ( $\pm 0.2^\circ$ ). The *brucine* salt of the *l*-compound, obtained from the methyl alcohol filtrate, yields *formyl-l-phenylalanine*,  $[\alpha]_D^{20} + 75.2^\circ$  ( $\pm 0.2^\circ$ ). The optically active formylphenylalanines crystallise from water in plates, soften at 163° (corr.), m. p. 167° (corr.), and are slightly more soluble than the *r*-compound. The optically active phenylalanines are prepared by boiling the formyl derivatives with *N*-hydrobromic acid and treatment of the resulting hydrobromides with ammonia. *d*-Phenylalanine prepared in this manner has m. p. 283° (corr.) (decomp.),  $[\alpha]_D^{20} + 35.14^\circ$  ( $\pm 0.5^\circ$ ) (Fischer and Mouneyrat, *Abstr.*, 1900, i, 647), and has a sweet taste. *l*-Phenylalanine, m. p. 283° (corr.) (decomp.),  $[\alpha]_D^{20} - 35.09^\circ$  ( $\pm 0.5^\circ$ ) ( $[\alpha]_D^{16} - 38.1^\circ$  to  $-40.2^\circ$ ; Schulze and Winterstein, *Zeitsch. physiol. Chem.*, 1902, 35, 299), has a bitter taste, and when heated with formic acid yields the formyl derivative,  $[\alpha]_D^{20} + 72.4^\circ$ .

*d*- $\alpha$ -Bromohydrocinnamic acid, prepared by the action of nitric oxide on *d*-phenylalanine hydrobromide in hydrobromic acid in

presence of bromine at  $-10^{\circ}$ , or in a more impure state by the action of sodium nitrite on *d*-phenylalanine hydrobromide in 25% hydrobromic acid solution cooled by ice, has  $[\alpha]_D^{20} + 9^{\circ}$ , and contains therefore about 13% of its optical isomeride. In the same manner, *l*-leucine hydrobromide on treatment with sodium nitrite in 49% hydrobromic acid solution yields *l*- $\alpha$ -bromoisohexioic acid containing about 22% of the *d*-acid.

*l*-Phenylalanine ethyl ester hydrochloride, prepared by the action of hydrogen chloride on *l*-phenylalanine in alcoholic solution, crystallises in long, colourless needles,  $[\alpha]_D^{20} - 7.6^{\circ}$  ( $\pm 0.2^{\circ}$ ). On treatment with hydrobromic acid and bromine, the *l*-ester forms a dark red oil, and on treatment with nitric oxide in cooled hydrobromic acid solution yields impure ethyl *d*- $\alpha$ -bromohydrocinnamate, b. p.  $110^{\circ}/0.35$  mm.,  $[\alpha]_D^{20} + 20^{\circ}$ . Ethyl *l*- $\alpha$ -bromohydrocinnamate, prepared by esterification of a specimen of the *l*-acid containing 18% of the *d*-acid, has  $[\alpha]_D - 15.5^{\circ}$ . Hence the pure *l*-acid has  $[\alpha]_D$  about  $-24^{\circ}$ , and Walden's transformation does not take place in the formation of ethyl  $\alpha$ -bromohydrocinnamate by the action of bromine and nitric oxide on *l*-phenylalanine ethyl ester.

*d*- $\alpha$ -Bromo- $\beta$ -phenylpropionyl chloride, prepared in an 85% yield from *d*- $\alpha$ -bromohydrocinnamic acid,  $[\alpha]_D^{20} + 9^{\circ}$ , is obtained as a colourless oil, b. p.  $90^{\circ}/0.25$  mm., has a suffocating odour, and contains at least 25% of the *r*-compound. *d*- $\alpha$ -Bromo- $\beta$ -phenylpropionylglycine,



obtained by the action of the chloride and sodium hydroxide on glycine and extraction of the product with ether, crystallises on addition of light petroleum to the ethereal solution in long needles, m. p.  $145\text{--}146^{\circ}$  (corr.),  $[\alpha]_D^{20} - 14.65^{\circ}$  ( $\pm 0.3^{\circ}$ ). The portion of the product insoluble in ether is the *r*-compound. On treatment with aqueous ammonia, the *d*-compound yields *l*-phenylalanylglycine,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which crystallises in needles, commences to sinter at about  $219^{\circ}$  (corr.), m. p.  $224^{\circ}$  (corr.) (decomp.),  $[\alpha]_D^{20} + 54.20^{\circ}$  ( $\pm 0.4^{\circ}$ ), or after precipitation by addition of alcohol to the aqueous solution and drying at  $80^{\circ}$  over phosphoric oxide in a vacuum,  $[\alpha]_D^{20} + 53.63^{\circ}$  ( $\pm 0.4^{\circ}$ ), and has a bitter taste; the aqueous solution has a slight acid reaction, and when boiling dissolves copper oxide, becoming blue.

Chloroacetyl-*l*-phenylalanine,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ , softens at about  $123^{\circ}$  (corr.), m. p.  $126^{\circ}$  (corr.),  $[\alpha]_D^{20} + 51.25^{\circ}$  ( $\pm 0.5^{\circ}$ ), or after recrystallisation from water,  $[\alpha]_D^{20} + 51.80^{\circ}$  ( $\pm 0.5^{\circ}$ ).

Glycyl-*l*-phenylalanine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ , crystallises in colourless needles, m. p.  $267^{\circ}$  (corr.) (decomp.),  $[\alpha]_D^{20} + 41.4^{\circ}$  ( $\pm 0.5^{\circ}$ ), or after recrystallisation from water,  $[\alpha]_D^{20} + 42.0^{\circ}$  ( $\pm 0.5^{\circ}$ ), has a bitter taste, forms a slightly acid aqueous solution, and yields a blue solution when boiled with water and copper oxide; the copper salt forms an amorphous, blue mass. The anhydride,



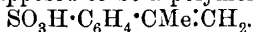
formed from *l*-phenylalanylglycine or glycyl-*l*-phenylalanine by conversion into the methyl ester and treatment of this with alcoholic ammonia, crystallises in needles, m. p. about  $265.5^{\circ}$  (corr.) (decomp.),



$[\alpha]_D^{20} + 100.5^\circ (\pm 0.4^\circ)$ , or after recrystallisation from water,  
 $[\alpha]_D^{20} + 99.5^\circ (\pm 0.5^\circ)$ . G. Y.

**The Liberation of Carbon Monoxide from the Simplest Tertiary Acids, Trimethylacetic [*αα*-Dimethylpropionic] and Phenyltrimethylacetic [*α*-Phenyl-*α*-methylpropionic] Acids.** AUGUSTIN BISTRZYCKI and LOUIS MAURON (*Ber.*, 1907, 40, 4370—4378. Compare *Abstr.*, 1901, i, 701; 1904, i, 44, 315; 1905, i, 285; 1906, i, 135).—It has been shown already that triphenylacetic acid, on dissolution in sulphuric acid, gives triphenylcarbinol, and carbon monoxide is eliminated quantitatively. On treating methyl diarylacetic acids similarly, carbon monoxide is again liberated quantitatively, but in these cases no carbinol is formed, the corresponding diarylolefine being obtained. The investigation has been extended to phenyltrimethyl- and trimethylacetic acids. In these cases also, carbon monoxide is evolved quantitatively, but neither olefine nor carbinol is obtained. The elimination of carbon monoxide proceeds with most ease, and is most complete, in the case of tertiary acids, and least readily with monobasic primary acids, the secondary acids occupying an intermediary position.

*α*-Phenyl-*α*-methylpropionic acid (m. p. 80—81°; Wallach, *Nach. Wiss. Göttingen*, 1899, 126, gives 77—78°), on dissolution in sulphuric acid and heating for thirty minutes at 60—70° after being kept for thirty hours, yields, on neutralisation of the aqueous solution with barium carbonate, the barium salt of polymerised (?) *α*-methylstyrenesulphonic acid,  $[(C_9H_9 \cdot SO_3)_2Ba, 6H_2O]_x$ , crystallising in microscopic prisms; the potassium salt,  $(C_9H_9O_3SK, H_2O)_x$ , forms slender, silky needles. It is only very slowly hydrolysed by acids, and is therefore not an ester of sulphuric acid, and is supposed to be a polymeride of



*αα*-Dimethylpropionic acid, when heated with sulphuric acid at 105—110° for three to four hours, yields isobutylenedisulphonic acid,  $C_4H_6(SO_3H)_2$ , in 35% yield as potassium salt,  $C_4H_6O_6S_2K_2$ , crystallising in leaflets. The ammonium salt,  $C_4H_6O_6S_2(NH_4)_2$ , forms plates, decomp. 248—251°; lead salt,  $C_4H_6O_6S_2Pb, 2H_2O$ , large, rectangular plates. The acid itself, prepared from the lead salt, forms hexagonal plates, m. p. 63—64°, and is not hydrolysed. Further, it behaves like an unsaturated substance towards bromine water and potassium permanganate. It may have either of the four possible formulæ:  $CH_2:C(CH_2 \cdot SO_3H)_2$ ,  $SO_3H \cdot CH:CMe \cdot CH_2 \cdot SO_3H$ ,  $CMe_2:C(SO_3H)_2$ ,  $CH_2:CMe \cdot CH(SO_3H)_2$ . W. R.

**General Reaction for Differentiating between Multiple Linkings in Unsaturated Compounds of the Aromatic and Aliphatic Series.** ETTORE MOLINARI (*Ber.*, 1907, 40, 4154—4161).—Ozone is quantitatively absorbed by compounds containing double linkings in the proportion of 1 mol. of ozone for each double linking, ozonides being formed; compounds, on the other hand, containing triple linkings do not absorb ozone. With benzenoid derivatives, where in the ring there is no "true" double linking, no ozone is absorbed; with those benzenoid derivatives which contain a "true" double linking, ozone is absorbed.

The behaviour of ozone towards stearolic acid, phenylpropionic acid, and *o*-nitrophenylpropionic acid was studied.

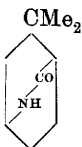
With aromatic compounds, the author draws the conclusion that, if a given substance does not take up ozone, the centric formula should be assigned to the compound in question; if ozone is absorbed, then the compound contains "true" double linkings. The following compounds absorb much ozone: resorcinol, quinol, phloroglucinol, pyrogallol, *p*-benzoquinone, cinnamic acid, phenanthrene, anthracene, hydrazobenzene, aminoazobenzene, benzidine, naphthalene,  $\alpha$ -naphthylamine,  $\beta$ -naphthylamine, and quinoline. The following compounds do not absorb ozone: benzene, toluene, the xylenes, nitrobenzene, phenetole, hydrocinnamic acid, phenylpropionic acid, *o*-nitrophenylpropionic acid, diphenyl, benzophenone, diphenylmethane, fluorene, phenanthraquinone, azobenzene, naphthaquinone, anthraquinone, pyridine, and *iso*-quinoline. Phenol and catechol absorb small quantities.

From the behaviour of benzene with ozone, the author concludes that the centric formula should be assigned to it, since benzene and ozone scarcely interact; this is opposed to the experience of Harries.

A. McK.

**Esters of Hydroaromatic Amino-carboxylic Acids.** ALADAR SKITA (*Ber.*, 1907, 40, 4167—4182).—The object of this investigation was to ascertain if the substances are similar to the aliphatic amino-esters, to study *cis*- and *trans*-isomerism, and also to see if the property of local anaesthesia, possessed by ethyl aromatic *p*-amino-carboxylates, was characteristic of similar hydroaromatic compounds.

The compounds examined were all 4-aminocarboxylates. Ethyl isophoronecarboxylate (ethyl 2:6:6-trimethylcyclo- $\Delta^2$ -hexene-4-one-1-carboxylate) was prepared by the patented method (D.R.-P. 148080. Compare also Abstr., 1905, i, 349). When left in a methyl-alcoholic solution of hydroxylamine hydrochloride for eight days, and the solvent then distilled, ethyl oximinisophoronecarboxylate hydrochloride is obtained in needles, m. p. 125°. The sodium salt of the oxime is hydrolysed by water; the oxime,  $C_{12}H_{19}O_3N, \frac{1}{2}H_2O$ , crystallises from dilute alcohol in slender needles, m. p. 78°. The oxime behaves differently towards various reducing agents. With sodium amalgam in alcohol, a 46% yield of ethyl *cis*-4-amino-2:6:6-trimethylcyclohexane-1-carboxylate,  $C_{12}H_{23}O_2N$ , is obtained as an oil, b. p. 124—125°/8 mm. (There is also a small fraction, b. p. 118—120°/9 mm., and 15% of the crude oil remains behind.) The platinichloride,  $C_{24}H_{48}O_4N_2Cl_6Pt$ , decomp. 248°; the hydrogen citrate,  $C_{30}H_{54}O_{11}N_2$ , forms hygroscopic crystals; the normal citrate,  $C_{42}H_{77}O_{13}N_3$ , is very hygroscopic. When the ester is boiled with sodium ethoxide for four hours and the alcohol removed, a lactam,  $C_{10}H_{15}ON$ , is obtained, crystallising from acetone in needles, m. p. 138—139°, b. p. 159—160°/9 mm. Not only have the elements of alcohol been lost, but two hydrogen atoms as well. This lactam formation shows the compound to be the *cis*-compound and to have the annexed grouping. Ethyl isophoronecarboxylate and ammonium formate, when heated in a sealed tube at 200° for five hours, give

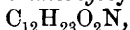


the formate of the amino-ester, and this on hydrolysis with 30% sulphuric acid yields the *cis*-modification.

Ethyl isophoronecarboxylate, when treated with six times the theoretical amount of sodium amalgam in alcohol and acetic acid, gives an oil, which on fractional distillation is separated into two main fractions: (1) b. p. 127—130°/9 mm., solidifies on cooling; (2) b. p. 130—133°, and does not solidify. Both have the composition,  $C_{12}H_{20}O_8$ , of *ethyl dihydroisophoronecarboxylates*; the two forms are probably derived from the ethylenic linkings becoming reduced.

The *oxime* of ethyl dihydroisophoronecarboxylate (b. p. 148—150°/9 mm.) on reduction with sodium amalgam or with ammonium formate gives the *cis*-modification.

*Ethyl trans-4-amino-2:6:6-trimethylcyclohexane-1-carboxylate*,



obtained by the reduction of ethyl oximinisophoronecarboxylate with sodium and alcohol, is an oil, b. p. 127—128°/11 mm., and is unchanged by twelve hours' boiling with sodium ethoxide solution. The *hydrochloride*,  $C_{12}H_{24}O_2NCl$ ; *tartrate*,  $C_{28}H_{52}O_{11}N_2$ , and *platinichloride*,  $C_{24}H_{48}O_4N_2Cl_6Pt$ , decomp. 279°, have been prepared.

Another fraction, b. p. 150—160°/11 mm., obtained during the above reduction consists of a *bimolecular ethyl aminotrimethylcyclohexanecarboxylate*,  $C_{24}H_{44}O_4N_2$ , and the solid ethyl dihydroisophoronecarboxylate has also been isolated.

By the reduction of the ethyl oximinisophoronecarboxylate with sodium and methyl alcohol, a *lactimide-carboxylate*,  $C_{10}H_{17}O_3N$ , is obtained, crystallising from acetone in slender, white needles, m. p. 153—154°, b. p. 125°/8 mm. Hydroxylamine is not liberated from it by the action of hydrochloric acid.

*Ethyl 4-hydroxy-2:6:6-trimethylcyclohexane-1-carboxylate*,  $C_{12}H_{23}O_3$ , obtained by the action of nitrous acid on the corresponding amino-compound, is an oil, b. p. 144—148°/12 mm. Another substance obtained is ethyl *cyclogeraniolenecarboxylate*,  $C_{12}H_{20}O_2$ , b. p. 87—88°/8 mm., due to removal of the elements of water (D.R.-P. 148080).

The *oxime hydrochloride* of ethyl dimethylcyclohexanonecarboxylate,  $C_{11}H_{18}O_3NCl$ , has m. p. 115°; the *oxime* itself is oily. Its reduction by sodium amalgam and acetic acid in the presence of sodium ethoxide yields the corresponding *amino-ester*,  $C_{11}H_{21}O_2N$ , an oil, b. p. 118—121°/8 mm., which has been characterised by preparing the *platinichloride*,  $C_{22}H_{44}O_4N_2Cl_6Pt$ , decomp. 250°, and the *citrate*,  $C_{39}H_{71}O_{13}N_3$ . This ester is a *cis*-form, because with sodium ethoxide it gives an oil, b. p. 156—158°/10 mm., which is apparently a lactam or mixture of lactams.

A physiological examination of the tartrates and citrates show them to be analogous to the aromatic amino-acids in possessing the property of local anaesthesia.

W. R.

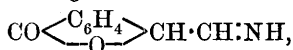
**Preparation of Glyceryl Salicylate.** CARL SORGER (D.R.-P. 186111).—Glyceryl monosalicylate,  $C_3H_6(OH)_2 \cdot O \cdot CO \cdot C_6H_4 \cdot OH$ , is readily obtained by heating methyl or ethyl salicylate with glycerol containing a trace of sodium hydroxide or some salt of sodium; the temperature is gradually raised to 220° and maintained until methyl or ethyl

alcohol ceases to distil off. The glyceryl ester crystallises from ether in white needles. G. T. M.

**Barium *p*-Hydroxybenzoate.** WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1907, 711—713. Compare this vol., i, 532).—This salt dissolves easily in water, and the specific gravities of a number of solutions of different strengths are tabulated in the original. Unlike calcium *p*-hydroxybenzoate, it does not exhibit triboluminescence. The calcium salt dissolves easily in alcohol (95°), but the barium salt is soluble with difficulty in this solvent, and the solution becomes turbid on standing, depositing a mixture of the anhydrous and monohydrated salts. A solution of calcium *p*-hydroxybenzoate in alcohol, on the contrary, remains clear indefinitely.

Barium *p*-hydroxybenzoate does not dissolve in, and is not appreciably acted on by, either ethyl formate or acetate. T. A. H.

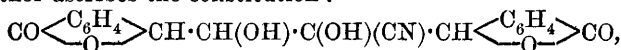
**$\omega$ -Bromoacetophenone-*o*-carboxylic Acid.** SIEGMUND GABRIEL (*Ber.*, 1907, 40, 4227—4239. Compare this vol., i, 214).—*Aminomethylenephthalide*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}:\text{CH}\cdot\text{NH}_2$  or



prepared by the action of ammonia on methyl  $\omega$ -bromoacetophenone-*o*-carboxylate in presence of alcohol, crystallises from alcohol in yellow, quadratic leaflets, m. p. 176—178°, and is transformed into the oxime, m. p. 154—155°, of hydroxymethylenephthalide (*loc. cit.*) by the action of hydroxylamine. When treated with concentrated hydrochloric acid at 0°, aminomethylenephthalide is converted into hydroxymethylenephthalide and an isomeric *amino*-compound,  $\text{C}_9\text{H}_7\text{O}_2\text{N}$ , which separates from alcohol in oblong plates, sintering at 200°, m. p. 207°, and is also obtained by the action of aqueous ammonia on  $\omega$ -bromoacetophenone-*o*-carboxylic acid.

$\omega$ -*Aminoacetophenone-*o*-carboxylamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2$ , obtained by the action of aqueous ammonia on methyl  $\omega$ -bromoacetophenone-*o*-carboxylate, separates from acetone in glistening crystals resembling whetstone, m. p. 144—145° (decomp.), is soluble in water, forms a crystalline *hydrochloride*, *hydrobromide*, and *picrate* (m. p. 214—215°), but yields no precipitate with auric or platonic chloride. In the same reaction is formed a *compound*,  $(\text{C}_9\text{H}_5\text{ON})_x$ , which crystallises from aniline in bundles of orange-red, flat needles, m. p. 415° (decomp.).

To the compound,  $\text{C}_9\text{H}_{13}\text{O}_6\text{N}$ , m. p. 223°, formed by the action of potassium cyanide on  $\omega$ -bromoacetophenone-*o*-carboxylic acid (*loc. cit.*) the author ascribes the constitution:



which is supported by the following transformations. When treated with dilute sodium hydroxide solution, it yields hydrogen cyanide

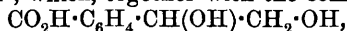
and hydroxymethylenephthalide. When treated with cold concentrated hydrochloric acid or heated with 50% acetic acid, it is converted into the *trilactone*, which separates in oblique-ended prisms or six-sided plates, m. p. 245°, and reduces Fehling's solution when dissolved in alkali.

The action of dilute potassium hydroxide solution on this trilactone, followed by the addition of excess of hydrochloric acid, yields: (1) the  $\alpha$ -lactonic acid,  $C_{19}H_{14}O_8$ , which crystallises in oblique-ended prisms, sintering at 190°, m. p. 199—200°; this lactonic acid is formed by the opening of one of the two end lactonic rings, and, when heated with acetic acid, yields a lactone, separating in colourless, cubical crystals, m. p. 191—194°, which is isomeric with the trilactone, m. p. 245°, and is termed the *isolactone*; the  $\alpha$ -lactonic acid yields a sparingly soluble *ammonium* salt,  $C_{19}H_{13}O_8 \cdot NH_4$ , m. p. 188°, and a still less soluble *barium* salt; (2) the  $\beta$ -lactonic acid,  $C_{19}H_{14}O_8$ , separating as a crystalline powder, which froths at 180°, forming a pale yellow, turbid mass which becomes clear at 190°; it is readily soluble in water or alcohol, and, when treated with glacial acetic acid, loses water, giving the trilactone, m. p. 245°; the *silver* salt,  $C_{19}H_{13}O_8Ag$ , of the  $\beta$ -lactonic acid was prepared.

When the trilactone, m. p. 245°, is treated with an excess of cold barium hydroxide solution and the solution subsequently acidified with hydrochloric acid, it yields the  $\alpha$ -lactonic acid and an isomeric  $\gamma$ -lactonic acid,  $C_{19}H_{14}O_8 \cdot 1\frac{1}{2}H_2O$ , m. p. varying from 188—189° to 190—195°, according to the rapidity of heating; this  $\gamma$ -acid forms a crystalline *silver* salt,  $C_{19}H_{13}O_8Ag$ , and is converted by concentrated acetic acid into the original trilactone, m. p. 245°. When the latter is shaken in a closed flask with about three equivalents of dilute barium hydroxide, it yields the *barium* salt,  $(C_{19}H_{15}O_{10})_2Ba_3$ , of the tribasic acid,

$CO_2H \cdot C_6H_4 \cdot CH(OH) \cdot CH(OH) \cdot C(OH)(CO_2H) \cdot CH(OH) \cdot C_6H_4 \cdot CO_2H$ , which could, however, not be obtained in the free state, the barium salt giving the  $\beta$ -lactonic acid when treated with dilute sulphuric acid.

When heated with dilute barium hydroxide solution, the trilactone, m. p. 245°, is converted into formic and phthalidecarboxylic acids (*loc. cit.*), m. p. 152°, which, together with the compound,



are the expected products of the tribasic acid referred to above.

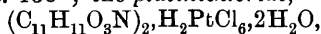
When heated with phosphorus pentachloride, the trilactone loses water, yielding the *compound*,  $C_{19}H_{10}O_6$ , which crystallises from acetic acid in colourless, quadratic or oblong plates, sintering at 240°, m. p. 261—263°; the constitution of this compound is to be investigated.

T. H. P.

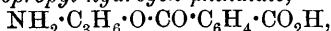
**Derivatives of Imides of Dibasic Acids.** PAUL MENDELSSOHN BARTHOLDY (*Ber.*, 1907, 40, 4400—4408).—The transformation of  $\beta$ -bromopropylphthalimide into the  $\beta$ -hydroxy-compound is shown to take place through the same intermediate stages as in the case of the isomeric  $\gamma$ -compound (compare Gabriel, *Abstr.*, 1905, i, 649).

*β-Bromopropylphthalamic acid*,  $C_3H_6Br \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ , prepared by the action of alcoholic potassium hydroxide on *β*-bromopropylphthimide, crystallises in rhombic plates, m. p. 126°. The imino-base,  $C_6H_4 \begin{matrix} \diagup CO \cdot NH \cdot CH_2 \\ \diagdown CO - O - CHMe \end{matrix}$ , obtained in the form of its hydro-

chloride,  $C_{11}H_{11}O_3N \cdot HCl$ , deliquescent, white needles, m. p. 134–135°, by the action of dilute hydrochloric acid on the corresponding nitrosoamine (compare Gabriel, Abstr., 1905, i, 950), crystallises in rectangular prisms, m. p. 138°; the *platinichloride*,



forms brilliant, golden, rhombic crystals, m. p. 190° (decomp.). The imino-base decomposes when its aqueous solution is heated, with the formation of *β*-aminopropyl hydrogen phthalate,



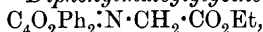
crystallising in rhombic plates, m. p. 168° (decomp.); the *hydrochloride*,  $C_{11}H_{13}O_4N \cdot HCl \cdot 2H_2O$ , crystallises in pointed needles, melts partially at 87°, and is completely molten at 165°; the *platinichloride*,  $(C_{11}H_{13}O_4N)_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , forms large, prismatic needles, m. p. 204° (decomp.). *β-Hydroxypropylphthalimide*,  $C_6H_4(CO)_2N \cdot C_3H_6 \cdot OH$ , results when *β*-bromopropylphthalimide is boiled with alcoholic potassium hydroxide; it crystallises in long prisms, m. p. 73°. *β-Bromoethylsuccinimide*,  $C_4H_4O_2 \cdot N \cdot CH_2 \cdot CH_2Br$ , prepared by the action of ethylene bromide on sodium succinimide, forms white needles, m. p. 56–57°. It is converted by cold potassium hydroxide solution and subsequent treatment with hydrobromic acid into *β-bromoethylsuccinamic acid*,  $C_2H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , crystallising in leaflets, m. p. 101°. This substance is very unstable, and does not give a nitrosoamine when treated with potassium nitrite.

*γ-Bromopropylsuccinimide*,  $C_4H_4O_2 \cdot N \cdot C_3H_6Br$ , forms brilliant leaflets, m. p. 52°; the corresponding succinamic acid could not be obtained. An attempt to prepare *β*-bromopropylsuccinimide by the action of hydrogen bromide on allylsuccinimide was unsuccessful.

*γ-Bromopropyl diphenylmaleinimide*,  $\begin{matrix} CPh \cdot CO \\ || \\ CPh \cdot CO \end{matrix} > N \cdot C_3H_6Br$ , resulting

from the interaction of sodium diphenylmaleinimide and trimethylene bromide, crystallises in broad, yellow needles, m. p. 112°. *β-Bromoethyl diphenylmaleinimide*,  $C_4O_2Ph_2 \cdot N \cdot C_2H_4Br$ , forms small, yellow crystals, m. p. 94°. These two derivatives of diphenylmaleinimide are more stable than the analogous phthalimide derivatives towards potassium hydroxide and hydrobromic acid.

Unlike phthalyl glycine ester, neither succinylglycine ester nor diphenylmaleylglycine ester is converted by sodium ethoxide into an isoquinoline derivative. *Diphenylmaleylglycine ester*,



prepared by the action of ethyl chloroacetate on sodium diphenylmaleinimide, crystallises in yellowish-green needles, m. p. 109°. W. H. G.

**Intramolecular Condensation of Phthalanilic Acid and of Certain Allied Compounds. II.** J. BISHOP TINGLE and B. F. LOVELACE (*Amer. Chem. J.*, 1907, 38, 642–652).—Tingle and Cram (this vol., i, 692) found that succinanilic acid readily combines

with aniline to form the anilide, whilst phthalanilic acid in presence of aniline and alcohol is converted into phthalanil even at the ordinary temperature. It is now shown that the latter change is due to the intermediate formation of aniline phthalanilate, which easily loses water and aniline with production of the anil. It has been found that pyridine and quinoline react with the acid in a similar manner to give a quantitative yield of the anil.

$\beta$ -Naphthylphthalamic acid reacts with aniline at  $100^\circ$  with formation of a mixture of phthalanil and  $\beta$ -naphthylphthalimide. Pyridine and quinoline under similar conditions give a quantitative yield of  $\beta$ -naphthylphthalimide. By the action of  $\beta$ -naphthylamine on the acid at  $100^\circ$ , a compound (probably di- $\beta$ -naphthylphthalimide), m. p.  $250^\circ$  (decomp.), is obtained. Benzylamine similarly yields *dibenzylphthalamide*,  $C_6H_4(CO \cdot NH \cdot CH_2Ph)_2$ , m. p.  $178-179^\circ$ .

When benzylphthalamic acid is heated with aniline at  $65^\circ$ , benzylphthalimide is produced together with a small quantity of a substance, m. p.  $177^\circ$ , which is probably dibenzylphthalamide. Pyridine and quinoline react with the acid at  $100^\circ$  with formation of a quantitative yield of benzylphthalimide. Similarly,  $\beta$ -naphthylamine appears to give  $\beta$ -naphthylphthalimide. Benzylamine reacts with the acid at  $65^\circ$  or  $100^\circ$  with formation of dibenzylphthalamide. E. G.

**2:4(3:5)-Dihydroxytritanolactone and *m*-Hydroxytritanolactone.** HANS VON LIEBIG (*J. pr. Chem.*, 1907, [ii], 76, 367—368).—The substance described as *m*-hydroxytritanolactone (this vol., i, 930) is now found to be identical with Baeyer and Diehl's *o*-hydroxytriphenylmethane (this vol., i, 759), and therefore is *o*-hydroxytritanolactone. It follows that the substance previously termed 3:5- is 2:4-dihydroxytritanolactone and that described as the 2:4- is the 2:6-dihydroxycompound (Abstr., 1905, i, 781).

*o*-Hydroxytritanolactone is formed when *o*-methoxytritanolactone is boiled with concentrated hydriodic acid and glacial acetic acid. G. Y.

**Anomalies in the Condensation of Benzilic Acid with Homologues of Benzene.** AUGUSTIN BISTRZYCKI and LOUIS MAURON (*Ber.*, 1907, 40, 4060—4065).—Benzilic acid in the presence of stannic chloride reacts in different ways with benzene and its monoalkyl homologues. Benzene and toluene yield the corresponding triarylated acetic acid; cumene reacts very slightly, the main product being diphenylacetic acid. This acid is also the main product of the reaction with ethylbenzene or propylbenzene in the presence of excess of benzene. *Ethyltriphenylacetic acid*,  $C_6H_4Et \cdot CPh_2 \cdot CO_2H$ , m. p.  $212-213^\circ$ , is obtained when benzilic acid, stannic chloride, and ethylbenzene are heated for two to three hours; it crystallises from dilute alcohol in aggregates of colourless leaflets, and loses carbon monoxide quantitatively by treatment with concentrated sulphuric acid (Abstr., 1904, i, 315). *p*-Propyltriphenylacetic acid, m. p.  $256-257^\circ$ , behaves in a similar manner, forming *p*-propyltriphenylcarbinol, m. p.  $153-155^\circ$ .

C. S.

**Preparation of Methylenecitrylsalicylic Acid.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 185800).—*Methylene-*  
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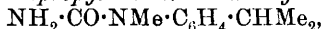
*citrylsalicylic acid*,  $\text{CH}_2 \begin{smallmatrix} \text{O} \\ \diagup \text{CO}_2 \end{smallmatrix} \text{C}(\text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$ , colourless crystals, m. p. 150—155°, is obtained by condensing methylenecitryl chloride with salicylic acid in the presence of an agent for taking up hydrogen chloride, such as dimethylaniline or quinoline. It is also produced by digesting in benzene equivalent amounts of dipotassium salicylate and methylenecitryl chloride. It is more beneficial as an antirheumatic than acetylsalicylic acid, and has the additional property of yielding formaldehyde when hydrolysed by the alkaline intestinal juices. G. T. M.

**Preparation of *o*-Nitrobenzaldehyde.** ARNOLD REISSERT (D.R.-P. 186881. Compare this vol., i, 908).—The processes formerly employed to convert *o*-nitrotoluene into *o*-nitrobenzaldehyde either do not give a complete oxidation or lead to the formation of *o*-nitrobenzoic acid. It has now been found that the dimercury derivative of *o*-nitrotoluene (*loc. cit.*) is readily oxidised by dilute nitric or nitrous acid to *o*-nitrobenzaldehyde. To bring about this change, the dimercury compound is boiled with a 10% aqueous solution of potassium nitrate while 20% sulphuric acid is slowly added; the *o*-nitrobenzaldehyde is extracted with benzene or ether. A similar result is obtained when 20% nitric acid, or an aqueous solution of sodium nitrite, is added to a boiling mixture of 10% sulphuric acid and the dimercury compound. G. T. M.

***p*-Dimethylaminobenzaldehyde.** VI. FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, 40, 4356—4361. Compare, *Abstr.*, 1903, i, 37; 1904, i, 506; 1905, i, 190, 202; 1906, i, 575).—It has been shown previously that, when magnesium methyl iodide and *p*-dimethylaminobenzaldehyde interact in the usual manner, the product is dimethylaminophenyl methyl carbinol,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{OH}$ . When, however, this product was heated at 100° with an excess of the Grignard reagent according to Klages' method, the corresponding unsaturated hydrocarbon,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH}_2$ , was not formed, but, in place of it, *p*-dimethylaminoisopropylbenzene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , was produced. That the latter compound has the constitution formerly assigned to it is, in the present paper, still further proved, since cumidine is formed from it by the elimination of two of the alkyl groups by the method of von Braun.

*N*-Dimethylcumidine (*p*-dimethylaminoisopropylbenzene) was prepared as previously described; its *picrate* has m. p. 112°, and its *methiodide*, m. p. 165°.

*p*-isoPropylphenylmethylcyanamide,  $\text{CN} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , obtained by the action of cyanogen bromide on *N*-dimethylcumidine and subsequent elimination of methyl bromide, is a yellow oil, b. p. 165°/10 mm. When boiled with 30% sulphuric acid for ten minutes, it forms *N*-methyl-*p*-isopropylaniline-*N*-carboxylamide,



which separates in rod-shaped crystals, m. p. 118°. When boiled for two to three hours with 30% sulphuric acid, the latter compound is converted into *N*-methylcumidine,  $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , which is a

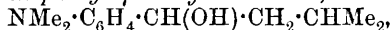


colourless oil, b. p. 111—112°/11 mm.; its *hydrochloride* forms glistening crystals, m. p. 128°; its *platinichloride* has m. p. 192°; its *picrate* has m. p. 147°; its *benzoyl* derivative separates from light petroleum in prisms, m. p. 58°. When acted on by phosphorus pentachloride, the benzoyl derivative is presumably first converted into the compound  $\text{CPhCl}_2 \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , from which methyl chloride is eliminated with formation of the imide chloride,  $\text{CPhCl} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , which readily gives *N*-benzoylcumidine,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ ; the latter compound crystallises from alcohol in glassy, spear-shaped crystals, m. p. 162°, and not 114° as given by Louis. The *N*-benzoylcumidine obtained was hydrolysed by heating at 150° for twelve hours with concentrated hydrochloric acid, and the resulting benzoic acid and *p*-cumidine identified. A. McK.

***p*-Dimethylaminobenzaldehyde.** VII. FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, 40, 4361—4367. Compare preceding abstract). — When magnesium organic compounds react with *p*-dimethylaminobenzaldehyde, three different products may be obtained: (1) carbinols, according to the normal action; (2) unsaturated hydrocarbons, when the carbinols are distilled under diminished pressure; (3) compounds, where the aldehydic oxygen atom is displaced by two alkyl groups. The method of conducting the latter change is as follows. The aldehyde (1 mol.) is gradually added to the ethereal solution of magnesium alkyl bromide (4 mol.). After some time, the ether is removed by heating the mixture, first on the water-bath, and finally under diminished pressure. The resulting grey, viscid mass is then heated in an oil-bath for about eight hours at 110°, and the product manipulated in the customary manner. The action of various magnesium organic compounds on *p*-dimethylaminobenzaldehyde is described in the present paper.

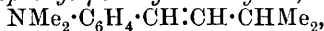
*p*-Dimethylaminophenylpropylcarbinol [ $\alpha$ -*p*-dimethylaminophenylbutane- $\alpha$ -ol],  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Me}$ , obtained by the action of magnesium propyl bromide on *p*-dimethylaminobenzaldehyde under normal conditions, melts at 35°, but was not obtained quite pure, owing to its tendency to form the corresponding styrene derivative; its *methiodide* separates from a mixture of alcohol and ether in glistening leaflets, m. p. 161°. When distilled under diminished pressure, the preceding secondary alcohol forms  $\alpha$ -*p*-dimethylaminophenyl- $\Delta^{\alpha}$ -butylene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{Me}$ , which boils at 275° under ordinary pressure, and has m. p. 25°; the *platinichloride* melts indefinitely at 140°; the *picrate* has m. p. 114.5°, and the *methiodide*, m. p. 212°.

$\alpha$ -*p*-Dimethylaminophenyl- $\gamma$ -methylbutane- $\alpha$ -ol,



obtained by the action of magnesium isobutyl bromide on *p*-dimethylaminobenzaldehyde, separates from light petroleum in stellate needles, m. p. 77°; its *methiodide* has m. p. 150°.

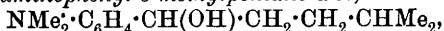
$\alpha$ -*p*-Dimethylaminophenyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -butylene,



boils at 148—149°/15 mm., is a liquid at the ordinary temperature, but

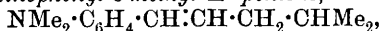
solidifies when immersed in a freezing mixture; its *picrate* has m. p. 137°, and its *platinichloride*, m. p. 154°.

*α-p-Dimethylaminophenyl-δ-methylpentane-α-ol*,



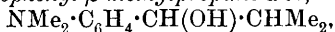
obtained from magnesium *isoamyl* bromide and *p*-dimethylaminobenzaldehyde, has m. p. 48°, and forms the *methiodide*, m. p. 141°.

*α-p-Dimethylaminophenyl-δ-methyl-Δ<sup>α</sup>-pentene*,



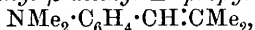
is a yellow oil at the ordinary temperature, b. p. 164—166°/9 mm., but solidifies when immersed in a freezing mixture; its *picrate* has m. p. 111°; its *platinichloride*, m. p. 167°, and its *methiodide*, m. p. 180°.

*α-p-Dimethylaminophenyl-β-methylpropane-α-ol*,



obtained from magnesium *isopropyl* bromide and *p*-dimethylaminobenzaldehyde, has m. p. 39°.

*α-p-Dimethylaminophenyl-β-methyl-Δ<sup>α</sup>-propylene*,



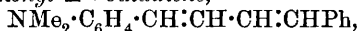
boils at 134—135°/11 mm., and has m. p. 37°; its *picrate* has m. p. 140°, and its *methiodide*, m. p. 170°.

*α-p-Dimethylaminophenyldiisopropylmethane* [*γ-p-dimethylaminophenyl-βδ-dimethylpentane*],  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CHMe}_2)_2$ , obtained from magnesium *isopropyl* bromide and *p*-dimethylaminobenzaldehyde, has m. p. 268°; its *picrate* has m. p. 150°, and its *methiodide* m. p. 171°.

*α-p-Dimethylaminophenyldiisoamylmethane* [*ε-p-dimethylaminophenyl-βθ-dimethylnonane*],  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe}_2)_2$ , obtained from magnesium *isoamyl* bromide and *p*-dimethylaminobenzaldehyde, is a colourless oil, b. p. 184—185°/13 mm.; its *methiodide* has m. p. 175°.

A. McK.

**Action of Magnesium Organic Compounds on *p*-Dimethylaminocinnamaldehyde.** FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, 40, 4368—4369. Compare preceding abstract).—The authors have studied the action of magnesium organic compounds on *p*-dimethylaminocinnamaldehyde. When magnesium ethyl bromide is used, the corresponding carbinol is not obtained, but the product, when distilled under diminished pressure, gives *α-p-dimethylaminophenyl-Δ<sup>αγ</sup>-pentadiene*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} : \text{CH} : \text{CHMe}$ , which separates from alcohol in yellow crystals, m. p. 65°. Its solution in concentrated sulphuric acid is brown, and in dilute sulphuric acid red; its *picrate* has m. p. 145°. *γ-Phenyl-α-p-dimethylaminophenyl-Δ<sup>α</sup>-propene-γ-ol(3)*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CHPh} \cdot \text{OH}$ , obtained from magnesium phenyl bromide and *p*-dimethylaminocinnamaldehyde, has m. p. 160° (decomp.); its ethereal solution is yellow; its solution in glacial acetic acid is red; its solutions in chloroform and alcohol respectively brown. *δ-Phenyl-α-p-dimethylaminophenyl-Δ<sup>αγ</sup>-butadiene*,



obtained from magnesium benzyl chloride and *p*-dimethylaminocinnamaldehyde, separates from light petroleum in yellow crystals, m. p. 171°.

A. McK.

[Arylsulphonic Esters of Salicylaldehyde and its Homologues.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 185547).—The arylsulphonic esters of salicylaldehyde are produced by shaking together at 70° an arylsulphonyl chloride and the aqueous solution of the sodium derivative of salicylaldehyde. The *p*-toluenesulphonyl derivatives of salicyl-, *o*-homosalicyl-, and *p*-homosalicylaldehydes are well-defined crystalline compounds melting respectively at 52–60°, 62°, and 68–69°. *Benzenesulphonyl-p-homosalicylaldehyde*, m. p. 63°, crystallises from petroleum in rectangular plates. When these arylsulphonyl derivatives are heated with the alkylbenzyl-anilinesulphonic acids in the presence of aqueous acids, leucodisulphonic acids are produced, which, on oxidation with acetic acid and lead dioxide, give rise to coloured disulphonic acids of the malachite-green series. G. T. M.

Preparation of 4-Benzoylaminoaceto-1:2-dialkyloxybenzenes. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 185598).—The action of hippuryl chloride on catechol leads to the attachment of the hippuryl group to one of the hydroxylic oxygens, with the formation of monohippuryl catechol. When this condensation is effected in the presence of aluminium chloride with a 1:2-dialkyloxybenzene instead of catechol, the hippuryl group enters the ring in the para-position to one of the oxygen atoms, so that compounds having the general formula  $C_6H_3(OR)_2 \cdot CO \cdot CH_2 \cdot NH \cdot CPh$  are produced, these substances being utilised in the preparation of physiologically active compounds. 4-Benzoylaminoacetylveratrole,  $C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot NH \cdot CPh$ , felted needles, m. p. 155°, and 4-benzoylaminoacetyl-1:2-diethoxybenzene,  $C_6H_3(OEt)_2 \cdot CO \cdot CH_2 \cdot NH \cdot CPh$ , needles, m. p. 162°, are thus obtained from veratrole and 1:2-diethoxybenzene respectively. G. T. M.

Hexahydroacetophenone, Dodecahydrobenzophenone, Dodecahydrodiphenyl, and other Hydroaromatic Derivatives. CARL HELL and OSCAR SCHAAL (*Ber.*, 4162–4166. Compare von Braun, this vol., i, 893).—The best method of preparation of cyclohexyl methyl ketone is from cyclohexanol by first preparing cycloiodohexane, then causing the magnesium cyclohexyl iodide to condense with acetaldehyde, and oxidising the secondary alcohol so obtained to the ketone. The yield is 50% of the cyclohexanol employed. Contrary to von Braun's statement, this ketone gives a hydrogen sulphite compound. cycloHexyl methyl ketone is also obtained in small yield by the distillation of a mixture of barium cyclohexanecarboxylate and acetate; acetone, and dicyclohexyl ketone,  $CO(C_6H_{11})_2$ , an oily liquid, b. p. 158–161°/14 mm., are also formed. Attempts to prepare cyclohexyl methyl ketone by reducing acetophenone by sodium and amyl alcohol, by the condensation of acetyl chloride and cyclohexanol, and by the interaction of acetonitrile and magnesium cyclohexyl iodide were without result.

The yield of iodocyclohexane from cyclohexanol is quantitative, whereas that of the bromo- and chloro-derivatives is only 50% (compare Freundler and Dammond, *Abstr.*, 1905, i, 890).

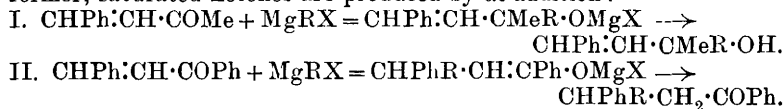
All three haloid compounds give by the Grignard reaction the normal organomagnesium compound, *cyclohexene*, and, in addition, the iodide yields *dodecahydrodiphenyl* [*dicyclohexyl*],  $C_6H_{11} \cdot C_6H_{11}$ , an agreeable-smelling liquid, m. p.  $4^\circ$ , b. p.  $234^\circ/760$  mm. A cryoscopic determination shows the mol. wt. to be 164, calc. 166; it reacts in sunlight very energetically with bromine.

Magnesium methyl iodide and ethyl *cyclohexanecarboxylate* give *cyclohexyldimethylcarbinol*, b. p.  $85-86^\circ/14$  mm. (compare Sabatier and Mailhe, Abstr., 1904, i, 810); the corresponding *diethyl* compound,  $C_6H_{11} \cdot C_2H_5 \cdot OH$ , has b. p.  $104-106^\circ/14$  mm. The *diphenyl* compound is an oily liquid, which loses water at  $210-220^\circ/14$  mm., and by several distillations the unsaturated *hydrocarbon*,  $C_6H_{10} \cdot CPh_2$ , is obtained, crystallising from methyl alcohol in prisms, m. p.  $84^\circ$ . W. R.

**Halogen Derivatives of Benzophenone and of Di- and Tri-phenylmethane.** FRANS M. JAEGER (*Zeitsch. Kryst. Min.*, 1907, 44, 50—60).—Determinations of the crystalline forms of the following compounds: 2-bromobenzophenone; 2:4'-dichlorobenzophenone; 2:4:6-trichlorobenzophenone; 4:4'-dichlorodiphenylmethane;  $\alpha$ -4:4'-trichlorodiphenylmethane;  $\alpha$ -bromodiphenylmethane; phenylindoxazen; 4:4':4''-tribromotriphenylmethane; 4:4':4''-trinitrotriphenylcarbinol; reduction product from 4:4':4''-4'''-tetrachlorobenzopinacolin; 4:4':4''-4'''-tetrachlorotetraphenylethane.

L. J. S.

**Reaction Between Unsaturated Compounds and Organic Magnesium Compounds. XII. Aldehydes and Ketones.** ELMER P. KOHLER (*Amer. Chem. J.*, 1907, 38, 511—561).—In an earlier paper (Abstr., 1904, i, 595), an account was given of the action of organic magnesium compounds on  $\alpha\beta$ -unsaturated ketones containing phenyl in combination with the carbonyl group. On comparing the reactions of these phenyl ketones with those of corresponding methyl ketones, it has been observed that in the latter  $\alpha\beta$ -addition takes place with formation of unsaturated alcohols, whilst, in the former, saturated ketones are produced by  $\alpha\delta$ -addition:



An investigation has been made with the object of ascertaining whether all unsaturated ketones behave in one or other of these ways, or whether substances could be found which would give both reactions. It has been found that certain ketones react in both ways, but that the relative proportions in which the  $\alpha\beta$ - and  $\alpha\delta$ -addition takes place depend on the nature of the unsaturated compound, the number and arrangement of the hydrocarbon residues and the character of the magnesium derivative. Experiments have been made to determine the relative importance of these factors, and attempts have been made to estimate the amounts of the various products.

In carrying out the experiments, the unsaturated compound was added gradually to a large excess of the reagent, cooled in a freezing mixture. The product was poured on ice and treated with hydro-

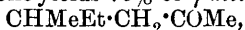
chloric acid to remove basic salts. The ethereal layer was separated, dried, and distilled; the residue was dissolved in acetone and treated with powdered potassium permanganate, the temperature being kept below 20°. In this way, the unsaturated products were destroyed and the saturated ketone could be collected and weighed. The quantitative results are expressed as the percentage of the unsaturated compound represented by the amount of  $\alpha\delta$ -additive product obtained. Most ketones yield both unsaturated alcohols and saturated ketones, whilst aldehydes yield the former only.

It is shown that the activity of the carbonyl group in unsaturated ketones varies in the same way as that of the corresponding saturated compounds, and that it merely determines the rate of the reaction. The final result depends quite as much on the rate of  $\alpha\delta$ -addition, and substances in which the activity of the carbonyl group is approximately the same may give almost entirely different products with the same reagent. The reactivity of the unsaturated compounds undergoes a gradual diminution as the hydrogen atoms are successively replaced by hydrocarbon residues, and the phenomena observed can be satisfactorily explained as being due to steric hindrance. The effect produced on the reaction by the nature of the magnesium derivative is shown by the different relative amounts of  $\alpha\beta$ - and  $\alpha\delta$ -additive products obtained with magnesium ethyl and magnesium phenyl bromides. Variations in the temperature and solvent do not appreciably affect the result.

The behaviour of unsaturated compounds resembles that of tautomeric substances, but in the case of the unsaturated ketones the results cannot be explained by intermediate compounds or by assuming that only one of the products is formed directly. In this case, the two additive reactions are so independent of each other that their rates are governed by quite different factors. The only satisfactory explanation therefore is that these unsaturated compounds can exist in two modifications, such as  $C:C:C:C$  and  $-C:C:C-C-$ .

By the action of magnesium ethyl bromide on acraldehyde, ethyl-vinylcarbinol is produced, whilst with magnesium phenyl bromide, phenylallyl alcohol is formed.

Ethylideneacetone reacts with magnesium methyl bromide with formation of dimethylisobutylcarbinol and methyl isobutyl ketone, the latter forming about 75% of the product. With magnesium ethyl bromide, ethylideneacetone yields 75% of  $\gamma$ -methylhexane- $\epsilon$ -one,



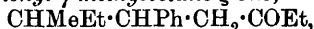
b. p. 146—147°, whilst with magnesium phenyl bromide it gives 40% of  $\beta$ -phenylpropyl methyl ketone,  $CHPhMe \cdot CH_2 \cdot COMe$ , b. p. 132°/22 mm., which furnishes an *oxime*, b. p. 160°/22 mm., as a viscous liquid.

In the case of mesityl oxide,  $\alpha\delta$ -addition does not take place.

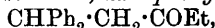
Benzylideneacetone (styryl methyl ketone) reacts with magnesium ethyl bromide or iodide with production of 60% of phenylhexanone,  $CHPhEt \cdot CH_2 \cdot COMe$ , b. p. 130°/18 mm., which yields an *oxime*, b. p. 170°/20 mm. With magnesium phenyl bromide, it gives 12% of  $\beta\beta$ -diphenylethyl methyl ketone,  $CHPh_2 \cdot CH_2 \cdot COMe$ , b. p. 194°/20 mm.

(compare Abstr., 1904, i, 596). The *keto*oxime exists in two forms, m. p. 91° (plates) and 128° (needles).

Styryl ethyl ketone, on treatment with magnesium ethyl bromide, yields 71% of  $\gamma$ -phenylheptanone,  $\text{CHPhEt}\cdot\text{CH}_2\cdot\text{COEt}$ , b. p. 255°, which gives an *oxime*, b. p. 172°/18 mm. With magnesium isobutyl bromide, a similar yield of  $\delta$ -phenyl- $\gamma$ -methyl-octane- $\zeta$ -one,

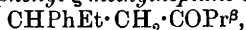


b. p. 152°/17 mm., is obtained, which furnishes an *oxime*, b. p. 185°. With magnesium phenyl bromide, *aa*-diphenylpentane- $\gamma$ -one,

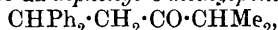


b. p. 334—335°, is produced in a yield of 40% of the unsaturated ketone; its *oxime* exists in two stereoisomeric modifications, m. p. 146° (needles) and 117° (plates).

Styryl isopropyl ketone reacts with magnesium ethyl bromide with formation of 100% of  $\gamma$ -phenyl- $\zeta$ -methylheptane- $\epsilon$ -one,

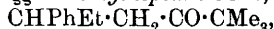


b. p. 138°/15 mm.; the *oxime* has b. p. 175°/18 mm. With magnesium phenyl bromide, 88% of *aa*-diphenyl- $\delta$ -methylpentane- $\gamma$ -one,

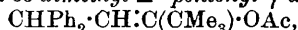


m. p. 66°, is produced, which forms colourless prisms and yields two isomeric *oximes*, m. p. 151° (needles) and 99° (plates); the  $\beta$ -bromo-derivative,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{Pr}^\beta$ , m. p. 108°, crystallises in needles, and is converted by potassium hydroxide into *aa*-diphenyl- $\delta$ -methyl- $\Delta^a$ -pentene- $\gamma$ -one,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CHMe}_2$ , b. p. 210—211°/15 mm.

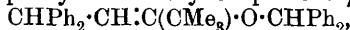
Benzylidenepinacolone, on treatment with magnesium ethyl bromide, yields 100% of  $\gamma$ -phenyl- $\zeta\zeta$ -dimethylheptane- $\epsilon$ -one,



b. p. 145°/15 mm., m. p. 34°, which crystallises in needles, and yields a mixture of *oximes*, m. p. 83° (needles) and 36° (prisms). With magnesium phenyl bromide, 100% of *aa*-diphenyl- $\delta\delta$ -dimethylpentane- $\gamma$ -one,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_3$ , m. p. 85°, is obtained, and forms slender needles. If acetyl chloride is added to the magnesium compound produced by the action of magnesium phenyl bromide on benzylidenepinacolone, *aa*-diphenyl- $\delta\delta$ -dimethyl- $\Delta^\beta$ -pentenyl  $\gamma$ -acetate,

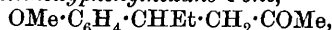


m. p. 165°, is obtained, and crystallises in brilliant plates. The magnesium compound does not react with simple alkyl halides, but reacts with diphenylbromomethane with formation of the *diphenyl-methyl ether* of *aa*-diphenyl- $\delta\delta$ -dimethyl- $\Delta^\beta$ -pentene- $\gamma$ -ol,



m. p. 224°, which crystallises in plates.  $\beta$ -Bromo-*aa*-diphenyl- $\delta\delta$ -dimethylpentane- $\gamma$ -one,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CMe}_3$ , m. p. 145°, crystallises in plates, and is converted by potassium hydroxide into *aa*-diphenyl- $\delta\delta$ -dimethyl- $\Delta^a$ -pentene- $\gamma$ -one,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CMe}_3$ , m. p. 66°, which forms pale yellow plates.

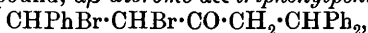
*p*-Methoxybenzylidenacetone reacts with magnesium ethyl bromide to form 63% of  $\gamma$ -*p*-methoxyphenylhexane- $\epsilon$ -one,



b. p. 170°/18 mm., which yields an *oxime*, b. p. 195°/18 mm.

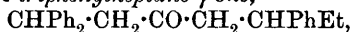
Dibenzylidenacetone and magnesium ethyl bromide react with formation of 91% of benzylidenephenylhexanone [*aa*-diphenyl- $\Delta^a$ -heptene-

$\gamma$ -one],  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPhEt}$ , b. p. 224—228°, m. p. 87°, which forms long needles; the *oxime*, m. p. 117°, crystallises in needles. With magnesium phenyl bromide, 73% of *benzylidenediphenylbutanone* [ $\alpha\epsilon$ -triphenyl- $\Delta^a$ -pentene- $\gamma$ -one],  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ , m. p. 136°, is produced, which forms pale yellow needles, and yields an *oxime*, m. p. 144°, which crystallises in needles. By the action of bromine on the preceding compound,  $\alpha\beta$ -dibromo- $\alpha\epsilon$ -triphenylpentane- $\gamma$ -one,

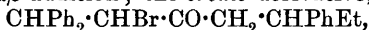


is obtained, and forms colourless needles.

Diphenylheptenone reacts with magnesium ethyl bromide to form 100% of  $\gamma\gamma$ -diphenylnonane- $\epsilon$ -one,  $\text{CHPhEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPhEt}$ , m. p. 56°, which crystallises in needles. With magnesium phenyl bromide, 93% of  $\alpha\alpha$ -triphenylheptane- $\gamma$ -one,



m. p. 72°, is produced together with about 7% of an unsaturated compound formed by  $\alpha\beta$ -addition; the *bromo*-derivative,

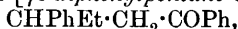


m. p. 153°, crystallises in needles.

Triphenylpentenone and magnesium ethyl bromide yield 100% of triphenylheptanone. With magnesium phenyl bromide, 99% of tetraphenylpentanone is produced together with a very small proportion of unsaturated compounds formed by  $\alpha\beta$ -addition.  $\beta$ -Bromo- $\alpha\alpha\epsilon$ -tetraphenylpentane- $\gamma$ -one,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ , m. p. 160°, crystallises in needles.

Trichloroethylideneacetophenone reacts with magnesium phenyl bromide with formation of 95% of *aaa-trichloro- $\beta$ -phenylbutyrophenone*,  $\text{CCl}_3\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$ , m. p. 137°.

Benzylideneacetophenone and magnesium ethyl bromide yield 99% of  $\beta$ -phenylvalerophenone [ $\gamma\epsilon$ -diphenylpentane- $\epsilon$ -one],



m. p. 63°, which forms thin needles and gives an *oxime*, m. p. 87°. With magnesium phenyl bromide, 94% of diphenylpropiofenone is produced.

Anisylideneacetophenone and magnesium ethyl bromide react with formation of 98% of *p-methoxyphenylvalerophenone*,



m. p. 58°, which crystallises in thick, lustrous needles; the *oxime*, m. p. 92°, forms prisms. With magnesium phenyl bromide, 96% of *anisylphenylpropiofenone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$ , m. p. 93°, is produced and forms stout needles.

Anisyl styryl ketone and magnesium ethyl bromide yield 100% of  $\beta$ -phenylbutyl anisyl ketone,  $\text{CHPhEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p. 85°, which crystallises in long, thin needles, and furnishes an *oxime*, m. p. 72°. With magnesium phenyl bromide, 99% of *diphenylethyl anisyl ketone*,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 118°, is produced; its *bromo*-derivative, m. p. 144°, is converted by potassium hydroxide into  $\beta$ -phenylstyryl anisyl ketone,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 103°, which yields a *bromo*-derivative,  $\text{CPh}_2\cdot\text{CBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 157°.

*Cinnamoylmesitylene*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , m. p. 63°, prepared by adding aluminium chloride to a solution of mesitylene and

cinnamoyl chloride in carbon disulphide, forms large, yellow plates, and is converted by bromine into  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionylmesitylene,  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , m. p.  $122^\circ$  (decomp.). It reacts with magnesium phenyl bromide with formation of 100% of  $\beta\beta$ -diphenylpropionylmesitylene,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , which yields a bromo-derivative,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , m. p.  $172^\circ$ . When the bromo-derivative is treated with potassium hydroxide, it is converted into phenylcinnamoylmesitylene,  $\text{CHPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , m. p.  $104^\circ$ , which forms dark yellow plates.

By the reactions of bromobenzylidenacetophenone, benzylidenepropiophenone, and benzylidenedeoxybenzoin with magnesium alkyl halides, unsaturated compounds formed by  $\alpha\beta$ -addition are not produced, and it is evident therefore that substituents in the  $\alpha$ -position interfere with the addition to the carbonyl group.

Dypnone reacts with magnesium ethyl bromide with formation of 44% of  $\beta$ -phenyl- $\beta$ -methylvalerophenone,  $\text{CPhMeEt}\cdot\text{CH}_2\cdot\text{COPh}$ , b. p.  $202^\circ/18$  mm.; its oxime, b. p.  $222^\circ/15$  mm., is amorphous. The quantity of diphenylbutyrophenone formed by the action of magnesium phenyl bromide on dypnone (Abstr., 1904, i, 596) is 41%.

Phenylbenzylidenacetophenone and magnesium ethyl bromide yield 18% of  $\beta\beta$ -diphenylvalerophenone,  $\text{CHPh}_2\text{Et}\cdot\text{CH}_2\cdot\text{COPh}$ , b. p.  $252^\circ/15$  mm.; its oxime was prepared. With magnesium phenyl bromide, a saturated ketone is not produced, but the unsaturated alcohol and hydrocarbon are obtained, which have been described by Vorländer, Siebert, and Osterburg (Abstr., 1906, i, 346).

Diphenylbenzylidenacetophenone,  $\text{CPh}_2\cdot\text{CPh}\cdot\text{COPh}$ , m. p.  $153^\circ$ , obtained by the action of potassium hydroxide on bromotriphenylpropiophenone, forms pale yellow needles and is very inactive. When treated with magnesium ethyl bromide, an unsaturated hydrocarbon is produced, and indications are obtained of the formation of a saturated ketone.

Magnesium phenyl bromide reacts with benzoylphenylacetylene with formation of hydroxytriphenylpropinene (benzophenonephenylacetylene) (Nef, Abstr., 1900, i, 21), but a saturated ketone is not produced.

E. G.

**Derivatives of Fluorenoneoxime. Contribution II. to the Theory of Colour.** JULIUS SCHMIDT and JULIUS SÖLL (*Ber.*, 1907, 40, 4257—4260. Compare this vol., i, 630).—The authors have prepared fluorenone and its oxime and various derivatives of the latter, and have repeatedly crystallised them from suitable solvents until their colours underwent no further change. Thus purified, fluorenone is reddish-yellow; fluorenoneoxime, bright yellow; its sodium salt, pale yellow; its acetyl and benzoyl derivatives, bright yellow; and its methyl ether, reddish-yellow. As with phenanthraquinone, so also with fluorenone, replacement of the ketonic oxygen by the hydroxyimino-group is accompanied by brightening of the colour. Not so distinct, but still appreciable, is the effect which the introduction of acetyl, benzoyl, or sodium into the molecule of fluorenoneoxime has in brightening the colour.



*Fluorenoneoxime methyl ether*,  $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}:\text{N} \cdot \text{OMe}$ , crystallises from alcohol in reddish-yellow needles, m. p. 145—146°, and dissolves readily in all the ordinary solvents except light petroleum.

The acetyl derivative of fluorenoneoxime has m. p. 79°; Wegerhoff (*Annalen*, 1888, 252, 36; *Abstr.*, 1889, 1066) gave 76°.

These derivatives of fluorenoneoxime are dissolved by concentrated sulphuric acid, giving reddish-brown solutions, from which they are precipitated by the addition of water. T. H. P.

**Constitution and Colour of Derivatives of *o*-Benzoquinone- and Naphthaquinone-dioximes.** ARTHUR HANTZSCH and WALTER H. GLOVER (*Ber.*, 1907, 40, 4344—4350. Compare this vol., i, 101).—Whilst *o*-benzoquinonedioxime is faintly coloured, it forms dark red salts and also a colourless anhydride. It could not be determined whether the alkyl (or acyl) derivatives of the type  $\text{OR} \cdot \text{N}:\text{C}_6\text{H}_4:\text{N} \cdot \text{OR}$  are colourless, since the salts are so readily transformed into the anhydrides, thus:  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{ONa} \\ \text{N} \cdot \text{OH} \end{smallmatrix} = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > \text{O} + \text{NaOH}$ . Analogous derivatives of  $\beta$ -naphthaquinonedioxime,  $\text{OR} \cdot \text{N}:\text{C}_{10}\text{H}_6:\text{N} \cdot \text{OR}$ , are yellow, in spite of the fact that the anhydride,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > \text{O}$ , is colourless. The intensity of the colour of these compounds depends largely on the solvent. The dioxime salts of the benzene series are red, those of the phenanthrene series yellow; the alkyl and acyl derivatives of the naphthalene series are yellow, those of the phenanthrene series are colourless. The intensity of colour during salt formation from derivatives of *o*-benzoquinonedioxime indicates that the latter are *pseudo*-acids.

Aqueous solutions of *o*-benzoquinonedioxime are yellow and faintly acid in reaction. Determinations of electrical conductivity showed that *o*-benzoquinonedioxime is 100 times as weak as acetic acid. The solutions of the dioxime in alkalis are blood-red; the salts are, however, very unstable, and from their aqueous solutions the colourless anhydride separates. When dry ammonia is passed into the yellow solution of the dioxime in absolute ether, there is no precipitate, and the colour does not change. The solutions of the dioxime in strong acids are also blood-red. Tetrabromo-*o*-benzoquinonedioxime benzyl ether was not formed from benzyl hydroxylamine and tetrabromo-*o*-benzoquinone; in place of it, *benzylhydroxylaminotribromo-o-quinone*,  $\text{C}_6\text{Br}_3\text{O}_2:\text{NH} \cdot \text{O} \cdot \text{C}_7\text{H}_7$ , was produced; it separates from glacial acetic acid or benzene in orange-coloured needles, m. p. 170° (decomp.).

Various salts of  $\beta$ -naphthaquinonedioxime  $\alpha$ -methyl ether were prepared, namely, the *normal potassium salt*, *hydrogen potassium salt*, and the *silver salt*. The *benzoyl derivative*,  $\text{OMe} \cdot \text{N}:\text{C}_{10}\text{H}_6:\text{N} \cdot \text{OBz}$ , has m. p. 116—119°; the yellow tint of the benzoyl derivative in various solvents is not so pronounced as that of the parent substance.

*$\beta$ -Naphthaquinonedioxime  $\alpha$ -benzyl ether*,  $\text{OH} \cdot \text{N}:\text{C}_{10}\text{H}_6:\text{N} \cdot \text{O} \cdot \text{C}_7\text{H}_7$ , obtained by the action of hydroxylamine on benzyl ether monoxime,

separates from a mixture of chloroform and acetone in yellow prisms, m. p.  $168^{\circ}$ ; its *benzoyl* derivative forms needles, m. p.  $116^{\circ}$ . The colour of these compounds in various solvents was studied.

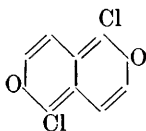
A. McK.

#### Quinonoid Compounds. XIV. *amphi*Naphthaquinones. II.

RICHARD WILLSTÄTTER and JAKOB PARNAS (*Ber.*, 1907, 40, 3971—3979. Compare this vol., i, 425).—An account of the formation of 1:5-dichloro*amphi*naphthaquinone and its derivatives.

1:5-Dichloro-2:6-dihydroxynaphthalene,  $C_{10}H_6O_2Cl_2$ , prepared by the action of chlorine on 2:6-dihydroxynaphthalene in glacial acetic acid solution, crystallises in needles containing  $2C_2H_4O_2$ , lost on exposure to air, or from benzene in hexagonal plates, m. p.  $223.5^{\circ}$  (corr.), and forms a *diacetate*,  $C_{14}H_{20}O_4Cl_2$ , crystallising in plates, m. p.  $179^{\circ}$  (corr.).

1:5-Dichloro*amphi*naphthaquinone (annexed formula), obtained in a 36—45% yield by oxidation of the 2:6-dihydroxy-compound with lead dioxide in benzene solution, crystallises from chloroform in reddish-yellow prisms, or from alcohol in golden needles, or from benzene-light petroleum in brownish-yellow needles, m. p.  $206.5^{\circ}$  (corr.) (intumesces), is not volatile, odourless, stable in air, and more stable than *amphi*naphthaquinone towards organic solvents; it dissolves only slowly in alkalis, gives an olive-green coloration with concentrated sulphuric acid, and is reduced to 1:5-dichloro-2:6-dihydroxynaphthalene by sulphurous acid, dilute hydriodic acid, or phenylhydrazine in benzene solution. The dichloro*amphi*naphthaquinone is an energetic oxidising agent; it gives a blue coloration with guaiacum resin solution, converts hydrocoerulignone into coerulignone, and forms malachite-green from the *leuco*-base. It yields a colourless, crystalline *acetate* with acetic anhydride in presence of sulphuric acid, and combines with 2:6-dihydroxy- and 1:5-dichloro-2:6-dihydroxynaphthalenes, forming *amphi*naphthaquinonehydrones, crystallising in dark green needles, and giving an intense emerald-green coloration with concentrated sulphuric acid.



The action of *as*-benzoylphenylhydrazine on 1:5-dichloro*amphi*naphthaquinone in glacial acetic solution leads to the formation of the *a*-benzoylphenylhydrazone of 5-chloro-6-hydroxy- $\beta$ -naphthaquinone,  $C_{23}H_{15}O_3N_2Cl$ , which crystallises in yellowish-red plates or red prisms, m. p.  $224^{\circ}$  (corr.), is extracted unchanged from its ethereal solution by dilute potassium hydroxide, is stable towards phenylhydrazine in boiling benzene solution, and forms a brilliant reddish-yellow solution in alcohol, which is decolorised by zinc dust and acetic acid. When treated with concentrated sulphuric acid, the benzoylhydrazone is hydrolysed, forming the *a*-phenylhydrazone,  $C_{16}H_{11}O_2N_2Cl$ , which crystallises from glacial acetic acid in yellowish-red needles, m. p.  $198^{\circ}$  (corr.), and dissolves in aqueous alkalis forming intense brownish-red, or in very dilute alkalis in bluish-red, solutions. The phenylhydrazone and benzoylphenylhydrazone on treatment with benzoyl chloride in pyridine solution yield the *dibenzoyl* derivative,  $C_{30}H_{19}O_4N_2Cl$ , which crystallises in brownish-yellow prisms, m. p.  $208.5^{\circ}$  (corr.), gives a cherry-red coloration.

tion with concentrated sulphuric acid, and forms benzanilide on reduction with zinc dust and acetic acid. G. Y.

**Preparation of Leucohydroxyanthraquinone.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 183332).—Leucoquinizarin is produced from 2:4-dinitro-1-anthraquinone by reducing this to the corresponding diamino-compound with stannous chloride and then boiling the mixture for eight hours; the *leuco*-base separates on cooling. A similar result is obtained on reducing 2:4-dinitro-1-hydroxyanthraquinone with sodium sulphide and then boiling the 2:4-diamino-1-hydroxyanthraquinone thus produced with stannous chloride and hydrochloric acid.

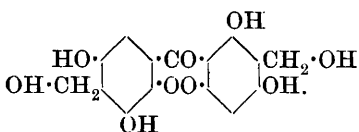
The reduction of the dinitrohydroxyanthraquinones containing one nitro-group in the ortho- and one in the para-position to the hydroxy-compound leads to the same result as the reduction of the mono-nitro-compounds, but, as the polynitro-derivatives are more readily obtained, there is a technical advantage in starting with the more highly nitrated products. G. T. M.

**Preparation of Alkylated 4:8-Diaminoanthrarufins.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 185546).—Alkylated 4:8-diaminoanthrarufins are obtained by treating the 4:8-halogen derivatives of anthrarufin with the monoalkylamines in the presence of a catalyst, such as copper. The products when sulphonated furnished valuable wool dyes.

s-4:8-Diethyldiaminoanthrarufin, bronze needles, m. p. 292°, and s-4:8-dimethyldiaminoanthrarufin, dark blue needles, m. p. above 300°, were prepared by heating at 100° in the presence of copper powder 4:8-dibromoanthrarufin and 20% alcoholic solutions of ethylamine and methylamine respectively. G. T. M.

**Preparation of 1:2:5-Trihydroxyanthraquinone and 1:2:5-Trihydroxyanthraquinone-3-sulphonic Acid.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 178631).—1:2:5-Trihydroxyanthraquinone is obtained readily by heating 5 parts of sodium alizarin-5-sulphonate with 15 parts of sodium hydroxide and 3 parts of water at 180–200°, and then acidifying the aqueous extract of the fused mass. The trihydroxy-compound is deposited in yellow flakes. The alkali fusion of sodium alizarin-3:5-disulphonate leads to the production of sodium 1:2:5-trihydroxyanthraquinone-3-sulphonic acid, which separates in yellow flakes, soluble in water, and reprecipitated by salting out. G. T. M.

**Preparation of  $\omega$ -Dihydroxydimethyl-2:6-anthrachrysone.**

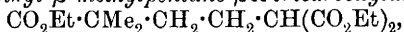


FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 184768).—Anthrachrysone readily reacts with formaldehyde in alkaline solution to yield an insoluble yellow condensation product, which is probably  $\omega$ -dihydro-

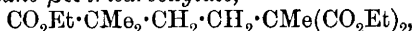
*oxydimethyl-2:6-anthrachryson*. The sodium salt is a well-defined, sparingly soluble compound, separating in garnet-red crystals.

G. T. M.

**Syntheses in the Camphor Group. Complete Synthesis of Campholene.** GUSTAVE BLANC (*Compt. rend.*, 1907, 145, 681—683).—The author has synthesised campholene by a similar method to that employed in the synthesis of its lower homologue, *isolaurolene* (Abstr., 1906, i, 523). *Ethyl β-methylpentane-β,ε-tricarboxylate*,



obtained by the condensation of ethyl γ-bromo-αα-dimethylbutyrate with ethyl sodiomalonate, is a colourless liquid, b. p. 175°/12 mm., and reacts with methyl iodide in the presence of sodium ethoxide to yield *ethyl β-methylhexane-β,ε-tricarboxylate*,



b. p. 168°/14 mm.; the corresponding acid forms sparingly soluble, white needles, melts at 205°, losing carbon dioxide and forming *ααδ-trimethyladipic acid*,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , m. p. 113—114°, which is probably identical with the acid obtained by Wallach and Kempe in the oxidation of pulegone (Abstr., 1904, i, 74). *ααδ-Trimethyladipic anhydride* is converted by careful distillation into

*1:1:4-trimethylcyclopentane-5-one*,  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad \quad | \\ \text{CHMe} \cdot \text{CO} \end{array} > \text{CMe}_2$ , b. p. 152°, a

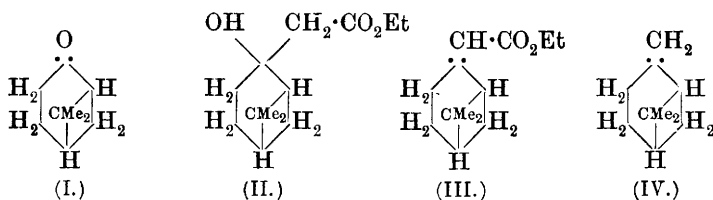
liquid having an odour similar to that of camphor or menthone; it forms an *oxime*, m. p. 62°, and condenses with magnesium methyl iodide to form the *tertiary alcohol*,  $\begin{array}{c} \text{CH}_2 - \text{CMe}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CHMe} \end{array} > \text{CMe} \cdot \text{OH}$ , an oily

liquid, b. p. 72°/18 mm., having an intense musty, camphoraceous odour, which yields campholene,  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad \quad | \\ \text{CMe} : \text{CMe} \end{array} > \text{CMe}_2$ , on distillation under ordinary pressure.

M. A. W.

**Terpenes and Etheral Oils. LXXXVIII.** OTTO WALLACH (*Annalen*, 1907, 357, 49—71).—I. *Synthesis from Nopinone of a Hydrocarbon related to β-Pinene*.—β-Pinene (nopinene) occurs commonly in small amounts in various turpentine oils, but, as it has not yet been isolated from these, its physical and other properties are not definitely known. It seemed therefore of interest to synthesise a hydrocarbon having the structure of β-pinene. Starting from nopinone (Wallach and Blumann, this vol., i, 936), this has now been accomplished by the method previously employed (Abstr., 1906, i, 563) for the introduction of a methylene group into cyclic hydrocarbons.

The action of zinc and ethyl bromoacetate on nopinone (I) in benzene solution leads to the formation of the *hydroxy-ester* (II), which has not been isolated, but when heated, after removal of the benzene, with potassium hydrogen sulphate at 150° yields the unsaturated *ester* (III). On hydrolysis of this, the acid is obtained as a syrup, b. p. 190—210°/13 mm.; the *silver salt*,  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{Ag}$ , was analysed. When distilled under atmospheric pressure, the acid loses carbon dioxide and forms a *β-pinene* (IV), b. p. 158°,  $D^{20}_D$  0.8630,  $[\alpha]_D + 15.93^\circ$  undiluted, or  $+12.76^\circ$  in ethereal solution,  $n^{20}_D$  1.4699:



On oxidation with potassium permanganate and sodium hydroxide at  $0^\circ$ , the hydrocarbon yields a sparingly soluble *sodium* salt, which resembles sodium nopate obtained from turpentine oil, but is dextrorotatory; the *silver* salt,  $C_{10}H_{15}O_3Ag$ , was analysed. The *acid* crystallises from benzene in needles, m. p.  $154-155^\circ$ , is dextrorotatory, and differs from nopic acid in recrystallising unchanged from dilute sulphuric acid. The benzene mother liquors from the acid contain small amounts of a *substance*, m. p.  $110-122^\circ$ . Oxidation of the acid with permanganic acid leads to the formation of a *ketone*,  $C_9H_{14}O$ , m. p. about  $60^\circ$ , which yields a *semicarbazone*,  $C_{10}H_{17}ON_3$ , m. p.  $206-207^\circ$ .

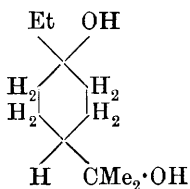
The action of hydrogen chloride on the hydrocarbon leads to the formation of liquid *additive* compounds, whilst that of sulphuric acid leads to the formation of a crystalline, saturated, secondary *alcohol*,  $C_{10}H_{17}OH$ , which has an odour of camphor, and on oxidation with chromic acid yields a *ketone*,  $C_{10}H_{16}O$ . This solidifies below  $0^\circ$ , has an odour of camphor and menthone, and forms a *semicarbazone*,  $C_{11}H_{19}ON_3$ , crystallising in needles, m. p.  $220-221^\circ$  (compare Aschan, this vol., i, 630).

The relation of the synthetical  $\beta$ -pinene to that occurring in turpentine oil is discussed; it is considered that a change in the configuration takes place during the conversion of the nopinone into the synthetical hydrocarbon. Of special interest is the formation of a secondary alcohol from a hydrocarbon containing the grouping:

$$\begin{array}{c} \cdot C > C : CH_2 \\ \cdot C > \end{array}$$

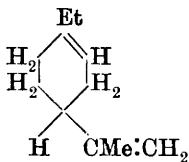
II. *Synthesis of Homologous Compounds of the Dipentene Series.*—It has been shown (Wallach and Blumann, *loc. cit.*) that methyl-nopinol is readily converted, on the one hand, into terpin hydrate and dipentene, and, on the other, into terpinolene and terpinene. Probably optically active limonene and  $\alpha$ -pinene also are formed. These reactions have now been employed in the formation of homologues of the terpene derivatives.

*Ethlynopinol*,  $C_{11}H_{20}O$ , prepared by the action of magnesium ethyl iodide on nopinone, forms large crystals, m. p.  $43-45^\circ$ , b. p.  $219-223^\circ$ , and when heated with formic acid loses water and yields homologous terpenes. When shaken with 5% sulphuric acid, ethlynopinol yields a *homologue* of terpin hydrate having the annexed constitution, which forms transparent crystals containing  $H_2O$ , m. p.  $75-76^\circ$ , and is readily converted into the *dihydrochloride*,  $C_{11}H_{18}, 2HCl$ , m. p.  $63-64^\circ$ . This is formed also by the action of hydrogen chloride on ethlynopinol in glacial acetic acid solution, and closely resembles



dipentene dihydrochloride. The *dihydrobromide*,  $C_{11}H_{18}, 2HBr$ , m. p. 82—84°; the *dihydriodide*, m. p. 63—64°.

The *hydrocarbon*,  $C_{11}H_{18}$ , b. p. 201—202°, prepared by treating the dihydrochloride with aniline, yields a crystalline *tetra-bromide*,  $C_{11}H_{18}Br_4$ , m. p. 124—125°, and a crystalline *nitrosochloride*, which loses hydrogen chloride, forming an *oxime*, converted by acids into an *oil* with an odour of carvone. The hydrocarbon is probably a homologue of dipentene having the annexed constitution, mixed with small amounts of an isomeride of the terpinolene series.

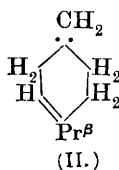
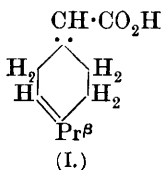


*n*-Propylnopinol,  $C_{12}H_{22}O$ , b. p. 225—235°, is formed in only small amount together with considerable quantities of nopinol by the action of magnesium *n*-propyl iodide on nopinone; it is converted by treatment with sulphuric acid into a *terpin*, which yields a crystalline *dihydrochloride*,  $C_{12}H_{20}, 2HCl$ .

III. *Synthesis in the Terpinene Series.*—*Methylsabinaketol* (*sabinene hydrate*), m. p. 38—39°, b. p. 195—201°, prepared by the action of magnesium methyl iodide on sabinaketone, has a terpineol odour, is stable towards permanganate, and on treatment with hydrogen bromide in glacial acetic acid solution yields terpinene dihydrochloride, m. p. 58—59°. When shaken with 5% sulphuric acid, sabinene hydrate yields terpineneterpin, m. p. 137° (this vol., i, 228).

*Ethylsabinaketol*,  $C_{11}H_{20}O$ , b. p. 100—104°, containing small amounts of an unsaturated substance, is prepared by the action of magnesium ethyl iodide on sabinaketone; dilute sulphuric acid converts it into a *homologue* of terpineneterpin, which crystallises in white leaflets, m. p. 141—142°, and yields a *dihydrobromide*,  $C_{11}H_{18}, 2HBr$ , m. p. 88—89°, formed also by the action of hydrogen bromide on ethylsabinaketol in glacial acetic acid solution. The *dihydrochloride*,  $C_{11}H_{18}, 2HCl$ , crystallises in plates, m. p. 67—68°; the *dihydrobromide*, m. p. 88—89°; the *dihydriodide* forms prisms, m. p. 89—90°.

The action of zinc and ethyl bromoacetate on sabinaketone, elimination of water from the resulting *hydroxy-ester*, and subsequent hydrolysis of the unsaturated *ester* leads to the formation of the unsaturated *acid* (I), m. p. 47—48°. The *silver salt*,  $C_{11}H_{15}O_2Ag$ , was analysed. On distillation, the acid loses carbon dioxide, forming a  $\beta$ -*terpinene* (II), b. p. 176°,  $D_{20} 0.843$ ,  $n_D 1.4773$ , which with hydrogen chloride in glacial acetic acid solution yields terpinene dihydrochloride, m. p. 52°, and is converted by nitrous acid into terpinene nitrosite.



**Terpenes and Ethereal Oils. LXXXIX.** OTTO WALLACH (*Annalen*, 1907, 357, 72—84).—I. *Oxygenated Derivatives of Sylvestrene*.—The method previously described (this vol., i, 64) for substituting hydroxyl groups for halogen atoms in terpene compounds has now been applied to the formation of oxygenated derivatives of sylvestrene.

The prolonged action of hot aqueous potassium hydroxide on sylvestrene dihydrochloride leads to the formation of sylvesterpineol, which distils with steam, in a 70% yield, and sylvesterpin, which remains in the alkaline distillation residue in a 25% yield.

*Sylvesterpin*,  $C_{10}H_{18}(OH)_2$ , separates from ethyl acetate in crystals, m. p. 135—136°,  $[\alpha]_D^{20} + 27.43^\circ$ .

*Sylvesterpineol*,  $C_{10}H_{17}OH$ , b. p. 210—214°, has an intense odour; with concentrated hydrochloric acid, it yields sylvestrenedihydrochloride, and is oxidised by 1% permanganate solution in the cold, yielding the *glycerol*,  $C_{10}H_{17}(OH)_3$ , which is obtained as a viscid, colourless oil, b. p. 165°/11 mm. This, on oxidation with chromic and dilute sulphuric acid, yields an oil which has an aldehyde-like odour, and reduces silver solutions.

*Sylvecarvone*,  $C_{10}H_{14}O$ , formed by removal of hydrogen chloride from sylvestrene nitroschloride and hydrolysis of the resulting *oxime* by boiling oxalic acid, is obtained as an oil, and forms a *semicarbazone*,  $C_{10}H_{14} \cdot N \cdot NH \cdot CO \cdot NH_2$ , crystallising in needles, m. p. 175—177°.

II. *Synthesis of Anethole from Anisaldehyde and of isoSafrole from Piperonal*.—[With EDGAR EVANS.]—The action of zinc and ethyl  $\alpha$ -bromopropionate on anisaldehyde in benzene solution leads to the formation of the *hydroxy-ester*,  $OMe \cdot C_6H_4 \cdot CH(OH) \cdot CHMe \cdot CO_2Et$ , b. p. 235—245°/13 mm., which, when heated with potassium hydrogen sulphate at 150°, loses water and forms *ethyl  $\beta$ -anisyl- $\alpha$ -methylacrylate*,  $OMe \cdot C_6H_4 \cdot CH : CHMe \cdot CO_2Et$ , b. p. 170—180°/25 mm. The acid (Perkin, this Journ., 1877, i, 411), when slowly distilled, loses carbon dioxide and forms anethole.

*$\beta$ -Piperonyl- $\alpha$ -methylacrylic acid*,  $CH_2 \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} C_6H_3 \cdot CH : CHMe \cdot CO_2H$ , prepared in the same manner from piperonal and ethyl  $\alpha$ -bromopropionate, when heated loses carbon dioxide and yields *isosafole*.

III. *Occurrence of Sabinene in Ceylon Cardamom Oil and in Majorana Oil*.—A hydrocarbon, b. p. 165—167°,  $D_{20} 0.846$ , obtained from cardamom and majorana oils was considered previously (this vol., i, 64) to be sabinene. As this is now confirmed by oxidation of the hydrocarbon by means of permanganate with formation of sabinic acid, it is probable that the terpene obtained from these oils by Weber (Abstr., 1887, 596) and Biltz (Abstr., 1899, i, 535) was formed by transformation of the sabinene present (this vol., i, 229).

IV. *Isomeric Camphenes and a New Camphenecamphoric Acid*.—[With PAUL GUTMANN.]—Various observations have suggested that naturally occurring camphene melts at a lower temperature than does synthetical camphene. To determine whether this difference results from the presence of impurities in the naturally occurring hydrocarbon or from the existence of different camphenes, the authors have investigated a camphene, m. p. 39°, b. p. 160—161°,  $D_{40} 0.8555$ ,

$[\alpha]_D - 84.9^\circ$ ,  $n_D^{40} 1.46207$ , obtained from Siberian pinewood oil. This, on oxidation with permanganate, yields a new *camphenecamphoric acid*,  $C_{10}H_{16}O_4$ , which crystallises in needles or leaflets, m. p.  $142^\circ$ ,  $[\alpha]_D - 1.66^\circ$ ; the *silver* salt,  $C_{10}H_{14}O_4Ag_2$ , was analysed. On conversion into the *chloride* and treatment with ammonia, the acid yields the *amide*,  $C_{10}H_{18}O_2N_2$ , crystallising in needles, m. p.  $197^\circ$ . The *dianilide*,  $C_{32}H_{26}O_2N_2$ , m. p.  $218^\circ$ . The action of acetyl chloride on the acid in chloroform solution leads to the formation of a syrupy *anhydride*, which reacts with aniline, forming an *anilic acid*.

Small amounts of a *glycol* and of an *acid*, which forms a sparingly soluble *sodium* salt, are formed together with the camphenecamphoric acid by oxidation of the naturally occurring camphene. This is converted into isoborneol by Bertram's reaction, and forms a solid *hydrochloride*, which, on treatment with aniline, yields a camphene, m. p.  $51^\circ$ ; on bromination by Reychler's method, the camphene, m. p.  $39^\circ$ , yields a *dibromide*, m. p.  $89^\circ$ . In view of these facts, the naturally occurring camphene is considered to be a physical isomeride of the synthetical hydrocarbon.

A specimen of camphene obtained from citronella oil yielded on oxidation the camphenecamphoric acid, m. p.  $142^\circ$ . Another camphene, m. p.  $50^\circ$ , b. p.  $160-161^\circ$ ,  $[\alpha]_D + 103.89^\circ$ , prepared by the action of sodium nitrite on pure bornylamine in acetic acid solution, on oxidation yields a camphenecamphoric acid, m. p.  $141-142^\circ$ , which is not identical with the acid obtained from the naturally occurring camphene.

G. Y.

**Constituents of Ethereal Oils. Teresantallic Acid,  $C_{10}H_{14}O_2$ ;**  
**a New Norcamphor and its Derivatives.** FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 4465-4472. Compare this vol., i, 703).—It has been shown by Müller (*Abstr.*, 1900, i, 677) that teresantallic acid (I) is decomposed by sulphuric acid with formation of  $\alpha$ -santene. An endeavour has now been made to study the course of this complicated reaction by employing formic in place of sulphuric acid. Here also the reaction is complicated, and leads to the formation of two products.

(a) The *formate* of  $\pi$ -norborneol,  $C_{10}H_{16}O_2$ , b. p.  $87-94^\circ/9$  mm.,  $D^{20} 1.0092$ ,  $n_D 1.46559$ ,  $[\alpha]_D - 10.15^\circ$ , when boiled with alcoholic potassium hydroxide is hydrolysed to  $\pi$ -norborneol (II), m. p.  $68-70^\circ$ , b. p.  $87-88^\circ$ , which is optically inactive. The *acetate*,  $C_{11}H_{18}O_2$ , b. p.  $89-90.5^\circ/9$  mm.,  $D^{20} 0.987$ ,  $n_D 1.45962$ .

$\pi$ -Norcamphor,  $C_9H_{14}O$ , formed by oxidation of  $\pi$ -norborneol with chromic acid in glacial acetic acid solution, has m. p. about  $30^\circ$ , b. p.  $75-76^\circ/9$  mm.,  $D^{20} 0.966$ ,  $n_D 1.46900$ , is optically inactive, and on treatment with sodium and *isoamyl* formate in ethereal solution yields an *oxymethylene* derivative,  $C_{10}H_{14}O_2$ , b. p.  $110-113^\circ/9$  mm.,  $D^{20} 1.066$ ,  $n_D 1.50045$ , which gives an intense bluish-violet coloration with ferric chloride.

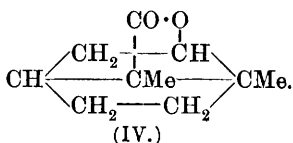
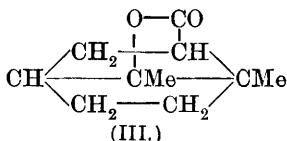
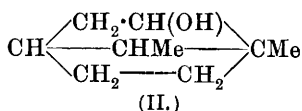
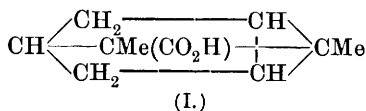
$\pi$ -Norisoborneol,  $C_9H_{16}O$ , m. p.  $91-92^\circ$ , b. p.  $88^\circ/9$  mm., is prepared by reduction of the ketone with sodium and alcohol.

(b) The *lactone* (III), m. p.  $190^\circ$ , on reduction with sodium and alcohol forms a *glycol*, m. p.  $254^\circ$ , which when distilled with steam in



presence of sulphuric acid yields a volatile *oxide*,  $C_{10}H_{16}O$ , m. p.  $148^{\circ}$ . The *hydroxy-acid*,  $C_{10}H_{16}O_3$ , m. p.  $196^{\circ}$ , corresponding to the lactone, forms a *methyl ester*,  $C_{11}H_{18}O_3$ , b. p.  $125^{\circ}/9$  mm.,  $D^{20}_D$  1.098  $n_D$  1.48616.

The lactone (IV), m. p.  $103^{\circ}$ , obtained by Müller (*loc. cit.*) from teresantallic acid hydrochloride, is reduced to a *glycol*,  $C_{10}H_{18}O_2$ , b. p.  $160-163^{\circ}/10$  mm. Hydrolysis of the lactone leads to the formation of a *hydroxy-acid*,  $C_{10}H_{16}O_3$ , m. p.  $159^{\circ}$ , which forms an ethyl ester, b. p.  $120-123^{\circ}/9$  mm.,  $D^{20}_D$  1.089,  $n_D$  1.48228.



It remains undecided whether the two lactones and their hydroxy-acids are structurally or stereo-chemically isomeric. The constitutional formulæ given are ascribed to teresantallic acid and its derivatives on the former supposition, which necessitates the assumption that various hypothetical intermediate products are formed by the action of formic acid on teresantallic acid.

G. Y.

**The Present Position of the Chemistry of Rubber.** SAMUEL S. PICKLES (*Brit. Assoc. Reports*, 1906, '76, 233-257).—A résumé of the different methods employed in attacking the problem of the chemical constitution of rubber.

G. T. M.

**The Cyanogenetic Glucoside of Flax. (Linseed.)** WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Bull. Acad. roy. Belg.*, 1907, 790-793). **Linamarin.** ARMAND JORISSEN (*ibid.*, 793-798).—Polemical, in reference to the question whether the name phaseolunatin or linamarin should be used for this glucoside (see Jorissen and Hairs, *Abstr.*, 1885, 181; 1892, 502; Jouck, *Diss. Strasbourg*, 1902; Dunstan and Henry, *Abstr.*, 1904 ii, 711; Jorissen, this vol., i, 434).

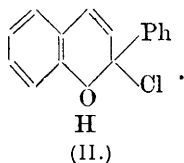
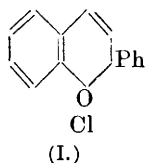
T. A. H.

**Bromo-derivatives of Dimethyl- and Trimethyl-furandicarboxylic Acids.** HYPOLYT TREPHILIEFF (*Ber.*, 1907, 40, 4388-4389).—Complicated changes occur when these acids are brominated in aqueous solution. Tetrabromo-derivatives are, however, obtained from methronic acid, ethyl methronate, and methyl methronate by exposing these substances to the action of bromine vapour at the ordinary temperature for two to three weeks. Nitric acid oxidises tetrabromo-methronic acid to oxalic acid; lead peroxide oxidises this acid to succinic acid.

Condensation of maleic acid and ethyl acetoacetate in the presence

of acetic anhydride results in the formation of a compound,  $C_{11}H_{14}O_3$ , of m. p.  $137^\circ$ .  
W. R.

**Benzopyryonium and Higher Homologous and Isologous Pyryonium Rings.** HERMAN DECKER and THEODOR VON FELLEBERG (*Annalen*, 1907, **356**, 281—342. Compare this vol., i, 950).—The oxygen-free salts of triphenylcarbinol having been recognised as carbonium salts, the constitution of the substances described as salts of xanthonium (Bünzly and Decker, *Abstr.*, 1904, i, 912) and coeroxonium (Decker, *Abstr.*, 1906, i, 687) and their sulphur isologues, and of dinaphthoxonium and coerdioxonium (Decker, *ibid.*, 874), became doubtful, since these possess the atomic groupings of di- and tri-phenylcarbinol and may equally be carbonium salts. In favour of the oxonium constitution is the difference in the basicities of tri-phenylcarbinol and phenylxanthanol; whilst salts of the former are not formed by the action of hydrochloric acid and are decomposed by 70% sulphuric acid, phenylxanthonium salts are stable in 10% sulphuric acid and are readily formed by means of hydrochloric acid. Moreover, the sulphur isologues are more strongly basic than the oxygen compounds in agreement with the known greater stability of thionium than oxonium salts. It is now found that the action of magnesium phenyl bromide on coumarin or of concentrated hydrochloric acid on *o*-hydroxybenzylideneacetophenone leads to the formation of a substance which must be 2-phenylpyryonium chloride (I), as a substance having the other possible constitution (II) would not be a salt:



It is argued that as the benzopyryonium salts are isologues of the quinolonium series, so the salts of xanthonium and thioxanthonium must be isologous with the acridonium and those of coeroxonium and coerthionium with the coeramidonium (Decker, Ferrario, and Schenk, *Abstr.*, 1906, i, 690) derivatives. The preparation and properties of a number of salts of benzopyryonium, xanthonium, coeroxonium, and their isologues are described.

*Benzopyryonium chloride*, prepared by heating gluco-*o*-coumaraldehyde with concentrated hydrochloric acid, is readily soluble; the *ferrichloride*,  $C_9H_7OCl, FeCl_3$ , forms a yellow, crystalline powder, m. p.  $199^\circ$  (corr.), and when heated with aqueous acetone gives an odour of fennel; the *aurichloride*,  $C_9H_7OCl, AuCl_3$ , crystallises in brownish-yellow, microscopic needles, m. p.  $198-200^\circ$  (corr.).

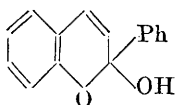
*2-Methylbenzopyryonium ferrichloride*,  $C_{10}H_9OCl, FeCl_3$ , prepared from *o*-hydroxycinnamyl methyl ketone, crystallises in yellow needles, m. p.  $118-119^\circ$  (corr.). The *cadmiobromide*,  $C_{10}H_9OBr, CdBr_2$ , forms a yellow, crystalline powder. The free base is unstable and readily changes into a dye. The *iodide*,  $C_{10}H_9OI$ , prepared from coumarin and magnesium methyl iodide, crystallises in greenish-brown needles,

m. p. 56—60°, readily loses iodine, and when heated with aqueous sulphurous acid is decomposed, forming coumarin.

2-Phenylbenzopyryronium chloride,  $C_{15}H_{11}OCl$ , crystallises in yellow leaflets, m. p. 69—70° (corr.), and is hygroscopic. The ferrichloride,

$C_{15}H_{11}OCl, FeCl_3$ ,  
yellow needles, m. p. 125—129° (corr.), aurichloride,  
 $C_{15}H_{11}OCl, AuCl_3$ ,

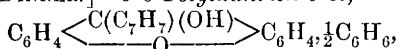
m. p. 200—202°, mercurichloride, brownish-yellow needles, m. p. 183—185°, cadmiobromide,  $C_{15}H_{11}OBr, CdBr_2$ , brownish-yellow needles, m. p. 190—192°, perbromide,  $C_{15}H_{11}OBr, Br_2$ , orange-red crystals, m. p. 122°, periodide,  $C_{15}H_{11}OI, I_2$ , m. p. 147—148°, unstable, and iodide, orange-red crystals, are described. A by-product from the action of



magnesium phenyl bromide on coumarin, which is insoluble in hydrochloric acid, will be described later (compare Houben, Abstr., 1904, i, 302, 334). The action of sodium hydroxide and much water on the chloride leads to the formation of a greenish-brown

precipitate containing the carbinol base, which has the annexed constitution, and is obtained also by the action of ammonia on the chloride in ethereal solution.

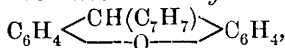
[With FRITZ DINNER.]—9-o-Tolylxanthen-9-ol,



prepared from xanthone and magnesium o-tolyl bromide (compare Bünzly and Decker, loc. cit.), crystallises from benzene in colourless needles, and loses  $\frac{1}{2}C_6H_6$  at 110°; m. p. 150·5°. o-Tolylxanthonium

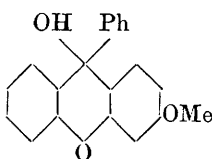
ferrichloride,  $C_6H_4 \left\langle \underset{\text{OCl}(FeCl_3)}{\text{C}(C_7H_7)} \right\rangle C_6H_4$ , crystallises in yellowish-

brown needles, m. p. 208—209°. o-Tolylxanthen,



prepared by boiling o-tolylxanthenol with hydriodic acid and red phosphorus in acetic anhydride solution, crystallises in colourless needles, m. p. 119°, and dissolves in cold sulphuric acid, forming the xanthonium salt. A substance,  $C_{23}H_{19}O_2$  or  $C_{23}H_{20}O_2$ , crystallises in large plates, m. p. 162°, a hydrocarbon,  $(C_{14}H_{13})_x - (C_9H_8)_x$ , m. p. 214°, and a substance, crystallising in leaflets, m. p. 170°, are obtained as by-products of the action of magnesium o-tolyl bromide on xanthone.

3-Methoxy-9-phenylxanthonium ferrichloride,  $C_{20}H_{15}O_2Cl, FeCl_3$ ,



prepared from 3-methoxyxanthone and magnesium phenyl bromide, forms dark red crystals, m. p. 124°, and on treatment with water yields 3-methoxy-9-phenylxanthen-9-ol, m. p. 133°.

This has the annexed constitution, and with acids yields oxonium salts which are stable in 10% hydrochloric acid and form deep red,

fluorescent solutions.

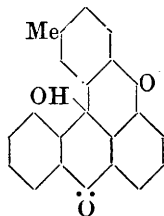
2-Methoxy-9-phenylxanthonium ferrichloride, prepared from 2-methoxyxanthone, crystallises in needles, m. p. 154°, and is more stable to water and more deeply coloured than its isomeride.

[With ENOS FERRARIO.]—The green, fluorescent solution obtained on dissolving fluoran in concentrated sulphuric acid contains 9-o-carboxyphenylxanthonium sulphate, which is stable only in the concentrated acid. The ferrichloride,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}_{13}\text{H}_8\text{OCl}\cdot\text{FeCl}_3$ , prepared by adding hydrochloric acid containing solid ferric chloride to a hot solution of fluoran in acetic acid, crystallises in yellow needles, m. p.  $200^\circ$ . Fluoran does not form a xanthonium salt with fuming hydrochloric acid; this difference in behaviour from the other members of the group results, not only from the negative influence of the carboxylic group, but also from the tendency of the carbinol base to lactone formation.

Dimethylfluoran forms a xanthonium ferrichloride,  $\text{C}_{22}\text{H}_{17}\text{O}_3\text{Cl}\cdot\text{FeCl}_3$ , crystallising in orange needles, m. p.  $215^\circ$ .

Coeroxonol (Abstr., 1906, i, 688) forms ethers when boiled with the corresponding alcohols. The methyl ether,  $\text{C}_{21}\text{H}_{14}\text{O}_3$ , crystallises in colourless needles, m. p.  $133^\circ$ . The n-propyl ether,  $\text{C}_{23}\text{H}_{18}\text{O}_3$ , m. p.  $151^\circ$ . The isobutyl ether,  $\text{C}_{24}\text{H}_{20}\text{O}_3$ , m. p.  $132^\circ$ . These ethers are convertible into each other; thus the methyl ether is formed when the ethyl ether is boiled with a large excess of methyl alcohol. Coeroxonol condenses readily with acetone, forming acetonylcoeroxone, m. p.  $146^\circ$ , which yields coeroxonium salts when heated with hydrochloric or sulphuric acid.

[With LEO STERN.]—Erythroxyanthraquinone p-tolyl ether,  $\text{C}_{21}\text{H}_{14}\text{O}_3$ , prepared as described in D.R.-P. 158531 (Abstr., 1905, i, 797), crystallises in yellow needles, m. p.  $128.5^\circ$ , and, when heated with fuming sulphuric acid and treated with ferric chloride, yields 14-methylcoeroxonium ferrichloride,  $\text{C}_{21}\text{H}_{13}\text{O}_2\text{Cl}\cdot\text{FeCl}_3$ , which is obtained in reddish-brown crystals, m. p.  $232.5\text{--}235.5^\circ$ , has the properties characteristic of coeroxonium salts, and becomes colourless on treatment with water. 14-Methylcoeroxone-9-ol (annexed formula) separates from benzene in colourless crystals, m. p.  $176^\circ$ , and reacts with acids, forming the dark red oxonium salts. The ethyl ether,  $\text{C}_{23}\text{H}_{18}\text{O}_3$ , crystallises in needles, m. p.  $139^\circ$ .

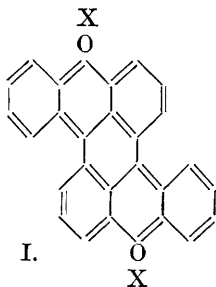


[With ENOS FERRARIO.]—4:14-Dimethylcoeroxone-9-ol, previously described (Abstr., 1906, i, 688) as 3:13-dimethylcoeroxonol, has m. p.  $170^\circ$  ( $152^\circ$ : loc. cit.). The methyl ether,  $\text{C}_{23}\text{H}_{18}\text{O}_3$ , forms colourless crystals, m. p.  $105^\circ$ . The ethyl ether,  $\text{C}_{24}\text{H}_{20}\text{O}_3$ , m. p.  $145^\circ$ . The action of mineral acids on the carbinol leads to the formation of oxonium salts; the ferrichloride, m. p.  $210^\circ$  ( $160^\circ$ : loc. cit.). Reduction of the carbinol base or of the oxonium salts leads to the formation of 4:14-dimethylcoeroxen-10-ol, which has a strong green fluorescence, dissolves in aqueous sodium hydroxide, forming an orange-red solution, and is very readily oxidised. The acetate is obtained in yellow crystals, m. p.  $230^\circ$ .

[With AUGUST WÜRSCH.]—1-Thiolanthraquinone p-tolyl ether,  $\text{C}_{21}\text{H}_{14}\text{O}_2\text{S}$ , prepared from potassium  $\alpha$ -anthraquinonesulphonate, p-thiocresol, and potassium hydroxide, or from nitroanthraquinone, crystallises in orange-red needles,  $223\text{--}225^\circ$ , and when heated with fuming sulphuric acid yields the 14-methylcoerthionium salt, which is

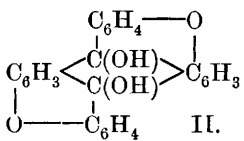
isolated as the *ferrichloride*,  $C_{21}H_{13}OSCl.FeCl_3$ , obtained in blackish-green crystals, m. p.  $240^\circ$ . 14-*Methylcoerthione-9-ol*,  $C_{21}H_{14}O_2S$ , formed by the action of water on the thionium salt, separates from benzene as a white, crystalline powder, m. p.  $235^\circ$ , and on reduction yields 14-*methylthiene-10-ol*,  $C_{21}H_{14}OS$ , m. p.  $247^\circ$ , which forms yellow solutions with green fluorescence, and is soluble in alkalis.

[With ENOS FERRARIO.]—When heated with phosphoric acid or a mixture of phosphoric and sulphuric acids, anthra-rufin diphenyl ether is converted into coerdioxonium salts having the constitution (I). The *ferrichloride*,  $C_{26}H_{14}O_2Cl_2.2FeCl_3$ , is obtained as a black, crystalline precipitate. The *sulphate*, *hexabromide*, and *iodide* are described. When treated with water, the ferrichloride yields *coerdioxendiol* (II), which separates as a violet, crystalline powder, forms violet-blue to violet-red solutions with intense, brownish-red fluorescence, and is reduced to *coerdioxen*. This forms an orange-red precipitate, sublimes, forming a



red sublimate, dissolves in ether or benzene to an orange solution with intense green fluorescence, and is readily oxidised, yielding the dioxonium salts.

1:5-Dithiolanthraquinone diphenyl ether,  $C_{26}H_{16}O_2S_2$ , prepared by boiling dinitroanthraquinone, thiophenol, and potassium hydroxide in alcoholic solution, crystallises in orange-red



plates, m. p.  $247^\circ$ , and on prolonged heating at  $200^\circ$  and treatment with sulphuric acid and ferric chloride yields *coerdithionium ferrichloride*,  $C_{26}H_{14}S_2Cl_2.2FeCl_3$ , which forms black crystals, with a green shade when powdered, m. p.  $258-260^\circ$ ; the *hexabromide* forms an olive-green precipitate. *Coerdithiendiol*, formed by the addition of water to the coerdithionium salts, separates from glacial acetic acid in colourless crystals, m. p.  $248^\circ$ , yields a coloured, fluorescent solution if strongly heated in acetic acid, and is reduced to *coerdithien*, which is obtained as an orange precipitate, sublimes unchanged, forms fluorescent solutions, and is readily oxidised to the dithionium salts.

1:5-Dithiolanthraquinone di-*p*-tolyl ether,  $C_{28}H_{20}O_2S_2$ , prepared from thio-*p*-cresol, potassium hydroxide, and dinitroanthraquinone, forms reddish-brown crystals, m. p.  $249^\circ$ . *Dimethylcoerdithionium ferrichloride* forms black crystals, m. p.  $204^\circ$ . *Dimethylcoerdithienol* is colourless. *Dimethylcoerdithien* is yellowish-red, forms solutions with green fluorescence, and is readily oxidised to the dithionium salts.

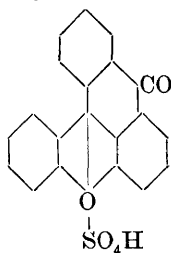
The isologous coerdiamidonium compounds have been previously described (Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1902, i, 501).

The relation of the coeroxonium salts to the coeroxonols and the similar relations in the isologous series are discussed in the light of Thiele's theory of partial valencies. G. Y.

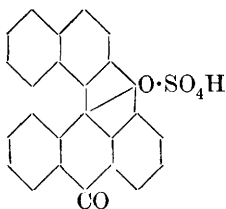
**Preparation of Coeroxonium and Coerthionium Derivatives.** FARBEFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 186882. Compare Abstr., 1905, i, 797; 1906, i, 687).—The aryl ethers and aryl

thioethers of the anthraquinone series when condensed with neutral or acid dehydrating agents give rise to coeroxonium and coerthionium derivatives, which are used in the preparation of colouring matters.

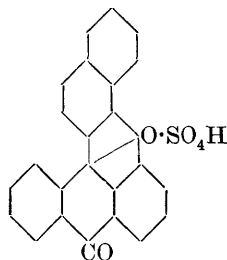
*Coeroxonium sulphate* (I) results from the dehydrating action of 70% sulphuric acid or zinc chloride on 1-phenoxyanthraquinone (erythroxyanthraquinone phenyl ether):



(I.)



(II.)

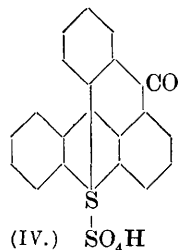


(III.)

The free coeroxonium base (coeroxonol; *loc. cit.*), a white, crystalline precipitate, is set free from the sulphate by ammonia; its ethyl ether,  $C_{22}H_{16}O_3$ , m. p.  $145^\circ$ , is a well-defined, crystalline substance.

*Coeroxonium ferrichloride*,  $C_{20}H_{11}O_2Cl, FeCl_3$ , m. p.  $233^\circ$ , is obtained in dark red crystals on adding ferric chloride and strong hydrochloric acid to the sulphate solution.

Benzocoeroxonium salts are obtained when the  $\beta$ -naphthyl ether of 1-hydroxyanthraquinone are employed in the foregoing condensation.



(IV.)

*Benzocoeroxonium sulphate* (II), the corresponding chloride, and the ferrichloride,  $C_{24}H_{13}O_2Cl, FeCl_3$ , are sparingly soluble, dark violet, crystalline salts. The free base, *benzocoeroxonol*, m. p.  $186-187^\circ$ , separates in almost colourless crystals.

*isoBenzocoeroxonium sulphate* (III) is obtained in a similar manner from  $\alpha$ -naphthyl-1-oxyanthraquinone.

*Coerthionium sulphate* (IV) is a violet-red salt resulting from the condensation of phenyl-1-thioanthraquinone; its carbinol base may be crystallised from alcohol. The coerthionium salts are generally more intensely coloured than the corresponding coeroxonium derivatives.

G. T. M.

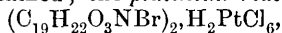
**Action of Grignard's Reagent on Cinchonine.** EZIO COMANDUCCI (*Boll. chim. Farm.*, 1907, 46, 753-756).—With magnesium ethyl iodide, cinchonine yields a pale yellow, amorphous, additive compound, which is stable when kept in a sealed tube or over sulphuric acid. This compound no longer contains the ketonic or vinyl group, and, when treated with dilute sulphuric acid, it yields a product which, after repeatedly dissolving in hydrochloric acid and precipitating with ammonia, has the composition  $NH \cdot C_{16}H_{18}N(CEt \cdot OH) \cdot CH_2 \cdot CH_2Et$  or  $NH \cdot C_{16}H_{18}N(CEt \cdot OH) \cdot CHMeEt$ .

T. H. P.

**Action of Halogen on Morphine Derivatives.** EDUARD VONGERICHTEN and O. DENSDOFF (*Ber.*, 1907, 40, 4146-4154).—A

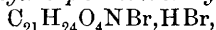
continuation of the work of Vongerichten and Hübner (this vol., i, 718), who studied the action of bromine on morphine, codeine,  $\alpha$ - and  $\beta$ -methylmorphimethines and dihydromethylmorphimethine respectively.

Acetyl- $\alpha$ -methylmorphimethine, in dilute acetic acid solution, behaves like  $\alpha$ -methylmorphimethine in uniting with only 1 mol. of bromine; in more concentrated acetic acid solution, 3 atoms of bromine are added on. *Acetyldibromodihydro- $\alpha$ -methylmorphimethine hydrobromide*,  $C_{21}H_{25}O_4NBr_2 \cdot HBr$ , has m. p. about  $202^\circ$  (decomp.); the *platinichloride*,  $(C_{21}H_{24}O_4NBr)_2 \cdot H_2PtCl_6$ , was prepared. By the action of sodium methoxide on acetylbromo- $\alpha$ -methylmorphimethine, *bromo- $\alpha$ -methylmorphimethine* was obtained; the *platinichloride*,



and the *methiodide*  $C_{19}H_{22}O_3NBr \cdot MeI$ , were prepared.

*Acetylbromoiso- $\alpha$ -methylmorphimethine hydrobromide*,



obtained by boiling acetyldibromodihydro- $\alpha$ -methylmorphimethine hydrobromide with acetic anhydride, separates from water in glistening needles, decomposing at  $235^\circ$ .

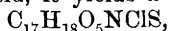
*Acetylnor-p-thebaine methobromide*,  $C_{21}H_{21}O_4NBr$ , obtained by heating acetoxybromodihydro- $\alpha$ -methylmorphimethine with acetic anhydride, crystallises in needles or prisms, m. p.  $231$ — $233^\circ$ . *Acetylnor-p-thebaine methiodide*, formed by the addition of potassium iodide to the preceding compound, has m. p.  $236^\circ$ . *Nor-p-thebaine methiodide*,  $C_{19}H_{22}O_3NI$ , has m. p.  $220^\circ$ .  
A. MCK.

**Preparation of Sulphonic Acids of Acetyl Derivatives of Morphine.** KNOLL & Co. (D.R.-P. 195601. Compare this vol., i, 235).—When morphine is gently heated with a mixture of acetic anhydride and sulphuric acid which no longer gives the reactions of sulphuric acid, it is converted into triacetylmorphine. When, however, the reaction is carried out at temperatures lower than that required to convert acetyl sulphuric acid into sulphoacetic acid, then the base is simultaneously acetylated and sulphonated. The product, *diacetyl-morphinesulphonic acid*, is precipitated by ether from its aqueous or alcoholic solutions as a white powder, which on acidifying separates from its alkaline solution in clusters of needles not melting below  $280^\circ$ . As is generally the case, the introduction of the sulphonic group greatly diminishes the toxic action of morphine.  
G. T. M.

**Intermediate Product in the Formation of apoMorphine.** LORENZ ACH and HERMANN STEINBOCK (*Ber.*, 1907, 40, 4281—4285).—The restricted action of hydrochloric acid on morphine yields a compound, termed by the authors  $\beta$ -chloromorphide, which is isomeric with Schryver and Lees' chloromorphide (*Trans.*, 1900, 77, 1024), and can also be prepared from the latter by the gentle action of hydrochloric acid.

*$\beta$ -Chloromorphide*,  $C_{17}H_{18}O_2NCl$ , crystallises from ether in a drusy mass of prisms or from alcohol in prisms, m. p.  $188^\circ$ , and is more readily soluble in alcohol or benzene than its isomeride. When freshly precipitated from its salts,  $\beta$ -chloromorphide is readily soluble in ether, but after one crystallisation it dissolves only sparingly in this solvent.

Its salts are mostly readily soluble, but the *nitrate* separates easily in prisms. With sulphuric acid, it yields a *sulpho-derivative*,



which crystallises from water in glassy prisms containing  $1\text{H}_2\text{O}$ , and has a neutral reaction in aqueous solution; the sulpho-compound yields a crystalline *acetyl* derivative, and, when heated with water at  $140^\circ$ , it is converted into a crystalline *sulpho-compound* free from chlorine.

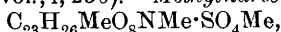
The isomeric chloromorphide (*loc. cit.*) yields no crystalline sulpho-derivative.

*$\beta$ -Chloromorphide methiodide*,  $\text{C}_{18}\text{H}_{21}\text{O}_2\text{NCII}$ , separates from water in dense crystals, m. p.  $210^\circ$  (decomp.), and is decomposed when heated with an aqueous alkali, yielding a volatile base.

*Acetyl- $\beta$ -chloromorphide*,  $\text{C}_{19}\text{H}_{20}\text{O}_3\text{NCl}$ , crystallises from alcohol in needles, m. p.  $163^\circ$ , and yields a *methiodide*, m. p.  $177^\circ$  (decomp.).

T. H. P.

**Preparation of Additive Products of Alkyl-narceine or Alkyl-homonarceine and their Alkyl Ethers.** KNOLL & Co. (D.R.-P. 186884. Compare this vol., i, 236).—*Methylnarceine methosulphate*,



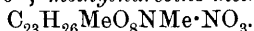
m. p.  $184\text{--}186^\circ$ , formed by the interaction of narceine (1 mol.) and methyl sulphate (2 mols.) in alcoholic potassium hydroxide; its hydrochloride decomposes at  $196^\circ$ . The following compounds are also described.

*Ethyl-narceine ethiodide*,  $\text{C}_{23}\text{H}_{26}\text{EtO}_8\text{NEtI}$ , m. p.  $140\text{--}144^\circ$ , produced by the combination of ethylnarceine and ethyl iodide at  $80^\circ$ ; *diethylnarceine methiodide*,  $\text{C}_{23}\text{H}_{25}\text{Et}_2\text{O}_8\text{NMeI}$ , m. p.  $184\text{--}185^\circ$ ; *dimethyl*

*methylnarceine methophosphate*,  $\text{C}_{23}\text{H}_{26}\text{MeO}_8\text{NMe}\cdot\text{PO}_4\text{Me}_2$ , its hydrochloride, m. p.  $136^\circ$ ; *methylnarceine methobenzenesulphonate*,

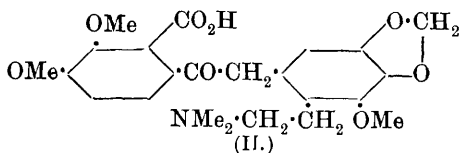
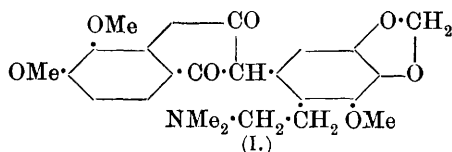


hydrochloride, m. p.  $136^\circ$ ; *methylnarceine methonitrate*,



G. T. M.

**Preparation of apoNarceine.** KNOLL & Co. (D.R.-P. 187138. Compare this vol., i, 236).—*apoNarceine* (I), yellow needles, m. p.  $112\text{--}115^\circ$ , is obtained by treating narceine (II) with dehydrating



agents, such as mineral acids, acid chlorides, or acid anhydrides; it is extracted with ether and converted into its *hydrochloride*,

$\text{C}_{23}\text{H}_{25}\text{O}_7\text{N}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , yellow needles, m. p.  $144^\circ$ . This salt is only sparingly soluble in cold water, but dissolves more readily on warming; it gives the ordinary alkaloid reactions. *apoNarceine* is insoluble in water, but dissolves readily in the ordinary

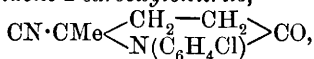
agents, such as mineral acids, acid chlorides, or acid anhydrides; it is extracted with ether and converted into its *hydrochloride*,



organic media, excepting light petroleum; when warmed with alkalis, it is reconverted into narceine. The *aponarceine methosulphate* crystallises from alcohol and ether in needles; it forms similar additive compounds with other alkyl halides, sulphates, and phosphates.  
G. T. M.

**Anisothobromine.** VON SZTANKAY (*Chem. Zentr.*, 1907, i, 1806; from *Pharm. Post*, 1907, 40, 322).—*Anisothobromine* (sodium theobromine anisate),  $\text{NaC}_7\text{H}_7\text{O}_2\text{N}_4 \cdot \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Na}$ , is a white, slightly deliquescent powder, melting and decomposing when carefully heated. Acids precipitate theobromine and anisic acid from its aqueous solution.  
W. H. G.

**Condensation Products of Ethyl Lævulate, Hydrogen Cyanide, and Para-substituted Anilines.** HERMANN WEBER (*Ber.*, 1907, 40, 4044—4052. Compare Kühling and Falk, *Abstr.*, 1905, i, 372).—The author's aim is to ascertain the influence of negative substituents on the stability of the pyrrolidone nucleus. The condensations are carried out in alcoholic solution on the water-bath. 1-*p*-Chlorophenyl-2-methylpyrrolidone-2-carboxylonitrile,



the *amide*, and the *carboxylic acid* have m. p. 40—42°, 207°, and 179° respectively. The corresponding *compounds*, obtained from *p*-bromoaniline, have m. p. 49—51°, 208°, and 189° respectively; the *barium* and *silver* salts and the *methyl ester* were prepared. The nitrile yields a thioamide with ammonium sulphide, and  $\gamma$ -oximinovaleic acid by treatment with hydroxylamine hydrochloride. 1-*p*-Iodophenyl-2-methylpyrrolidone-2-carboxylonitrile is an oil, from which the *amide*, m. p. 222°, and the *carboxylic acid*, m. p. 211—212°, are readily obtained. *p*-Aminobenzonitrile condenses with hydrogen cyanide and ethyl lævulate to form an oil from which well-defined derivatives have not been obtained. Ethyl *p*-aminobenzoate condenses readily to form the *substance*,  $\text{CN} \cdot \text{CMe}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ , m. p. 75°, from which the *dicarboxylic acid*,  $\text{CO}_2\text{H} \cdot \text{CMe} \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{N}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}) \end{array} \right\rangle \text{CO}$ , m. p. 228—229°, is obtained by hydrolysis; the *ethyl ester-amide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CMe} \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{N}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}) \end{array} \right\rangle \text{CO}$ , has m. p. 149°, and the corresponding *methyl ester-amide*, 171—172°.  
C. S.

[**Preparation of Amino-Ethers.**] EMANUEL MERCK (D.R.-P. 184968).—The amino-ethers having the general formula



are obtained by treating the halogenated ethers,  $\text{X} \cdot [\text{CH}_2]_x \cdot \text{O} \cdot \text{R}$ , with secondary amines. The hydrochlorides of these amino-ethers give neutral solutions and have a powerful anaesthetic action.

*Guaiacyl  $\epsilon$ -dimethylaminoamyl ether*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$ , m. p. 144—145°, was produced by mixing guaiacyl  $\epsilon$ -bromoamyl ether with dimethylamine in closed vessels; its hydrochloride is soluble.  $\gamma$ -*Piperidylpropyl phenyl ether*,  $\text{Ph} \cdot \text{O} \cdot [\text{CH}_2]_3 \cdot \text{C}_5\text{NH}_{10}$ , b. p. 150°/10 mm.,

$\epsilon$ -Piperidylamyl phenyl ether,  $\text{Ph}\cdot\text{O}\cdot[\text{CH}_2]_5\cdot\text{NC}_5\text{H}_{10}$ , b. p.  $172^\circ/3$  mm.  $\gamma$ -Piperidylpropyl guaiacyl ether,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_3\cdot\text{NC}_5\text{H}_{10}$ , b. p.  $173^\circ/10$  mm.  $\epsilon$ -Piperidylamyl guaiacyl ether,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_5\cdot\text{NC}_5\text{H}_{10}$ , b. p.  $190^\circ/5$  mm.  $\epsilon$ -Piperidylamyl menthyl ether,  $\text{C}_{10}\text{H}_{18}\cdot\text{O}\cdot[\text{CH}_2]_5\cdot\text{NC}_5\text{H}_{10}$ , b. p.  $170\text{--}172^\circ/4$  mm.  $\epsilon$ -Piperidylpropyl thymyl ether, b. p.  $197^\circ/6$  mm.  $\epsilon$ -Piperidylamyl thymyl ether, b. p.  $200\text{--}202^\circ/8$  mm., and  $\epsilon$ -camphidinylamyl thymyl ether,  $\text{C}_{10}\text{H}_{18}\cdot\text{O}\cdot[\text{CH}_2]_5\cdot\text{NC}_{10}\text{H}_{18}$ , hydrochloride, m. p.  $122\text{--}123^\circ$ , were all prepared in a similar manner from the corresponding brominated mixed ethers. G. T. M.

**Preparation of Pyrimidine Derivatives.** EMANUEL MERCK (D.R.-P. 185963).—Pyrimidine derivatives having the general formula:  $\text{R}^{\text{I}}\cdot\text{C}\begin{smallmatrix} \text{<NH}\cdot\text{C}\cdot\text{R}^{\text{II}} \\ \text{<NH}\cdot\text{C}\cdot\text{R}^{\text{V}} \end{smallmatrix} \text{>C}\begin{smallmatrix} \text{R}^{\text{III}} \\ \text{R}^{\text{IV}} \end{smallmatrix}$ , are obtained by condensing carbamide, thiocarbamide, guanidine, or their derivatives with alkyl malonates, malonamates, or cyanoacetates, or with malononitrile, or mono- and di-alkyl derivatives of substituted malonic acids in the presence of the carbides of the alkali or alkaline earth metals.

4-Iminobarbituric acid results from the condensation of carbamide, ethyl cyanoacetate, and sodium carbide in xylene solution, being precipitated from the resulting alkaline solutions with acetic acid. 5:5-Diethylbarbituric acid is similarly obtained from carbamide, ethyl diethylmalonate, and sodium carbide. G. T. M.

**Hydroxypyridinechromium Salts. Additive Salt Formation with Metallic Hydroxides.** PAUL PEIFFER [and W. OSANN] (*Ber.*, 1907, 40, 4026—4036).—The monohydroxylo-, dihydroxylo-, and trihydroxylo-compounds, derived from chromiumtetra-aquodipyridine, were found to form salts with acids by direct addition (*Abstr.*, 1906, i, 531). Such additive salt formation has been studied also in the case of other metallic hydroxides (this vol., i, 895; ii, 694; Werner, this vol., i, 189, 239; ii, 560). The present paper contains an account of further observations made with members of the pyridine-chromium series.

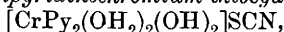
The hydroxylo-salts, derived from chromiumtetra-aquodipyridine, are prepared by three methods: (1) the removal of a mol. of acid from an aquo-salt by the action of a base; (2) the gradual addition of an acid to a polyhydroxylo-compound, which leads finally to the formation of the tetra-aquo-salt, and (3) the action of normal salts on tetra-aquo-salts in aqueous solution, which leads only in certain cases to the formation of hydroxylo-salts in consequence of partial hydrolysis of the tetra-aquo-salt in solution.

Hydroxylotriaquodipyridinechromium thiocyanate and sulphate have now been prepared by the action of ammonium thiocyanate and sulphate respectively on dihydroxylodiaquodipyridinechromium chloride in acetic acid solution.

*Dihydroxylodiaquodipyridinechromium iodide*,  $[\text{CrPy}_2(\text{OH})_2(\text{OH})_2]\text{I}$ , formed by addition of potassium iodide to the dihydroxylo-chloride in acetic acid solution or to the monohydroxylothiocyanate in aqueous solution, or of hydriodic acid to chromiumtrihydroxyloaquodipyridine,

is obtained as a greenish-grey powder, and on treatment with a mineral acid yields the corresponding tetra-aquo-salt.

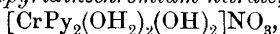
*Dihydroxylodiaquodipyridinechromium thiocyanate*,



prepared by adding pyridine to the monohydroxylo-thiocyanate in presence of water, or by addition of ammonium thiocyanate to an aqueous solution of a soluble dihydroxylo-salt, forms a greyish-brown powder, has a slight alkaline reaction in aqueous solution, and forms the red tetra-aquo-salt on treatment with mineral acids.

Dihydroxylodiaquodipyridinechromium sulphate forms a greyish-green aqueous solution, which appears reddish-brown in thick layers, becomes red on addition of mineral acids, and yields the chloride and iodide as greyish-green precipitates on addition of sodium chloride and potassium iodide respectively.

*Dihydroxylodiaquodipyridinechromium nitrate*,



is formed when chromiumtrihydroxyloaquodipyridine is treated with a small amount of nitric acid, or by the action of pyridine on tetra-aquodipyridinechromium nitrate in aqueous solution; it is obtained as a bluish-grey powder, has a very slight alkaline reaction, does not form silver oxide with aqueous silver nitrate, gives precipitates of the corresponding dihydroxylo-salts when treated with sodium chloride, potassium bromide and iodide, and ammonium thiocyanate, and is converted into red tetra-aquo-salts by the action of mineral acids.

*Tetra-aquodipyridinechromium nitrate*,  $[\text{CrPy}_2(\text{OH})_4](\text{NO}_3)_3$ , prepared by addition of concentrated nitric acid to the preceding salt and evaporation over soda-line, forms light red leaflets, is deliquescent, dissolves, forming red solutions in water and alcohol, and gradually decomposes to a dirty green, viscid mass.

G. Y.

[Preparation of Isatin Derivatives.] KALLE & Co. (D.R.-P. 182260 and 182261).—The condensation of isatin and 3-oxy-1-thionaphthen in hot aqueous sodium carbonate leads to the production of a very sparingly soluble colouring matter, having probably the constitution:  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NH}.$

This substance furnishes a soluble reduction product on treatment with alkaline reducing agents. When isatinacetic acid is substituted for isatin in this condensation, a colouring matter is produced which furnishes a soluble sodium salt separating in lustrous, bright red crystals. This substance is a wool dye of considerable fastness.

G. T. M.

**Asymmetric Nitrogen. XXX.** Resolution of a Cyclic Asymmetric Ammonium Base. EDGAR WEDEKIND and O. WEDEKIND (*Ber.*, 1907, 40, 4450—4456. Compare Buckney, this vol., i, 722).—The authors have resolved methylallyltetrahydroquinolinium *d*-bromocamphorsulphonate by recrystallisation from a mixture of solvents. The less soluble *l*-base *d*-acid salt has  $[\alpha]_D + 39.09^\circ$ ,  $[M]_D + 194.7^\circ$ , and on treatment with concentrated aqueous potassium iodide yields the *iodide*,  $[\alpha]_D + 20.57^\circ$ ,  $[M]_D - 64.98^\circ$ , which rapidly

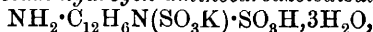
undergoes racemisation when dissolved in methyl alcohol. The more soluble *d*-base *d*-acid salt has  $[\alpha]_D + 76.48^\circ$ ,  $[M]_D + 380.7^\circ$ . These values give  $[M]_D - 80.3^\circ$  and  $+105.7^\circ$  for the *l*- and *d*-basic ions respectively. On further fractional recrystallisation, a fraction having  $[M]_D + 434^\circ$  was obtained; this yields an iodide which after recrystallisation is optically inactive.

*Benzylmethyltetrahydroquinolinium bromide* undergoes partial decomp. when recrystallised. The *d*-bromocamphorsulphonate crystallises in colourless prisms, m. p.  $180^\circ$  (decomp.). Attempts to resolve this salt were unsuccessful (compare Jones, Trans., 1903, 83, 1417).

[With ROBERT OECHSLER.]—*Ethyl N-methyltetrahydroquinolinium-acetate d-camphorsulphonate*,  $C_{24}H_{25}O_6NS$ , prepared from the iodide, crystallises in colourless needles, decomp. about  $95^\circ$ ,  $[\alpha]_D + 11.7^\circ$ ,  $[M]_D + 51.9^\circ$ , and is hygroscopic. Attempts to resolve this salt also were fruitless. G. Y.

**Carbazole.** GUSTAV SCHULTZ and L. HAUENSTEIN (*J. pr. Chem.*, 1907, [ii], 76, 336—349).—An investigation of the sulphonic acids of carbazole (compare Graebe and Glaser, this Journ., 1872, 25, 302; Bechhold, Abstr., 1890, 1297; Wirth and Schott, Abstr., 1903, i, 54).—Carbazole is sulphonated slowly at the ordinary temperature, more rapidly at  $70$ — $75^\circ$ , by concentrated sulphuric acid; the reaction product contains di- and tri-sulphonic acids together with unchanged carbazole. The disulphonic acid is isolated as the *barium* salt,  $C_{12}H_7N(SO_3)_2Ba \cdot 3H_2O$ , which loses  $2H_2O$  in a desiccator, and becomes anhydrous at  $180$ — $190^\circ$ . The free *acid* is obtained as a transparent, compact mass, m. p. below  $56^\circ$ , becomes blue on the surface, gives a brown coloration when fused with resorcinol, and on fusion with oxalic acid forms a blue *dye* soluble in water. The *sodium*,  $C_{12}H_7N(SO_3Na)_2$ , and *potassium* salts were analysed. *Carbazole-disulphonyl chloride*,  $C_{12}H_7N(SO_2Cl)_2$ , prepared by heating the potassium salt with phosphorus pentachloride in a water-bath, is hydrolysed by hot water, and reacts with ammonia, forming the *disulphonamide*,  $C_{12}H_7N(SO_2 \cdot NH_2)_2$ , which crystallises in colourless needles or triangular plates, m. p.  $220$ — $225^\circ$ . The sulphonic acid groups of carbazoledisulphonic acid are displaced only with difficulty; the acid remains almost unchanged when heated with alkalis at  $250^\circ$ , but yields a *phenolic* product at  $300$ — $320^\circ$ . Distillation of the potassium disulphonate with potassium ferrocyanide or cyanide leads to the formation of carbazole. When heated with concentrated nitric acid on the water-bath, the potassium disulphonate yields *potassium tetra-nitrocarbazolesulphonate*, which crystallises in yellow needles.

*Potassium nitrocarbazoledisulphonate*,  $C_{12}H_6O_2N_2(SO_3K)_2 \cdot 3H_2O$ , formed by heating potassium carbazoledisulphonate with the theoretical amount of dilute nitric acid, crystallises in yellow needles, loses about  $2H_2O$  in a desiccator, becomes anhydrous at  $160^\circ$ , intumesces when heated, and dyes wool in an acid-bath a shade resembling naphthol-yellow. Reduction of the nitrodisulphonate by means of hydrogen sulphide in ammoniacal solution leads to the formation of *potassium hydrogen aminocarbazoledisulphonate*,



which crystallises in colourless needles, loses  $3\text{H}_2\text{O}$  at  $120^\circ$ , and when treated with nitrous acid forms a *diaz*-salt; this couples with  $\beta$ -naphthol, forming a red *dye*, which crystallises in needles, and in an acid-bath dyes wool red.

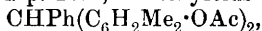
*Potassium carbazoletrisulphonate*, obtained from the filtrate from the barium disulphonate, crystallises in white needles containing  $3\text{H}_2\text{O}$ , which is lost at  $190$ — $195^\circ$ .

Nitration of the product of complete sulphonation of carbazole with excess of concentrated sulphuric acid on the water-bath leads to the formation of a mono- or di-nitrocarbazoledisulphonic acid, depending on the amount of nitric acid employed. The mononitro-acid is obtained in this manner in an almost quantitative yield, and, when reduced and diazotised, couples with  $\beta$ -naphthol, forming a red, or with  $\alpha$ -naphthylamine a violet, dye. G. Y.

**Derivatives of *p*-Xylidine.** GUSTAV SCHULTZ and A. PETENY (*J. pr. Chem.*, 1907, [ii], 76, 331—336).—The base, m. p.  $208^\circ$ , obtained as a by-product in the separation of *p*- and *m*-xylidine by means of benzaldehyde is found to be *phenyldi-p-aminodi-p-xylidmethane*,



and is best prepared by boiling benzaldehyde and *p*-xylidine with alcoholic hydrogen chloride. It crystallises in light yellow prisms, and forms a *diacetyl* derivative,  $\text{C}_{27}\text{H}_{30}\text{O}_2\text{N}_2$ , crystallising in white needles, m. p.  $217^\circ$ , and a *dibenzoyl* derivative,  $\text{C}_{37}\text{H}_{34}\text{O}_2\text{N}_2$ , m. p.  $249$ — $250^\circ$ . The action of nitrous acid on the base leads to the formation of a *phenol*, m. p.  $162^\circ$ , which yields a *diacetate*,



crystallising in white needles, m. p.  $158^\circ$ .

Similar bases are obtained by boiling *m*- and *p*-nitrobenzaldehyde with *p*-xylidine and alcoholic hydrogen chloride.

The *m*-nitro-compound,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NH}_2)_2\cdot\text{C}_6\text{H}_6$ , crystallises from benzene in yellow needles, m. p.  $216^\circ$ , and loses  $\text{C}_6\text{H}_6$  at  $120^\circ$ , forming orange needles, m. p.  $227^\circ$ . The *diacetyl* derivative,  $\text{C}_{27}\text{H}_{29}\text{O}_4\text{N}_3$ , crystallises in yellow needles, m. p.  $232^\circ$ ; the *dibenzoyl* derivative,  $\text{C}_{37}\text{H}_{33}\text{O}_4\text{N}_3$ , crystallises in needles, m. p.  $261$ — $262^\circ$ . The *dihydrochloride* was analysed.

The *p*-nitro-compound crystallises in prisms, m. p.  $162^\circ$ , or after losing  $\text{C}_6\text{H}_6$  at  $120^\circ$ , m. p.  $237^\circ$ . The *diacetyl* derivative crystallises in white needles, m. p.  $192^\circ$ ; the *dibenzoyl* derivative forms yellow needles, m. p.  $258$ — $259^\circ$ ; the *dihydrochloride* crystallises in yellow leaflets.

G. Y.

**Magnesium Alkylhalides and Carbodi-imides.** MAX BUSCH and RICHARD HOBEIN (*Ber.*, 1907, 40, 4296—4298).—Carbodi-imides form additive compounds with magnesium alkylhalides which are decomposed normally by water, forming amidines. Thus carbodiphenylimide and magnesium methyl iodide form colourless needles, m. p.  $132^\circ$ , of diphenylethenylamidine,  $\text{NHPh}\cdot\text{CMe}\cdot\text{NPh}$ . *Diphenylbenzenylamidine*,  $\text{NHPh}\cdot\text{CPh}\cdot\text{NPh}$ , forms colourless needles, m. p.  $144^\circ$ . Diphenyl- $\alpha$ -naphthenylamidine,  $\text{NHPh}\cdot\text{C}(\text{C}_{10}\text{H}_7)\cdot\text{NPh}$  (Bössneck, *Abstr.*, 1883, 595), forms silky, glistening needles, m. p.  $184^\circ$ ; the

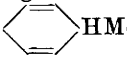
*hydrochloride* forms transparent, pointed crystals, m. p. 232°. Phenylcyanamide and magnesium phenyl bromide form phenylbenzenylamidine,  $\text{NPh}\cdot\text{CPh}\cdot\text{NH}$ , colourless needles, m. p. 112°. E. F. A.

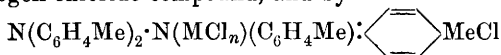
**Preparation of the Leuco-derivatives of the Indophenols.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 184601, 184651).—When the quinonemonoimines, obtained by oxidation of *p*-aminophenol and its derivatives, are condensed with aromatic bases in dilute hydrochloric acid, leuco-derivatives of the indophenols are produced, providing that the imine is not present in excess.

*p*-Aminophenol hydrochloride, when oxidised in aqueous solution with the calculated amount of ferric chloride, yields quinoneimine, and the addition of a solution of  $\alpha$ -naphthylamine hydrochloride leads to the precipitation of leucoindophenol. A similar result is obtained with *o*-chloro-*p*-aminophenol and  $\alpha$ -naphthylamine, or the sulphonic acids of this base may be employed.

The leucoindophenols are likewise produced when the phenols, having a free para-position, react with the quinonedi-imines in molecular proportions. Thus *s-p*-phenylenedimethyldiamine, oxidised with ferric chloride to quinonedimethylimine and then condensed with phenol in aqueous solutions, furnishes a leucoindophenol which is obtained by salting out. G. T. M.

**Tertiary Aromatic Hydrazines and Amines. III.** HEINRICH WIELAND (*Ber.*, 1907, 40, 4260—4281. Compare Abstr., 1906, i, 453, 830).—The blue or violet coloration obtained when tetraphenylhydrazine is treated with acids (Abstr., 1906, i, 453) is found to be due to the formation of salts of the hydrazine derivative. As tetraphenylhydrazine rapidly undergoes the benzidine rearrangement, the author has investigated the formation of the above salts with tetra-*p*-tolylhydrazine. These violet salts are obtained by the addition, not only of acids, but also of the halogens and of halogen compounds, such as phosphorus pentachloride, thionyl chloride, antimony pentachloride, and stannic, ferric, aluminium, and zinc chlorides. These salts are additive compounds, but not double salts, and are resolved by water or alkali into the tetratolylhydrazine and the decomposition products of the halogen compound employed.

The structure of these additive derivatives is regarded as expressed by the formula:  $\text{N}(\text{C}_6\text{H}_4\text{Me})_2\cdot\text{NCl}(\text{C}_6\text{H}_4\text{Me})\cdot$   HMe for the hydrogen chloride compound, and by

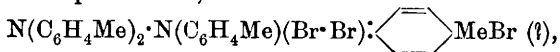


for the other halogen compounds,  $\text{MCl}_n$  representing  $\text{PCl}_4$ ,  $\text{FeCl}_3$ , &c. This quinonoid constitution is supported by the observation that tetraphenylhydrazine exhibits a tendency to form these additive derivatives much less marked than with tetra-*p*-tolylhydrazine, since, in the case of the simple quinols, the presence of a methyl group in the para-position greatly enhances the stability of the quinol form.

The reduction of these violet salts by stannous chloride yields di-*p*-tolylamine. Their spontaneous decomposition in solution also

yields di-*p*-tolylamine together with a pale red compound, which melts at a high temperature, and has the empirical composition of a haloid derivative of di-*p*-tolylamine, although it does not appear to have the simple molecular weight.

The addition of bromine to tetra-*p*-tolylhydrazine results in the formation of a perbromide,

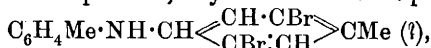


which decomposes into di-*p*-tolylamine and a dibromodi-*p*-tolylamine.

In its unchanged form, tetra-*p*-tolylhydrazine takes up 5 atoms of iodine, yielding a periodide, which has the colour of the associated iodine and shows none of the reactions characterising the violet salts.

Pure, colourless triphenylamine, when added to sulphuric acid either alone or in acetic acid solution, gives no coloration if the liquid is kept cool, but, on heating, an intense, blue coloration appears (compare Goldberg and Nimerovsky, this vol., i, 621); no compound analogous to those formed by tetra-*p*-tolylhydrazine is, however, obtained. Further, tri-*p*-tolylamine does not react with sulphuric, hydrochloric, or acetic acid, but gives with antimony pentachloride, bromine, or phosphorus pentachloride dark blue, crystalline, additive products, which, on decomposition, yield tri-*p*-tolylamine.

The *perbromide* of tetra-*p*-tolylhydrazine,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{Br}_3$ , separates from a benzene-chloroform solution in moderately stable, blackish-violet needles having a faint green, metallic lustre, and decomposes at about 58°. On decomposition, it yields a *dibromodi-p-tolylamine*,



separating from methyl alcohol in colourless, spear-like crystals, m. p. 59°.

The *compound*,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{PCl}_5$ , prepared from tetra-*p*-tolylhydrazine and phosphorus pentachloride, separates in slender needles. The *antimony pentachloride* compound,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{SbCl}_5$ , forms stable, broad needles with an intense green reflection, m. p. 107° (decomp.); the addition of pyridine to the violet solution causes the gradual disappearance of the colour, whilst the subsequent addition of water precipitates the violet compound. The *periodide*,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{I}_5$ , crystallises from benzene in shining, blue scales decomposing at 113°.

*Tri-p-tolylamine*,  $\text{C}_{21}\text{H}_{21}\text{N}$ , prepared by the interaction of di-*p*-tolylamine, *p*-iodotoluene, and potassium carbonate in presence of copper (compare Goldberg, Abstr., 1906, i, 426), separates from acetic acid as a faintly yellow, crystalline crust, m. p. 117°, and distils undecomposed; with concentrated sulphuric acid, it gives a colourless solution, which, when heated, assumes a bluish-green colour. With *bromine*, it gives an unstable compound separating in dark blue, bronzy needles, m. p. 40° (decomp.), and giving a dibromotri-*p*-tolylamine, m. p. 160–165°, on decomposition. With phosphorus pentachloride, it forms a *compound*,  $\text{C}_{21}\text{H}_{21}\text{N} \cdot \text{PCl}_5$ , crystallising in dark blue needles, and with antimony pentachloride the *compound*,  $\text{C}_{21}\text{H}_{21}\text{N} \cdot \text{SbCl}_5$ , crystallising in broad, dark blue needles having a metallic lustre, m. p. 116° (decomp.).

T. H. P.

### Action of Hydrazine Hydrate on Nitro-compounds. III. Action of Hydrazine Hydrate on 2:4-Dinitrobenzoic Acid.

THEODOR CURTIUS and HERMANN F. BOLLENBACH [and, in part, HANS CLEMM] (*J. pr. Chem.*, 1907, [ii], **76**, 281—301. Compare this vol., i, 969, 970).—The action of fuming nitric acid on *p*-nitrobenzoic acid leads to the formation of a mixture of 2:4- and 3:4-dinitrobenzoic acid. 2:4-Dinitrobenzoic acid is best prepared by oxidation of 2:4-dinitrotoluene with chromic acid in concentrated sulphuric acid solution at 45—50°. *Ethyl 2:4-dinitrobenzoate*, prepared by boiling the acid with alcoholic hydrogen chloride or by the action of ethyl iodide on the silver salt, crystallises in white needles, m. p. 41°, and readily changes into an oily modification.

*2-Nitro-4-aminobenzoic acid*,  $C_7H_6O_4N_2$ , prepared by boiling 2:4-dinitrobenzoic acid with hydrazine hydrate in alcoholic solution, crystallises in scarlet needles, m. p. 255°. The *silver*,  $C_7H_5O_4N_2Ag$ , and *sodium*,  $C_7H_5O_4N_2Na \cdot 2H_2O$ , salts were analysed. The *ethyl ester*, formed by boiling ethyl 2:4-dinitrobenzoate with alcoholic hydrazine hydrate, crystallises in yellow needles, m. p. 130°, and is hydrolysed by boiling dilute sodium hydroxide, forming 2-nitro-4-aminobenzoic acid.

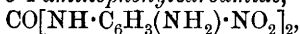
*2-Nitro-4-aminobenzoylhydrazide*,  $NO_2 \cdot C_6H_3(NH_2) \cdot CO \cdot NH \cdot NH_2$ , is formed by boiling ethyl 2-nitro-4-aminobenzoate with dilute hydrazine hydrate; it crystallises in golden leaflets or reddish-yellow columns, m. p. 212°, and reduces ammoniacal silver nitrate or Fehling's solution when heated. The *benzylidene* derivative,  $C_{14}H_{12}O_3N_4$ , forms yellow crystals, m. p. 187—189°; the *o-hydroxybenzylidene* derivative,  $C_{14}H_{12}O_4N_4$ , separates from alcohol in glistening crystals, m. p. 210°; the *isopropylidene* derivative,  $C_{10}H_{12}O_3N_4$ , forms golden crystals, m. p. 204—206°. The *dibenzoyl* derivative,  $NHBz \cdot C_6H_3(NO_2) \cdot CO \cdot NH \cdot NHBz$ , m. p. 239—241°, is prepared by shaking the hydrazide with benzoyl chloride in aqueous sodium hydroxide solution. The *triacetyl* derivative,  $C_{13}H_{14}O_6N_4$ , obtained by boiling the hydrazide with acetic anhydride, crystallises in leaflets, m. p. 255°.

*Bis-2-nitro-4-aminobenzoylhydrazide*,  $N_2H_2[CO \cdot C_6H_3(NH_2) \cdot NO_2]_2$ , formed by boiling the monohydrazide with alcoholic iodine solution or, together with ethyl 2-nitro-4-aminobenzoate, by the action of hydrazine hydrate on ethyl 2:4-dinitrobenzoate in ethereal or concentrated alcoholic solution, separates from aqueous alcohol in yellowish-brown crystals, m. p. 238°, and when heated with alcoholic hydrogen chloride at 110° yields hydrazine and 2-nitro-4-aminobenzoic acid.

*2-Nitro-4-aminobenzoylazoimide*,  $NO_2 \cdot C_6H_3(NH_2) \cdot CO \cdot N_3$ , prepared by the action of sodium nitrite on the hydrazide in acetic acid solution, is obtained as an unstable, red, flocculent precipitate, detonates when heated on platinum, is hydrolysed by dilute sodium hydroxide, forming azoimide and sodium 2-nitro-4-aminobenzoate, and is converted by boiling aniline into 2-nitro-4-aminobenzanilide,  $C_{13}H_{11}O_3N_3$ , which crystallises in white needles, m. p. 226°, and forms an *acetyl* derivative,  $NHAc \cdot C_6H_3(NO_2) \cdot CO \cdot NHPh$ , crystallising in yellow needles, m. p. 238°. The action of boiling alcohol on the azoimide leads to the formation of a dark red syrup, which is probably 2-nitro-4-aminophenylurethane,  $NO_2 \cdot C_6H_3(NH_2) \cdot NH \cdot CO_2Et$ , since, on successive treatment with an alkali and hydrochloric acid, it yields nitro-*p*-phenylene-



diamine. When boiled with water, the azoimide forms nitro-*p*-phenylenediamine and *bis*-2-nitro-4-aminophenylcarbamide,



which is hydrolysed by prolonged boiling with concentrated sodium hydroxide, forming nitro-*p*-phenylenediamine.

Experimental details as to the action of hydrazine hydrate on nitrobenzene, *m*-dinitrobenzene, nitrophenols, *m*- and *p*-nitrobenzoic acids, and *p*-nitrosodimethylaniline are now given (compare this vol., i, 969). G. Y.

#### Action of Hydrazine Hydrate on Nitro-compounds. IV.

**4-Nitro- and 4-Amino-phthalhydrazides.** THEODOR CURTIUS and ALFRED HOESCH (*J. pr. Chem.*, 1907, [ii], 76, 301—330. Compare this vol., 969, 970, and preceding abstract).—When boiled with alcoholic hydrazine hydrate, ethyl 4-nitrophthalate forms *hydrazonium*

4-nitrophthalylhydrazide,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{N}_2\text{H}_5$ , which is obtained in

yellow and red modifications, does not melt at 300°, forms a red aqueous solution, yields benzaldazine when shaken with aqueous benzaldehyde, and, on treatment with acetic acid, yields 4-nitrophthalylhydrazide (Bogert and Boroschek, *Abstr.*, 1902, i, 98). This is obtained in golden plates, m. p. 298°, sublimes slowly at 200°, has an acid reaction in aqueous solution, and dissolves in aqueous alkalis or alkali carbonates, forming a deep red solution which gives precipitates with salts of the heavy metals. The *potassium*,  $\text{C}_8\text{H}_4\text{O}_4\text{N}_6\text{K}\cdot 3\text{H}_2\text{O}$ , *calcium*,  $\text{C}_{16}\text{H}_8\text{O}_8\text{N}_6\text{Ca}$ , and *copper*,  $\text{C}_{16}\text{H}_8\text{O}_8\text{N}_6\text{Cu}$ , salts are described. The hydrazide remains unchanged when boiled with benzaldehyde or bromine and acetic acid, but yields hydrazine and β-nitrophthalic acid when heated with concentrated hydrochloric acid at 150°.

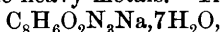
The *methyl* derivative,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NMe}$ , prepared by heating the potassium salt with methyl iodide at 150°, crystallises in yellow needles, m. p. 295°, and dissolves in aqueous alkalis, forming a red solution. The *diacetyl* derivative,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{N}(\text{Ac})\cdot\text{CO}\cdot\text{N}(\text{Ac})$ , obtained by

heating the hydrazide with acetic anhydride, forms white leaflets, m. p. 165°, and is hydrolysed by boiling water. *Ethyl* 4-nitrophthalylhydrazidecarboxylate,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CO}_2\text{Et}$ , formed by heating

the potassium salt with ethyl chlorocarbonate, crystallises in yellow leaflets, m. p. 115°, and is hydrolysed by boiling water, yielding the hydrazide. The action of ethyl chloroacetate on the potassium salt at 120—150° leads to the formation of a red powder,  $\text{C}_{12}\text{H}_{11}\text{O}_6\text{N}_3$ , m. p. 182°. 4-Nitrophthalylhydrazide is attacked by fuming nitric acid at -10°, but not by concentrated nitric acid at the ordinary temperature; the action of potassium permanganate, chromic acid, or potassium dichromate and concentrated sulphuric acid leads to the formation of 4-nitrophthalic acid.

4-Aminophthalylhydrazide,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , prepared by the re-

duction of the nitro-hydrazide with hydrogen sulphide in ammoniacal solution, or by heating the nitro-hydrazide with an excess of hydrazine hydrate at 130—140°, crystallises in yellow, microscopic needles, does not melt at 300°, has an acid reaction in aqueous solution, is precipitated from its brown alkaline solutions by carbon dioxide, dissolves in hot dilute acids, but separates unchanged on cooling, and gives precipitates with salts of the heavy metals. The *sodium*,



*calcium*,  $\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_6\text{Ca}$ , and *copper*,  $\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_6\text{Cu}$  and  $\text{C}_8\text{H}_6\text{O}_2\text{N}_3\text{Cu}\cdot\text{OH}$ , salts are described. When heated with concentrated hydrochloric acid at 150°, the hydrazide is hydrolysed, forming hydrazine and 4-aminophthalic acid; oxidation with nitric acid, permanganate, or dichromate leads to the complete destruction of the molecule. The

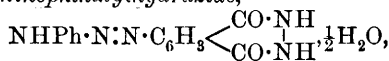
*ethyl* derivative,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{NEt} \end{smallmatrix}$ , formed from the sodium salt, separates from water in flocculent crystals, m. p. 155°. The *diacetyl*

derivative,  $\text{NHAc}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{N}^{\text{Ac}} \end{smallmatrix}$ , crystallises in yellow plates, m. p. 212°, and when boiled with water yields a white mixture of the *mono*- and *di*-acetyl derivatives, m. p. about 270°. *Ethyl 4-aminophthalyl-*

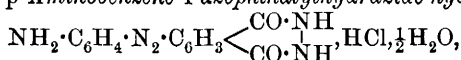
*hydrazidedicarboxylate*,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{N}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ , crystallises in yellow leaflets, m. p. 148—150°.

Diazotisation of 4-aminophthalhydrazide with sodium nitrite in sulphuric acid solution leads to the formation of a dark red *solution*, which, when heated on the water-bath, evolves nitrogen, and, on cooling, deposits 4-*hydroxyphthalylhydrazide*,  $\text{OH}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ ; this forms an amorphous, yellow powder, does not melt at 300°, and dissolves in aqueous alkalis or alkali carbonates to a yellowish-red solution. The diazo-sulphate solution couples with resorcinol in alkaline solution, forming a red *dye*,  $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_4$ , which in alkaline solution dyes vegetable and animal fibres yellow.

*Benzenediazoaminophthalylhydrazide*,



formed by the action of sodium acetate on a mixture of aniline hydrochloride and diazotised 4-aminophthalylhydrazide in hydrochloric acid solution, is obtained as a yellow precipitate, m. p. 185—187°, and evolves a gas and yields an odour of phenol when heated with dilute acids. *p-Aminobenzene-4-azophthalylhydrazide hydrochloride*,



formed by heating the preceding substance with aniline and aniline hydrochloride, crystallises in dark red prisms, m. p. about 240°, and, when treated with carbon dioxide in ammoniacal solution, yields the free *base*,  $\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_5$ , which is obtained as an amorphous powder, does not melt at 300°, and is soluble in acids and alkalis. G. Y.

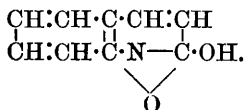
**Synthesis of Quinoline Derivatives. IV. Action of Ethyl Benzoylacetate on Anthranilic Acid.** STEFAN VON NIEMENTOWSKI (*Ber.*, 1907, 40, 4285—4294. Compare *Abstr.*, 1905, i, 611).—The compound,  $C_{30}H_{20}O_5N_2$ , m. p.  $308^\circ$  [ $1318^\circ$ ], described previously (*loc. cit.*) as a by-product of the interaction of ethyl benzoylacetate (1 mol.) and anthranilic acid (1 mol.), is shown to be 4-anilino-2-hydroxyquinoline,  $C_{15}H_{12}ON_2$ , which is obtained in better yield by the action of 2 mols. of anthranilic acid on 1 mol. of the ester. It crystallises from acetone, methyl alcohol (+ Me·OH), or acetic acid or anhydride (+  $C_2H_4O_2$ ) in microscopic, six-sided plates, m. p.  $318^\circ$ , and acts as a feeble, monobasic acid. Its *hydrochloride*,  $C_{15}H_{12}ON_2\cdot HCl$ , forms silky needles, m. p.  $160$ — $165^\circ$ . By the action of fused potassium or sodium hydroxide, or by heating with hydrochloric acid in a sealed tube, 4-anilino-2-hydroxyquinoline is resolved into aniline and 4-hydroxycarbostyryl (2 : 4-dihydroxyquinoline). The latter compound, when obtained from its sodium derivative and acetic acid, separates as a crystalline powder, m. p.  $340$ — $344^\circ$ , whilst, after long boiling with nitrobenzene or aniline, it forms stout crystals, m. p.  $355^\circ$ .

When distilled with zinc dust under very low pressure, 4-anilino-2-hydroxyquinoline yields 4-anilinoquinoline (compare Ephraim, *Abstr.*, 1893, i, 727).

2-Chloro-4-anilinoquinoline,  $C_{15}H_{11}N_2Cl$ , obtained by the action of phosphorus pentachloride and oxychloride on 4-anilino-2-hydroxyquinoline, crystallises from alcohol in concentric groups of white needles, m. p.  $156^\circ$ , forms a yellow *hydrochloride*, m. p.  $247^\circ$ , and, when boiled with excess of aniline, yields 2 : 4-dianilinoquinoline (Ephraim, *loc. cit.*), which separates from alcohol in rhombic crystals.

The mechanism of the formation of 4-anilino-2-hydroxyquinoline is probably as follows. One of the two mols. of anthranilic acid is resolved into carbon dioxide and aniline, the latter then immediately reacting with the second mol. of anthranilic acid giving aminobenzoyl-anilide. This then reacts either with ethyl benzoylacetate yielding 4-anilino-2-hydroxy-3-benzoylquinoline, the benzoyl group of which is removed by hydrolysis, or with ethyl acetate, a product of the decomposition of ethyl benzoylacetate, giving 4-anilino-2-hydroxyquinoline directly.

The compound,  $C_9H_7O_2N$ , termed hydroxycarbostyryl by Friedländer and Ostermaier (*Abstr.*, 1882, 201, 732), and obtained together with carbostyryl by reducing ethyl o-nitrocinnamate with alcoholic ammonium sulphide, is regarded by the author as having the constitution :

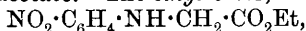


T. H. P.

**Preparation of 5-Hydroxy-3'-aminophenyl-1 : 2-naphthiminazoledisulphonic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 186883).—5-Hydroxy-3'-aminophenyl-1 : 2-naphthiminazole-7- $\lambda$ -disulphonic acid is an almost colourless, sparingly

soluble compound, obtained by sulphonating 5-hydroxy-3'-aminophenyl-1:2-naphthiminazole-7-sulphonic acid on the water-bath with fuming sulphuric acid (25%  $\text{SO}_3$ ). Its alkali salts are readily soluble, as are also those of barium, strontium, and calcium; the yellow copper salt dissolves in water only sparingly. G. T. M.

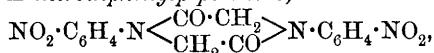
**2:5-Diketo-dinitro- and -diamino-diphenylpiperazines.** E. DEUTSCH (*J. pr. Chem.*, 1907, [ii], **76**, 350—363).—*m*-Nitrophenylglycine,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by heating *m*-nitroaniline with chloroacetic acid in sodium acetate and carbonate solution, crystallises in doubly refracting, yellow, rhombic prisms, m. p.  $156^\circ$  (corr.), decomp. slightly above its m. p., and dissolves in aqueous sodium carbonate or acetate. The *ethyl* ester,



prepared from *m*-nitroaniline and ethyl chloroacetate, forms pleochroic crystals, m. p.  $84^\circ$  (corr.).

Chloroacetyl-*m*-nitroanilide (Johnson and Cramer, *Abstr.*, 1903, i, 581) crystallises in doubly refracting plates, m. p.  $116^\circ$  (corr.), decomp.  $150$ — $160^\circ$ , and is hydrolysed by alcoholic potassium hydroxide, forming *m*-nitroaniline together with traces of the *m*-nitroanilide of glycollic acid if in presence of water.

**2:5-Diketodi-*m*-nitrodiphenylpiperazine,**

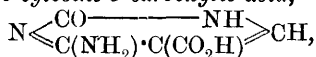


is obtained in a 20% yield when *m*-nitrophenylglycine, or in a 10% yield when chloroacetyl-*m*-nitroanilide, is heated at  $160$ — $170^\circ$ ; it forms a yellow, crystalline powder, m. p.  $157^\circ$  (corr.), and is hydrolysed to *m*-nitrophenylglycine by alcoholic potassium hydroxide.

The action of chloroacetyl chloride on *m*-nitrophenylglycine leads to the formation of *chloroacetyl-m-nitrophenylglycine*, which cannot be obtained free from unchanged *m*-nitrophenylglycine; when boiled with excess of *m*-nitroaniline in benzene, it forms small amounts of 2:5-diketodi-*m*-nitrodiphenylpiperazine. Reduction of this with tin and hydrochloric acid leads to the formation of 2:5-diketo-di-*m*-aminodiphenylpiperazine dihydrochloride,  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4\text{Cl}_2$ , which is obtained in colourless, doubly refracting crystals. The free base is colourless, but on exposure to air rapidly becomes yellow, changing to green and black. Orange-red to yellow dyes, which dye wool, but not cotton, are obtained by coupling the diazotised base with R-salt and salicylic acid.

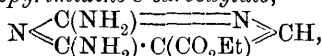
*Chloroacetyl-p-nitroanilide* crystallises in doubly refracting plates, m. p.  $152^\circ$  (corr.), and resembles the *m*-nitroanilide in its behaviour to hydrolysing agents. When heated at  $170^\circ$ , it yields 2:5-diketodi-*p*-nitrodiphenylpiperazine,  $\text{C}_{16}\text{H}_{12}\text{O}_6\text{N}_4$ , which is obtained as a yellow powder, m. p.  $147^\circ$  (corr.), and when boiled with alcoholic potassium hydroxide is hydrolysed to *p*-nitrophenylglycine. The dihydrochloride, obtained on reduction of the di-*p*-nitro-compound in hydrochloric acid solution, forms colourless, doubly refracting prisms; the free base is colourless, rapidly darkens on exposure to air, and, when diazotised and coupled with R-salt and salicylic acid, yields dyes which dye wool, but not cotton, a dirty, brown yellow. G. Y.

**Pyrimidines. XXVI. Synthesis of Cytosine-5-carboxylic Acid.** HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1907, **38**, 594—602).—When ethyl 2-ethylthiol-6-oxypyrimidine-5-carboxylate (Wheeler, Johnson, and Johns, this vol., i, 559) is boiled with phosphorus oxychloride, it is converted into *ethyl 6-chloro-2-ethylthiopyrimidine-5-carboxylate*,  $\text{N} \begin{smallmatrix} \text{C(SET)} \\ \text{C(Cl} \cdot \text{C(CO}_2\text{Et)} \end{smallmatrix} \text{N} \rangle \text{CH}$ , b. p. 203°/20 mm. This substance, on treatment with cold alcoholic ammonia, yields *ethyl 6-amino-2-ethylthiopyrimidine-5-carboxylate*,  $\text{N} \begin{smallmatrix} \text{C(SET)} \\ \text{C(NH}_2\text{)} \cdot \text{C(CO}_2\text{Et)} \end{smallmatrix} \text{N} \rangle \text{CH}$ , m. p. 102°, which forms rectangular plates; the corresponding *acid*, m. p. 230° (decomp.), crystallises in microscopic prisms, and when heated with concentrated hydrochloric acid is converted into *cytosine-5-carboxylic acid*,



m. p. 256—257° (decomp.). The *hydrochloride* of cytosine-5-carboxylic acid, m. p. 275—276°, forms pointed prisms containing 1H<sub>2</sub>O. The *ethyl ester* crystallises in needles, and decomposes slowly at 260—275°. The *amide* forms tufts of hair-like needles. When cytosine-5-carboxylic acid is heated with 20% sulphuric acid, it yields uracil-5-carboxylic acid (*loc. cit.*) together with a small quantity of cytosine. These results indicate that cytosine does not exist in the nucleic acids in the form of a 5-carboxyl derivative.

*Ethyl 2 : 6-diaminopyrimidine-5-carboxylate*,



m. p. 205—207°, obtained by heating ethyl 6-amino-2-ethylthiopyrimidine-5-carboxylate with alcoholic ammonia at 168—178°, crystallises in needles. E. G.

**Pyrimidines. XXVII. Synthesis of Thymine-5'-carboxylic Acid.** TREAT B. JOHNSON and CARL FRANK SPEH (*Amer. Chem. J.*, 1907, **38**, 602—613).—The study of the carboxylic acids of uracil, cytosine, and thymine has been undertaken with a view to obtain evidence as to whether these bases are linked in nucleic acid by means of an acid amide group (compare Wheeler, Johnson, and Johns, this vol., i, 559, and preceding abstract; Johnson, this vol., i, 879, and Wheeler, this vol., i, 972). The results so far obtained indicate that uracil is the only one of these pyrimidines which is capable of being united in this way and that this might exist as a 5-carboxyl compound.

*Ethyl formylsuccinate*, CO<sub>2</sub>Et·CH(CHO)·CH<sub>2</sub>·CO<sub>2</sub>Et, b. p. 158—160°/20 mm., is obtained by the condensation of ethyl formate and succinate in presence of sodium. By the action of its sodium derivative on *ψ*-ethylthiocarbamide, *ethyl 6-oxy-2-ethylthiopyrimidine-5-acetate*,  $\text{NH} \begin{smallmatrix} \text{C(SET)} \\ \text{CO} \cdot \text{C(CH}_2 \cdot \text{CO}_2\text{Et)} \end{smallmatrix} \text{N} \rangle \text{CH}$ , m. p. 146—147°, is produced which forms slender needles. The corresponding *acid*, m. p. 184°, crystallises in needles and square plates; its *potassium salt* forms long needles.

By the action of phosphorus oxychloride on ethyl 6-oxy-2-ethyl-



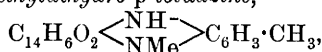
has the formula:  $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_4 \begin{smallmatrix} \diagup NH \diagdown \\ \diagdown NH \diagup \end{smallmatrix} C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_4$ , and is probably isomeric with the indanthrene of commerce.

Purpurin and 1:2-diaminoanthraquinone gives rise to hydroxy-indanthrene, which, on reduction, yields a blue vat-dye and gives greenish-blue shades on unmordanted cotton. The patent contains a tabulated description of nine of these indanthrene derivatives.

G. T. M.

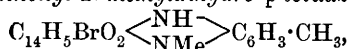
[Preparation of Azines Derived from Anthraquinone.]

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 184391).—When the aldehydes react with the aryl-*o*-diaminoanthraquinones, new coloured substances are produced, which are regarded as azine derivatives. 2-Amino-1-*p*-tolylaminoanthraquinone, when condensed with formaldehyde solution (40%) in glacial acetic acid at 100°, furnishes *anthraquinonyl-N-methyldihydro-p-toluzaine*,



which separates as a blue, crystalline precipitate.

3-Bromoanthraquinonyl-*N*-methyldihydro-*p*-toluzaine,



blue needles, is prepared in a similar manner from 3-bromo-2-amino-1-*p*-tolylaminoanthraquinone. The properties of these and seven other complex dihydro-azines are tabulated in the patent. The sulphonic acids of all these substances are wool dyes, giving various shades of blue.

G. T. M.

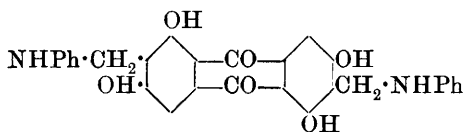
[Preparation of 2':2'-Dianthraquinonyl-1:5-diaminoanthraquinone.]

BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 184905).—When 1:5-diaminoanthraquinone is heated to boiling in naphthalene or nitrobenzene solution with 2-chloroanthraquinone in the presence of dry sodium acetate and cupric or cuprous chloride, 2:2'-*dianthraquinonyl-1:5-diaminoanthraquinone*,  $C_{10}H_6O_2(NH \cdot C_{10}H_7O_2)_2$ , is produced as a compound insoluble in the organic media; it dissolves in concentrated sulphuric acid to a green solution, and is reduced by alkaline hyposulphite to give a vat-dye producing very fast shades of red on cotton.

G. T. M.

[Preparation of  $\omega$ -Dianilinodimethyltetrahydroxyanthraquinone and *pp*-Tetramethyldiaminodibenzyltetrahydroxyanthraquinone.]

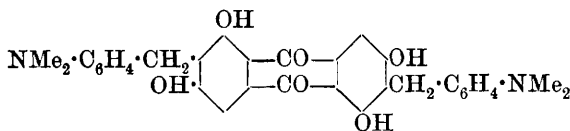
FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 184807, 184808).—The condensation product from anthra-



*tetrahydroxy-3:7-dimethylanthraquinone*, separating from the cooled

chrysone (tetrahydroanthraquinone) and formaldehyde, when heated with excess of aniline so long as steam is evolved, gives rise to  $\omega$ -*dianilino-2:4:6:8-*

solution in orange-yellow crystals, which on heating decompose without definite melting point. Corresponding compounds may be obtained with the toluidines and

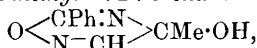


xylydines. *pp-Tetramethyldiamino-2:4:6:8-tetrahydroxy-3:7-dibenzyl-anthraquinone*, produced by substituting dimethylaniline for aniline in the foregoing condensation, separates in orange-yellow crystals, m. p. 272°. The corresponding tetraethyl derivative melts at 233°.

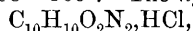
G. T. M.

**Oxadiazines.** II. OTTO DIELS and ERICH SASSE (*Ber.*, 1907, 40, 4052—4059. Compare *Abstr.*, 1905, i, 946).—*iso*Nitrosoacetone and *isonitrosoacetophenone* react like diacetylmonoxime with *syn*-benzaloxime hydrochloride forming oxadiazines. In the presence of anhydrous hydrogen chloride, the *isonitroso*-compound reacts with itself (or with its isomeric modification) yielding an oxadiazine containing a carbonyl group, from which an oxime is readily obtained. Thus from *isonitrosoacetophenone* is obtained an oxime of the formula  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_3$ , which appears to be identical with a substance prepared by Müller and von Pechmann (*Abstr.*, 1890, 51) and by Scholl (*Abstr.*, 1891, 287). The latter regarded the substance as the dioxime of 5-benzoyl-3-phenyl-4-*isooxazolone*. The author brings forward evidence to show that the preparation and properties of the substance harmonise better with the oxadiazine formula,  $\text{O} < \begin{array}{c} \text{N} \\ \text{C}(\text{CPh}:\text{NOH}) \end{array} \text{CH} > \text{N} > \text{CPh}:\text{OH}$ .

4-Hydroxy-6-phenyl-4-methyl-1:2:5-oxadiazine,

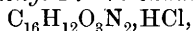


darkens at 170—180° and decomposes at 220—225°; the *methiodide*,  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_2\text{I}_3$ , has m. p. 108—109°. The *hydrochloride*,



m. p. 137—138°, softening at 134—135°, is prepared from *isonitrosoacetone* and *syn*-benzaloxime hydrochloride in methyl-alcoholic solution; with boiling water, it yields the preceding base.

4-Hydroxy-6-benzoyl-4-phenyl-1:2:5-oxadiazine hydrochloride,



is obtained by passing a rapid current of hydrogen chloride through an ethereal solution of *isonitrosoacetophenone*; it separates in stout, yellow, prismatic needles, which decompose violently at 215°. Boiling water liberates the base,  $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ , m. p. 220—226°, which forms a yellow, crystalline sodium salt, which decomposes at 215°, and the oxime, which decomposes at 221—222° (Müller and von Pechmann, m. p. 219°; Scholl, m. p. 207—211°).

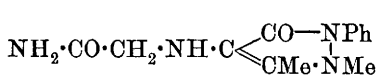
C. S.

**Preparation of 4-Antipyrldimethylamine.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 184850).—4-Cyanomethyl-amino-1-phenyl-2:3-dimethylpyrazolone (4-antipyrilcyanomethylamine),  $\text{CN} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NPh} \\ \text{CMe} \cdot \text{NMe} \end{array}$ , colourless leaflets, m. p. 112°, is pro-

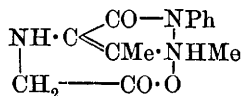


duced by treating an aqueous solution of 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone successively with formaldehyde, sodium hydrogen sulphite, and potassium cyanide, when it separates as an oil which becomes solid on cooling; it dissolves only sparingly in ether, but is readily soluble in hot water or benzene, or in cold alcohol or chloroform.

4-Antipyrilaminoacetamide (I), m. p. 194°, colourless prisms from alcohol or water, is obtained on boiling the preceding cyano-



(I.)



(II.)

compound with water, or on leaving it in contact with concentrated hydrochloric acid. On boiling either of the preceding compounds with concentrated hydrochloric acid, the betaine (II) is produced, which is only sparingly soluble in all organic media, and crystallises from alcohol in lustrous needles, m. p. above 300°.

4-Antipyrilcyanodimethylamine,  $\text{CN} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{C} \begin{array}{l} \diagup \text{CO-NPh} \\ \diagdown \text{CMe} \cdot \text{NMe} \end{array}$ ,

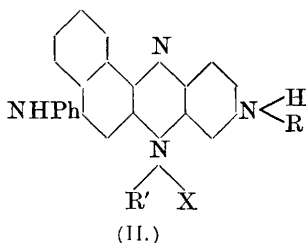
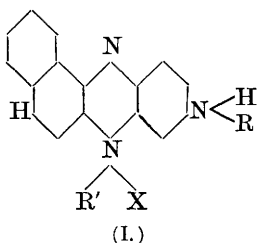
colourless crystals, m. p. 75°, is prepared by alkylating 4-antipyrilcyanomethylamine with methyl iodide in methyl-alcoholic solution.

4-Antipyrilmethylaminoacetamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{C} \begin{array}{l} \diagup \text{CO-NPh} \\ \diagdown \text{CMe} \cdot \text{NMe} \end{array}$ ,

leaflets from benzene, m. p. 158—159°, is similarly obtained by methylating 4-antipyrilaminoacetamide. 4-Antipyrilmethylaminoacetic acid, prepared by methylating the foregoing betaine, is a very soluble substance, having a hygroscopic sodium salt soluble in chloroform.

The last three compounds can be hydrolysed so as to yield the therapeutically important 4-antipyrildimethylamine. G. T. M.

[Preparation of Naphthaphenosafranine Derivatives.]  
FRIEDRICH KEHRMANN (D.R.-P. 183117).—The isorosinduline salts of the general type (I; where X is the acid ion) have the



hydrogen atom, indicated in the naphthalene residue, replaced by the group  $\text{NHR}''$  when the colouring matter is treated with an amine in the presence of an oxidising agent, such as

atmospheric air. Condensation with aniline would lead to the formation of substances indicated by the general formula (II).

Ethylisorosinduline chloride, obtained from nitrosoethylaniline and phenyl- $\beta$ -naphthylamine when treated with aniline and aqueous sodium hydroxide at 80–90° while a current of air is passed through the mixture, gives rise to a colour base separating in green crystals with a metallic lustre. Phenylisorosinduline chloride and *p*-aminoacetanilide yield a similar product, which separates in golden-yellow crystals. Sulphonation and hydrolysis of the acetyl group lead to the production of a soluble sulphonic dye. Phenylisorosinduline disulphonic acid furnishes similar condensation products on treatment with aromatic amines and sodium hydroxide. G. T. M.

### Action of Diazo-derivatives of Aliphatic Hydrocarbons on Cyanogen and its Derivatives. III. Halogenated Compounds.

ANTONIO TAMBURELLO and A. MILAZZO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 412–418. Compare Peratouer and Azzarello, this vol., i, 979).—The action of cyanogen chloride or bromide on diazomethane or diazoethane in ethereal solution yields a chloro-derivative of osotriazole, which usually undergoes subsequent etherification by the diazo-compound:  $\text{CH}_2\text{N} \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} + \text{CNCI} = \text{NH} \begin{smallmatrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{CCI} \end{smallmatrix}$ , and  $\text{NH} \begin{smallmatrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{CCI} \end{smallmatrix} + \text{CH}_2\text{N}_2 = \text{N}_2 + \text{NMe} \begin{smallmatrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{CCI} \end{smallmatrix}$ ; cyanogen chloride gives the best yields, whilst with the iodide no definite compounds were obtained.

4-Chloro-3-methylsotriazole,  $\text{NH} \begin{smallmatrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{CCI} \end{smallmatrix}$ , prepared from cyanogen chloride and diazoethane, crystallises from benzene in shining, white needles, m. p. 77–78°.

4-Chloro-3-methyl-1-ethylsotriazole,  $\text{NEt} \begin{smallmatrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{CCI} \end{smallmatrix}$ , is a colourless liquid, b. p. 86–88°/40 mm., which has a pleasing odour and is insoluble in water.

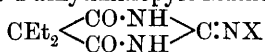
4-Bromo-3-methyl-1-ethylsotriazole,  $\text{C}_5\text{H}_8\text{N}_3\text{Br}$ , is a colourless liquid, b. p. 84–85°/30 mm., having a pleasant odour.

3-Chloro-1-methylsotriazole,  $\text{NMe} \begin{smallmatrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{CCI} \end{smallmatrix}$ , is a colourless liquid, b. p. 62–65°/39 mm., having a pleasant odour.

3-Bromo-1-methylsotriazole,  $\text{NMe} \begin{smallmatrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{CBr} \end{smallmatrix}$ , is a colourless liquid, b. p. 62–65°/22 mm., and has a pungent odour which excites to tears.

T. H. P.

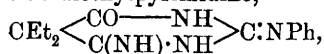
Preparation of 2-Alkyliminopyrimidines. EMANUEL MERCK (D.R.-P. 186456).—The 2-alkyliminopyrimidines,



(where X is an alkyl or aryl group), were obtained by condensing the corresponding guanidine,  $\text{NX}:\text{C}(\text{NH}_2)_2$ , with malonyl halides, alkyl

malonamates, alkyl cyanoacetates, or their mono- and di-alkyl derivatives.

Phenylguanidine and ethyl cyanodiethylacetate give rise to 4-imino-6-oxy-2-phenylimino-5:5-diethylpyrimidine,

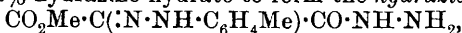


which is readily hydrolysed to 5:5-diethylbarbituric acid.

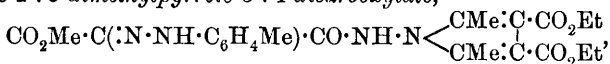
4-*Imino-6-oxy-2-phenyliminopyrimidine*, m. p. 244°, was produced by condensing phenylguanidine and ethyl cyanoacetate with alcoholic sodium ethoxide. 4-*Imino-6-oxy-2-methylimino-5:5-diethylpyrimidine*, m. p. 265°, was obtained from methylguanidine and ethyl cyanodiethylacetate. 4:6-*Dioxy-2-phenylimino-5:5-diethylpyrimidine*, needles, m. p. 255°, was prepared from phenylguanidine and diethylmalonyl chloride.

G. T. M.

**Derivatives of Methyl Mesoxalate-*p*-tolylhydrazone.** CARL BÜLOW and RICHARD WEIDLICH (*Ber.*, 1907, 40, 4326—4332. Compare Abstr., 1906, i, 981).—Methyl mesoxalate-*p*-tolylhydrazone (Bülow and Ganghofer, Abstr., 1905, i, 90) in cold alcoholic solution reacts with 50% hydrazine hydrate to form the *hydrazide*,

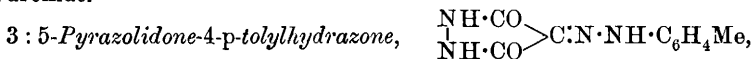


m. p. 160°, which separates from dilute alcohol in slender, yellow needles, and is converted by acetic anhydride into the *acetyl* derivative,  $\text{CO}_2\text{Me} \cdot \text{C}(\text{:N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}) \cdot \text{CO} \cdot \text{NH} \cdot \text{NHAc}$ , m. p. 186°. The hydrazide condenses with benzaldehyde in boiling alcohol to form the *benzylidene* compound,  $\text{CO}_2\text{Me} \cdot \text{C}(\text{:N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}) \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$ , m. p. 163°, and with acetone, yielding the corresponding *isopropylidene* compound,  $\text{CO}_2\text{Me} \cdot \text{C}(\text{:N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}) \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CMe}_2$ , m. p. 165°. The hydrazide and ethyl diacetylsuccinate in very slightly diluted glacial acetic acid form *methyl diethyl mesoxalyl-p-tolylhydrazone-1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate*,



m. p. 161—162°, which separates from dilute alcohol in stout, yellow needles.

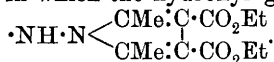
The *dihydrazide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{CO} \cdot \text{NH} \cdot \text{NH}_2)_2$ , m. p. 196°, is obtained by heating the mother liquor of the monohydrazide for five hours on the water-bath, or the calculated quantities of 50% hydrazine hydrate and methyl mesoxalate-*p*-tolylhydrazone for four hours; the *acetyl* derivative,  $\text{C}_{14}\text{H}_{18}\text{O}_4\text{N}_6$ , m. p. 247°, is a yellow powder. *Ethyl mesoxalyl-p-tolylhydrazone-bis-1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{CO} \cdot \text{NH} \cdot \text{N} \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array})_2$ , m. p. 241°, crystallises in slender, yellow needles, and dissolves in dilute sodium hydroxide.



m. p. 267°, is prepared by passing carbon dioxide through the mother liquor of the dihydrazide or through the cold filtrate obtained after heating methyl mesoxalate-*p*-tolylhydrazone and a slight excess of

hydrazine hydrate in alcohol for twelve hours. In alkaline solution, it reacts with methyl sulphate to form 1:2-dimethyl-3:5-pyrazolidone-4-p-tolylhydrazone, m. p. 170°, which crystallises in red needles.

The authors formulate the rule: hydrazides of organic acids react with ethyl diacetylsuccinate in acetic acid solution to form compounds in which the hydroxyl group of the acid is replaced by the complex:



C. S.

[Diazotisation of Acetyl-2:6-diaminophenol-4-sulphonic Acid.] KALLE & CO. (D.R.-P. 182853).—6-Nitro-2-acetylaminophenol-4-sulphonic acid is reduced without losing its acetyl group or undergoing condensation by means of iron filings and water acidified with acetic acid. The resulting acetyl-2:6-diaminophenol-4-sulphonic acid yields a very stable diazo-compound, which when warmed at 40–45° for six hours with dilute hydrochloric acid loses its acetyl group, whilst the diazo-complex remains intact.

G. T. M.

**Transformations of Azo-compounds into Hydrazones.** OTTO DIMROTH and MAX HARTMANN (*Ber.*, 1907, 40, 4460–4465).—Benzene-azo- and *p*-bromobenzeneazo-acetyldibenzoylmethane and *p*-bromobenzeneazotribenzoylmethane behave in the same manner as *p*-nitrobenzeneazoacetyldibenzoylmethane (this vol., i, 662), changing into colourless isomerides when heated alone or with indifferent solvents. The coloured substances are azo-compounds,  $\text{NR}:\text{N}\cdot\text{C}(\text{COR}')_2\cdot\text{COR}'$ , whilst the colourless isomerides are hydrazones,  $\text{COR}''\cdot\text{NR}\cdot\text{N}:\text{C}(\text{COR}')_2$ , which do not undergo the converse transformation in benzene, ether, or chloroform at 160°.

*Benzeneazoacetyldibenzoylmethane*,  $\text{C}_{23}\text{H}_{15}\text{O}_3\text{N}_2$ , prepared by addition of diazobenzene chloride and sodium acetate to the enolic modification of acetyldibenzoylmethane in alcoholic solution at 0°, forms yellow crystals, m. p. 90°, evolving gas. The isomeric *hydrazone* crystallises in white needles, m. p. 188°.

*p*-*Bromobenzeneazoacetyldibenzoylmethane*,  $\text{C}_{23}\text{H}_{17}\text{O}_3\text{N}_2\text{Br}$ , forms amber-coloured, monoclinic crystals, m. p. 113°. The *hydrazone*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NAc}\cdot\text{N}:\text{C}(\text{COPh})_2$ , crystallises in white needles, m. p. 218°, and when reduced with zinc dust and ammonia yields acet-*p*-bromoanilide. On treatment with sodium ethoxide at 0°, both isomerides yield *p*-bromobenzeneazodibenzoylmethane,  $\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_2\text{Br}$ , crystallising in golden leaflets, m. p. 147–149°.

*p*-*Bromobenzeneazotribenzoylmethane*,  $\text{C}_{28}\text{H}_{19}\text{O}_3\text{N}_2\text{Br}$ , forms yellow crystals, m. p. 130–135°. The *hydrazone* crystallises in colourless needles, m. p. 220–221°, and is reduced by zinc dust and acetic acid, forming benzo-*p*-bromoanilide.

G. Y.

[Combination of *o*-Diazo-oxides with 1:8-Dihydroxynaphthalene-3:6-disulphonic Acid.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 184689).—The nitro-*o*-aminophenols, containing the nitro-group in the para-position with respect to the amino-group, yield sparingly soluble, yellow diazo-oxides, which couple far more readily with 1:8-dihydroxynaphthalene-3:6-disulphonic acid (chromo-

tropic acid) in the presence of calcium hydroxide than when sodium hydroxide or carbonate is employed. The azo-sulphonic acids thus produced give various shades of blue on chrome-mordanted wool.

G. T. M.

**Etherification of Hydroxyazo-compounds by means of Methyl Sulphate.** AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 457—464).—As a rule, hydroxyazo-compounds can be converted quantitatively into the corresponding methoxyazo-derivatives by shaking their alkaline solutions for a short time with a slight excess of methyl sulphate. In some cases, for example, with azo-compounds derived from phenols in which the para-position is occupied by another radicle, the etherification is only effected on heating, and proceeds best when an absolute alcoholic solution of the alkali derivative of the hydroxyazo-compound is treated with methyl sulphate.

This method has been applied to the preparation of the methyl ethers of benzeneazophenol, 2 : 4 - bisbenzeneazophenol, benzeneazoguaiacol, m. p. 53—54° [Jacobson, Jaenicke, and Meyer gave m. p. 44·5—45° (Abstr., 1897, i, 143)], and the following new compounds.

The *methyl ether* of *o*-nitrobenzeneazoguaiacol,  $C_{14}H_{13}O_4N_3$ , separates from alcohol in reddish-brown crystals, m. p. 152°.

The *methyl ether* of  $\beta$ -naphthylazoguaiacol,  $C_{18}H_{16}O_2N_2$ , is deposited from alcohol in long, orange-red, acicular crystals, m. p. 103—105°.

The *methyl ether* of *p*-bromobenzeneazoeugenol,  $C_{17}H_{17}O_2N_2Br$ , separates from benzene in minute, pale-yellow crystals, m. p. 92—94°.

The *methyl ether* of *m*-xyleneazoeugenol,  $C_{19}H_{22}O_2N_2$ , forms minute, brick-red crystals, m. p. 56°.

T. H. P.

**Esterification of Azo-derivatives of Hydroxy-acids by means of Methyl Sulphate.** AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 547—551. Compare preceding abstract).—When an azo-derivative of *o*- or *m*-hydroxybenzoic acid is treated with rather more than 2 mols. of potassium hydroxide and rather more than 2 mols. of methyl sulphate, it yields a mixture of the esters:  $N_2R \cdot C_6H_3(OH) \cdot CO_2Me$  and  $N_2R \cdot C_6H_3(OMe) \cdot CO_2Me$ . In the cases examined, the methoxy-acid,  $N_2R \cdot C_6H_3(OMe) \cdot CO_2H$ , was not detected.

Thus benzeneazosalicylic acid [ $OH : CO_2H : N_2Ph = 2 : 1 : 5$ ] yields:

(1) *methyl 5-benzeneazo-2-methoxybenzoate*,

$N_2Ph \cdot C_6H_3(OMe) \cdot CO_2Me$  [ $N_2Ph : CO_2H : OMe = 5 : 1 : 2$ ], which separates from alcohol in crystals, m. p. 63—64°; (2) *methyl 5-benzeneazosalicylate*,  $N_2Ph \cdot C_6H_3(OH) \cdot CO_2Me$ , is deposited from alcohol in yellow crystals having a metallic lustre, m. p. 162—165°.

The *p*-chlorobenzeneazo-derivative of *m*-hydroxybenzoic acid gives:

(1) *methyl 6-p-chlorobenzeneazo-3-methoxybenzoate*,

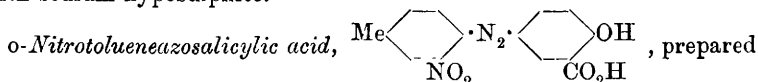
$C_6H_4Cl \cdot N_2 \cdot C_6H_3(OMe) \cdot CO_2Me$  [ $C_6H_4Cl \cdot N_2 : CO_2Me : OMe = 6 : 1 : 3$ ], which separates from alcohol in orange-yellow crystals, m. p. 89—90°;

(2) *methyl 6-p-chlorobenzeneazo-3-hydroxybenzoate*,

$C_6H_4Cl \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2Me$ , which is deposited from alcohol in shining red crystals, m. p. 155°.

T. H. P.

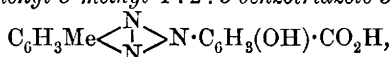
**Reduction of *o*-Nitroazosalicylic Acids by means of Sodium Hyposulphite.** EUGÈNE GRANDMOUGIN and J. R. GUISAN (*Ber.*, 1907, 40, 4205—4208. Compare this vol., i, 166).—Further investigation shows that the reduction of *o*-nitroazo-compounds by means of sodium hyposulphite does not always cease when the azoimino-oxide stage is reached, the corresponding triazole compounds being sometimes obtained directly by further action. In other cases, the two compounds are produced together. Both the *o*-nitroazosalicylic acids dealt with in the present paper give triazole derivatives on reduction with sodium hyposulphite.



either by the interaction of diazotised *m*-nitro-*p*-toluidine and salicylic acid in alkaline solution or by the nitration of *p*-tolueneazosalicylic acid in concentrated sulphuric acid, crystallises from aqueous alcohol in felted masses of long, yellow needles, m. p. 213°. The *acetyl* derivative crystallises from aqueous alcohol in pale yellow needles, m. p. 167°.

*p*-Tolueneazosalicylic acid,  $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$ , prepared either from the dye "flavazol," which is its sodium salt, or from diazotised *p*-toluidine and salicylic acid, crystallises from aqueous alcohol in brown leaflets, m. p. 212—213°, and yields an *acetyl* compound,  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_2$ , which forms pale yellow crystals, m. p. 157°.

4'-Hydroxy-2-phenyl-5-methyl-1:2:3-benzotriazole-3'-carboxylic acid,



prepared by reducing *o*-nitrotolueneazosalicylic acid in alkaline solution by means of sodium hyposulphite, crystallises from alcohol or acetic acid in white needles, m. p. 276° (slight decomp.). Its *acetyl* derivative,  $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}_3$ , crystallises from aqueous alcohol in slender, white needles, m. p. 198°.

The reduction of *o*-nitrobenzeneazosalicylic acid (compare Elbs and Keiper, *Abstr.*, 1903, i, 662) in alkaline solution by means of sodium hyposulphite yields benzotriazole-2-salicylic acid (Elbs and Keiper, *loc. cit.*).

T. H. P.

**Steric Hindrance.** HUGO KAUFFMANN and W. FRANCK (*Ber.*, 1907, 40, 3999—4015. Compare *Abstr.*, 1906, i, 841).—It is suggested in view of the hypothesis of the divisibility of valencies that the steric hindrance observed with ortho-substituted compounds may arise from mutual interference of the partial valencies. The following cases of steric hindrance have been observed with 2-substituted resorcinol dimethyl ethers. 2-Nitroresorcinol dimethyl ether is reduced only with great difficulty by zinc dust in alkaline solution. 2-Aminoresorcinol dimethyl ether cannot be acetylated by the ordinary methods, and does not form a benzylidene derivative; it is diazotised by nitrous acid, and reacts with carbon disulphide, forming a thiocarbamide only extremely slowly. The diazo-sulphate formed from 2-aminoresorcinol dimethyl ether is stable, can be recrystallised from alcohol, remains unchanged on prolonged boiling with water,

yields a nitro-derivative when heated with fuming nitric acid, and when boiled with a solution of cuprous cyanide in potassium cyanide forms a stable copper compound which again forms the diazo-salt on treatment with acids. On the other hand, substitution in the nucleus takes place readily; 2-nitroresorcinol dimethyl ether is easily brominated and nitrated, and condenses readily with aldehydes. The steric hindrance observed does not in any case amount to inhibition; its extent depends on the reagent, since 2-aminoresorcinol dimethyl ether reacts only with great difficulty with acetic acid, acetic anhydride, or benzaldehyde, but readily enters into reaction with phenylthiocarbimide or ethyl iodide.

2-Nitroresorcinol dimethyl ether is prepared in an 85% yield by the action of methyl sulphate on 2-nitroresorcinol in 10% aqueous sodium hydroxide solution at 70–80°; it remains almost unchanged when boiled with alcoholic potassium hydroxide. When treated with a limited amount of bromine in glacial acetic acid solution, it forms *bromo-2-nitroresorcinol dimethyl ether*,  $C_8H_8O_4NBr$ , m. p. 55–56°, or with an excess of bromine the *dibromo-derivative*,  $C_8H_7O_4NBr_2$ , which crystallises in white needles, m. p. 100–101°.

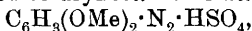
The action of fuming nitric acid on 2-nitroresorcinol dimethyl ether leads to the formation of two products. 2:4-*Dinitroresorcinol dimethyl ether*,  $C_8H_8O_6N_2$ , formed at the ordinary temperature, crystallises in yellowish-white needles, m. p. 72°, or after fusion and resolidification, m. p. 62°. 2:4:6-*Trinitroresorcinol dimethyl ether*, m. p. 124–125°, formed by the boiling acid, is identical with Hönig's styphnic acid dimethyl ether (Abstr., 1878, 727). Whilst the dinitro-ether is only slowly attacked by boiling aqueous sodium hydroxide, the trinitro-ether is rapidly hydrolysed, forming 2:4:6-trinitroresorcinol.

In presence of sulphuric acid, 2-nitroresorcinol dimethyl ether condenses with chloral hydrate, forming 3:3'-*dinitro-2:4:2':4'-tetramethoxydiphenyltrichloroethane*,  $CCl_3 \cdot CH[C_6H_2(OMe)_2NO_2]_2$ , which separates from benzene-light petroleum in yellow crystals, m. p. 181–182°.

2-Nitroresorcinol dimethyl ether is reduced only to a small extent by zinc dust in boiling alcoholic potassium hydroxide or by sodium and amyl alcohol, but readily by iron powder in glacial acetic acid or by tin and hydrochloric acid, forming 2-aminoresorcinol dimethyl ether,  $C_8H_{11}O_2N$ , which crystallises in white leaflets, m. p. 75°, b. p. 146°/23 mm. The *acetyl derivative*,  $C_{10}H_{13}O_3N$ , is formed by heating the base with acetic anhydride in a sealed tube at 150–160° for ten hours; it crystallises in white leaflets, m. p. 81°, and is hydrolysed by boiling hydrochloric acid. 2:6:2':6'-*Tetramethoxy-s-diphenylthiocarbamide*,  $C_{17}H_{20}O_4N_2S$ , m. p. 170°, is formed in only small amount when the amine is boiled with carbon disulphide and alcoholic potassium hydroxide, but in slightly better yields if sulphur is employed in place of potassium hydroxide (compare Hegershoff, Abstr., 1899, i, 886). 2:6-*Dimethoxy-s-diphenylthiocarbamide*,  $C_{15}H_{16}O_2N_2S$ , m. p. 150°, on the other hand, is formed rapidly with slight development of heat when the amine is shaken with phenylthiocarbimide.

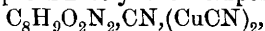
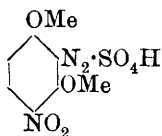
2:6-Dimethoxydiethylaniline, prepared by boiling 2-aminoresorcinol dimethyl ether with ethyl iodide in a reflux apparatus on the water-bath, is obtained as an almost colourless oil, b. p.  $130^{\circ}/12$  mm.; the *platinichloride*,  $(C_{12}H_{19}O_2N)_2 \cdot H_2PtCl_6$ , was analysed. With sodium nitrite in acid solution, the base forms a *dinitro-derivative*,  $C_{10}H_{13}O_6N_3$ , which is obtained in yellowish-brown crystals, m. p.  $108^{\circ}$ .

A soluble *diazo-chloride* is obtained when 2-aminoresorcinol dimethyl ether is treated with sodium nitrite and hydrochloric acid at the ordinary temperature and then heated gradually to  $60-70^{\circ}$ ; nitrogen is not evolved when the solution is nearly neutralised with sodium hydroxide and evaporated to dryness. The *diazo-sulphate*,



prepared by diazotisation with amyl nitrite in alcoholic solution, forms yellow crystals, is stable when free from amyl nitrite, burns quietly on platinum, can be recrystallised from benzoyl chloride, and remains unchanged when boiled with water or hydrochloric acid, or when heated at  $300^{\circ}$  with concentrated sulphuric acid, but is decomposed by aqueous alkalis, forming resorcinol dimethyl ether. On addition of a concentrated solution of the diazosulphate to 50% aqueous sodium hydroxide, a white *substance* separates, which couples only slowly with alkaline  $\beta$ -naphthol, behaving therefore as an *anti-diazo-oxide*. The diazo-salt couples with  $\beta$ -naphthol in alkaline solution, forming 2:6-dimethoxybenzeneazo- $\beta$ -naphthol,  $C_6H_3(OMe)_2 \cdot N_2 \cdot C_{10}H_6 \cdot OH$ , which crystallises in red needles, m. p.  $120-121^{\circ}$ , and is not fluorescent.

When boiled with fuming nitric acid, the diazo-sulphate yields a *nitro-derivative* having probably the annexed constitution, which couples with alkaline  $\beta$ -naphthol forming a *dye*,  $C_{18}H_{15}O_5N_3$ , crystallising in red needles, m. p.  $162-163^{\circ}$ . The *diazo-perbromide*,  $C_8H_9O_2N_2Br_3$ , prepared by adding potassium bromide and aqueous bromine to the diazo-sulphate, crystallises in needles, decomp.  $120^{\circ}$ , and loses bromine in contact with water slowly at the ordinary temperature, but quickly on heating. At the ordinary temperature, the perbromide changes slowly into a red *substance*, which couples to only a small extent. A yellowish-brown *salt*, having approximately the composition :



formed by the action of cuprous cyanide in potassium cyanide solution on the diazo-sulphate in presence of sulphuric acid, dissolves in hydrochloric acid, forming a solution which couples with  $\beta$ -naphthol and yields resorcinol dimethyl ether when heated with alkalis. A yellow *substance*, containing tin, formed by the action of stannous chloride and concentrated hydrochloric acid on the diazo-sulphate, behaves in the same manner. 2-Iodoresorcinol dimethyl ether,  $C_8H_9O_2I$ , prepared by heating the diazo-sulphate with concentrated aqueous hydriodic acid, crystallises in white needles, m. p.  $103^{\circ}$ , and does not react with "active" magnesium.

G. Y.

**Methods for the Removal of Proteins from Solution.** PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1907, 5, 365-367 Compare this vol., i, 667, and following abstract).—The precipitation



of proteins by mastic suspensions is incomplete when more than 1% of protein is present in the solution. As the mastic, however, always removes a large proportion of the protein, even from concentrated solutions, complete precipitation may be achieved by adding mastic two or three times at intervals. In many cases, precipitation by China clay is preferable to that by mastic. G. B.

**The Behaviour of Electrolytes in Mastic Precipitation.** LEONOR MICHAELIS, LUDWIG PINCUSOHN, and PETER RONA (*Biochem. Zeitsch.*, 1907, 6, 1—16. Compare Abstr., 1907, i, 667).—A study of the extent to which electrolytes are carried down from a solution in which mastic flocculation occurs. The problem is of practical importance in connexion with the method of removing proteins, described in the preceding abstract. Acids produce flocculation in very small concentrations, and are not at all carried down by the precipitate. Sodium hydroxide is not an efficient precipitating agent, and is not adsorbed either; baryta is more efficient, and is adsorbed to some extent. Mere traces of colloidal ferric hydroxide precipitate the mastic, and are thereby completely adsorbed. Sodium and ammonium chlorides resemble acids in not being adsorbed at all, but are less efficient precipitants. Other metallic salts are still less efficient, and with those of the heavy metals there is partial adsorption of the base. Dextrose, urea, glycine, and hippuric acid are not carried down at all. Very similar results were obtained with China clay instead of mastic.

G. B.

**Rotatory Power of Proteins Extracted from Cereal Flours by Aqueous Alcohol.** LÉON LINDET and LOUIS AMMANN (*Compt. rend.*, 1907, 145, 253—255; *Bull. Soc. chim.*, 1907, [iv], 1, 968—974).—By fractional precipitation of wheat gliadin dissolved in 70% alcohol by alcohol or water, two gliadins were obtained,  $\alpha_D$  -81.6° and -95.0°. The rotatory power of the mixed gliadins (twenty samples) varied between -81.6° and -92.7°.

Rye and barley yielded a protein, hordein,  $\alpha_D$  -137.5°.

Two of the three maisins ( $\alpha$  and  $\beta$ ) obtained by Donard and Labbé (Abstr., 1903, i, 215, 782) were separated from maize,  $\alpha_D$  -29.6° ( $\alpha$ ) and -40.0° ( $\beta$ ).

N. H. J. M.

**The Swelling of Fibrin.** MARTIN H. FISCHER and GERTRUDE MOORE (*Amer. J. Physiol.*, 1907, 20, 330—342).—An attempt to explain the variable affinity of colloids for water on physico-chemical lines. As a physiological outcome, it is found that substances which are most effective in diminishing the amount of swelling of fibrin in hydrochloric acid are those which most retard gastric digestion. The absorption of water by frog's muscles is entirely analogous to the absorption of water by fibrin.

W. D. H.

**The Products Obtained by Boiling Casein with 25% Sulphuric or Concentrated Hydrochloric Acid.** EMIL ABDERHALDEN and CASIMIR FUNK (*Zeitsch. physiol. chem.*, 1907, 53, 19—30).—The amount of glutamic acid produced by the hydrolysis of

casein with 25% sulphuric or concentrated hydrochloric acid is much the same, namely, some 10—11%, if the hydrolysis is continued for a sufficient length of time. Anhydrides of dipeptides are also formed in both cases; the amounts, however, are exceedingly small, under 1%. When sulphuric acid is used, the anhydride consists of a mixture of leucinimide and *l*-phenylalanyl-*d*-alanine anhydride, and probably *l*-leucyl-*d*-valine anhydride. The amounts of anhydrides tend to increase as the time of heating is decreased. When hydrochloric acid is used, leucinimide alone is formed.

Amino-acids do not yield diketopiperazine when heated with concentrated hydrochloric acid. J. J. S.

**Hydrolysis of the Sodium Salts of Casein.** LUCIUS L. VAN SLYKE and DONALD D. VAN SLYKE (*Amer. Chem. J.*, 1907, **38**, 619—626).—Determinations of the quantity of alkali hydroxide required for the neutralisation of casein give results which vary according to the indicator employed. Laqueur and Sackur (*Abstr.*, 1903, i, 300), in determining the equivalent weight of casein, arbitrarily regarded phenolphthalein as giving correct results.

In the hope of obtaining a method of ascertaining the true neutralisation point, the electrical conductivity of solutions of varying amounts of casein in 100 c.c. of *N*/100 sodium hydroxide has been determined. Usually when an acid is added to a solution of a strong base, the conductivity gradually decreases until the neutral point is reached, and by plotting the conductivities as ordinates and the amounts of acid added as abscissæ, a curve is obtained as a straight line sloping downwards to the neutral point, at which it breaks sharply. The curve for casein, however, like that for phosphoric acid, is concave and does not show any break. The minimum point is near that at which the solution is neutral to phenolphthalein, but cannot be regarded as representing the true point of neutralisation. E. G.

**Dissociation of Solutions of the Neutral Caseinates [Caseinogenates] of Sodium and Ammonium.** T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1907, **11**, 542—552).—Neutral solutions of the sodium and ammonium salts of caseinogen (termed casein by the author) have been prepared by shaking the respective alkalis with excess of caseinogen and filtering, and the electrical conductivity of these salts in various dilutions has been measured at 25°. The variation of the conductivity with dilution is such as to justify the assumption that caseinogen behaves to alkalis as a weak non-amphoteric monobasic acid. From the conductivity results, on the assumption that no complex ions containing sodium are present, the value  $2.6 \times 10^{-5}$  cm./sec. is obtained for the velocity of the caseinogen ion, but, when the results for the ammonium salt are calculated on the same assumption, it is found that the sum of the velocity of the  $\text{NH}_4^+$  and protein ions is less than the known velocity of the  $\text{NH}_4^+$  ion alone. It follows that the solution of the ammonium salt contains complex ion-protein compounds in which the non-protein ion (in this case  $\text{NH}_4^+$ ) is not dissociated as such; the formation of such compounds is thus proved for the first time, although their existence had been foreseen by Loeb.

The dissociation constants for the sodium and ammonium salts of caseinogen are 0.0395 and 0.0428 respectively. G. S.

**Molecular Weight of Oxyhæmoglobin.** GUSTAV HÜFNER and EMIL GANSSER (*Chem. Zentr.*, 1907, ii, 816; from *Arch. Anat. Physiol. Abt.*, 1907, 209—216).—By means of osmotic pressure measurements, the mol. weight of the hæmoglobin from horses and from oxen was found to be 15,115 and 16,321 respectively, it being still doubtful whether these mol. weights are really different. The authors conclude from their osmotic pressure experiments that crystalline oxyhæmoglobin is composed of one mol. of hæmoglobin combined with one mol. of oxygen. W. H. G.

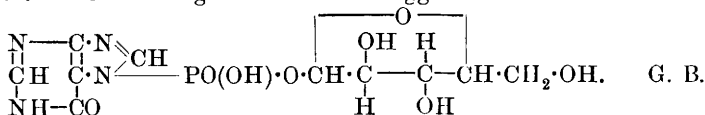
**Paranucleo-protagon.** MATTHEW STEEL and WILLIAM J. GIES (*Amer. J. Physiol.*, 1907, 20, 378—398).—This is the name given by Ulpiani and Lelli (*Abstr.*, 1902, ii, 573) to a compound in the brain in which they believe the protagon is combined. It is resolved by alcohol into protagon and paranuclein. They further adhere to the idea that protagon is a definite chemical individual. The material is extracted from the brain with chloroform. On the lines of Gies' previous work, the present paper again deals with the non-existence of protagon as a chemical unit, and similarly it is shown that paranucleo-protagon is a mixture also; it contains other substances as well as the two mentioned by Ulpiani and Lelli, and the products differ with the strength and temperature of the alcohol used to decompose it. Probably none of the constituents of protagon are combined with a nuclein-like substance. W. D. H.

### Composition of Nucleic Acids of Thymus and Herring-Roe.

II. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 53, 14—18. Compare this vol., i, 168).—In addition to guanine, adenine, cytosine and thymine, episaccharic acid (this vol., i, 739) has been isolated from the nucleic acid of thymus by hydrolysis with concentrated nitric acid. The *quinine* salt,  $2\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2, \text{C}_6\text{H}_{10}\text{O}_8$ , crystallises well.

It is suggested that the remaining residue in the nucleic acid is  $\text{C}_{21}\text{H}_{44}\text{O}_{26}\text{P}_4$  and not  $\text{C}_{21}\text{H}_{44}\text{O}_{26}\text{P}_4$ , and the formula for the acid then becomes  $\text{C}_{43}\text{H}_{57}\text{O}_{30}\text{N}_{15}\text{P}_4$ . The residue,  $\text{C}_{24}\text{H}_{44}\text{O}_{26}\text{P}_4$ , is supposed on hydrolysis to yield a sugar and metaphosphoric acid. J. J. S.

**Inosic Acid.** CARL NEUBERG and B. BRAHN (*Biochem. Zeitsch.*, 1907, 5, 438—450).—Inosic acid is the only nucleic acid which can at present be obtained pure (as a crystalline salt). Hauser (*Abstr.*, 1895, i, 580) stated that when hydrolysed it is decomposed into phosphoric acid, and probably a purine base and trihydroxyvaleric acid. The second of these products has now been identified as hypoxanthine, and the third as *l*-xylose. Hydrolysis takes place according to the equation:  $\text{C}_{10}\text{H}_{13}\text{O}_8\text{N}_4\text{P} + 2\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + \text{C}_5\text{H}_{10}\text{O}_5 + \text{C}_5\text{H}_4\text{N}_4\text{O}$ . Inosic acid is optically active,  $[\alpha]_D -18.5^\circ$ , a fact which has hitherto been overlooked. The following constitution is suggested:



**The Constitution of Inosic Acid and the Pentose of Muscle.** FRIEDRICH BAUER (*Beitr. chem. Physiol. Path.*, 1907, 10, 345—357).—The author has arrived independently and almost simultaneously at the same general conclusion as Neuberg and Brahn (preceding abstract), namely, that inosic acid is composed of a molecule of phosphoric acid and a molecule of hypoxanthine, which are united by an intermediate pentose molecule in such a way that the latter has lost its free aldehyde group. There is still some disagreement, or doubt, as to the nature of this pentose. The author, who did not observe the optical activity of inosic acid, obtained from it on hydrolysis an osazone, m. p. 158—159°, which he regards as derived from *i*-arabinose, whereas Neuberg and Brahn identify the sugar with *l*-xylose. The dextrorotation, which this latter substance might be expected to produce in the solution after hydrolysis, has, however, not been observed in either investigation.

A full account of the literature and details of a method of preparing crystalline barium inosate is given (yield 3 to 4 grams per kilo. of meat extract used). In meat extract, the sugar of inosic acid occurs in the free state, probably owing to partial hydrolysis during manufacture. G. B.

**Tanning and Adsorption Compounds of Gelatin.** LÜPPO-CRAMER (*Chem. Zentr.*, 1907, ii, 413—415; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 1, 353—364. Compare Biltz, *Abstr.*, 1904, ii, 324; A. and L. Lumière and Seyewetz, *Abstr.*, 1906, i, 916).—All metallic salts the solutions of which contain a colloidal hydroxide are capable of tanning gelatin. Dilute, but not strong, solutions of ferric salts produce coagulation when added to a solution of gelatin. No coagulation occurs if a ferric salt is added to an ammoniacal solution of gelatin. Ferrous salts, potassium ferrocyanide, and ferricyanide have no tanning action, whereas uranyl salts, auric chloride, and cerium sulphate tan readily. Copper salts and silver nitrate are adsorbed without coagulation. It is impossible to free gelatin treated with a solution of silver bromide in sodium thiosulphate from silver completely by washing; similarly, gelatin treated with mercuric chloride, mercuric iodide, lead iodide, lead nitrate, and barium chloride cannot be freed from these salts by washing.

Gum arabic and albumin behave like gelatin.

W. H. G.

**Alkaline Digestion.** HANS EULER (*Arkiv. Kem. Min. Geol.*, 1907, 2, No. 39, 1—13. Compare this vol., i, 574).—Experiments on the action of pancreatin extract on glycylglycine in presence of small proportions of sodium hydroxide show that the pancreatin combines with a considerable part of the alkali, and, as the effect of the latter on the action is great, extracts of commercial pancreatin and trypsin, unless extremely active, are unsuitable for physico-chemical investigations on dipeptides. The results also show that Schütz-Borissow's rule does not hold for the alkaline digestion of dipeptides.

The pancreatin employed yielded 5.4% of ash, consisting principally of sodium pyrophosphate, probably derived from disodium hydrogen phosphate by heating. The velocity of digestion of glycylglycine by

pancreatin in presence of sodium hydroxide is not, however, influenced by the addition of sufficient disodium hydrogen phosphate to double the phosphoric acid present originally. Also, this velocity is not changed by more than 10% of its value by the addition of 0.1 gram of mercuric chloride, 0.12 gram of formaldehyde, or 0.1 gram of potassium cyanide per 100 c.c. of liquid.

The course of the decomposition of glycylglycine by the pressed juice of soaked peas in presence of sodium hydroxide indicates that the excess of the latter is, in this case, far more completely neutralised than by erepsin.

The following results were obtained by the action of 4 grams of very active erepsin on 100 c.c. of 0.1*N*-glycylglycine solution in presence of varying proportions of alkali :

Concentration of alkali .....	0.035	0.04	0.05	0.06	0.075
Reaction constant, $K \times 1000$ ...	5.0	7.0	8.3	8.0	6.5

From these results, the conclusion is drawn that alkaline digestive enzymes are not rendered active by the alkali, which accelerates their action partly by neutralising the substrate and partly by preventing the retarding effect of free decomposition products.

The hydrolysis of casein by erepsin is similar to that of glycylglycine. In the former case, however, the destruction of the enzyme is unimportant in comparison with the retardation caused by the decomposition products, whilst with glycylglycine the opposite holds. The reaction coefficient in the case of casein diminishes rapidly as the action proceeds, but the initial velocities are very nearly proportional to the concentrations of the enzyme. Such enzyme solutions, hence, cannot be regarded as heterogeneous systems.

It was further found that the conductivity of faintly alkaline casein solutions gradually diminishes, even in absence of enzyme.

The intensity of the action of erepsin varies for different dipeptides, the values of  $1000K$  being 58.4 for alanylglycine, 13.1 for leucylglycine, and 7.0 for glycylglycine.

The decomposition of glycine anhydride by alkali was studied by measuring the conductivity, which was found to diminish considerably as the reaction proceeded, the alkali causing the opening of the ring and the formation of the sodium derivative of glycylglycine. By dilute hydrochloric acid, glycine anhydride is far more slowly decomposed, and here too the velocity rapidly diminishes owing to the combination of the acid with the decomposition products.

Experiments with germinating peas show that, during the ten days from the beginning of germination to the stage at which the lateral roots are developed, the quantity of enzyme capable of decomposing glycylglycine remains practically constant. The enzyme probably exists in the resting seed, either as active enzyme or as proenzyme. This is not the case with the other enzymes of germinating seeds, for instance, with those causing proteolysis.

T. H. P.

**Action of Arginase on Creatine and other Guanidine Derivatives.** HENRY D. DAKIN (*J. Biol. Chem.*, 1907, 3, 435—441).—Arginase is a specific enzyme for the exclusive hydrolysis of

*d*-arginine or of substances containing the *d*-arginine grouping. Creatine and other guanidine derivatives structurally similar to arginine are incapable of hydrolysis by this enzyme. W. D. H.

**Specific Accelerating Action of Sodium Fluoride on the Coagulation of Milk by Vegetable Rennet.** C. GERBER (*Compt. rend.*, 1907, 145, 689—692).—The rate of coagulation of milk by vegetable rennet is first slightly accelerated, then retarded by the addition of increasing quantities of sodium fluoride; when the salt is present in the proportion of 30—60 mg. molecules per litre of milk, there is no coagulation, but the process begins again as the proportion of the salt is increased, the rate of coagulation being first accelerated, then retarded. The irregularity of these results is attributed to the disturbing influence introduced by the precipitation of the calcium salts present by the sodium fluoride. If a small quantity of sodium chloride is added to the mixtures, the results are comparable with those previously obtained, and show that the specific action of sodium fluoride is similar to that of sodium chloride. M. A. W.

**Systematic Investigation of Oxydases in Animal Tissues.** OCTAVE DONY-HÉNAULT and Mlle. J. VAN DUUREN (*Bull. Acad. roy. Belg.*, 1907, 537—638).—In the first part of this memoir, a résumé of current theories explaining catalytic oxidation is given, and the analogies between such actions and those due to oxydases in living tissues are detailed. Attention is then directed to the tests which have been applied by various investigators in ascertaining the occurrence of oxidising ferments in animal organs. Schmiedeberg's test, which consists in estimating the amount of salicylaldehyde converted into salicylic acid by an extract of the organ under investigation, has been fully examined, and it is found that it is liable to three sources of error. In removing the excess of salicylaldehyde as a preliminary to the estimation of the amount of acid formed, a saturated solution of sodium hydrogen sulphite is used, and it is found that this in presence of salicylic acid and ether leads to the formation of some sulphuric acid and organic acids, the latter being apparently produced from the ether. The alkalimetric estimation of the salicylic acid formed gives therefore results which are usually too high. Colorimetric estimation of the salicylic acid by means of ferric chloride only gives trustworthy results when the amount of acid is small and there are no other free acids present. Elion's method (*Abstr.*, 1889, 195), which depends on the conversion of the salicylic acid into tribromophenol, gives good results in the case of pure mixtures of the aldehyde and acid, but it appears to be impossible to extract the whole of the acid by means of ether from albuminous solutions, such as aqueous extracts of organs, so that even using this method the results obtained are low, but a modified form of this method, described in detail in the original, was eventually adopted as the best available.

In the experiments, an extract of calves' livers in salt (0.9%), or sodium fluoride (0.65%) solution, was used. It was found that the oxidation of salicylaldehyde to salicylic acid by such extracts takes

place best in the absence of oxygen, and that the velocity of the reaction varies greatly and irregularly when the concentration of the extract varies and is conditioned mainly by the concentration of the aldehyde. The oxidising power of the extracts diminishes spontaneously on keeping, and this diminution in activity usually occurs more rapidly in presence of air, or when the temperature is raised. Some extracts remain active after being heated to 80°, whilst others show a marked lessening of activity after exposure to this temperature. These observations are insufficient to enable a decision to be arrived at as to whether the oxidation is due to an oxydase or is merely catalytic, but the authors are inclined to adopt the latter alternative.

The last portion of the memoir is devoted to a criticism of the views of Abelous and his collaborators (Abstr., 1896, ii, 119; 1898, ii, 36; 1900, i, 268, ii, 226; 1903, ii, 560, 561, 678; 1904, ii, 188) on the subject, and in this connexion it is pointed out that all the extracts used in the present set of experiments contained a small amount of oxyhæmoglobin, which rapidly disappeared when the extracts were exposed to air, but persisted for some time in its absence, which would probably not have been the case if an oxydase had also been present in the solution. Salicylaldehyde is not oxidised by oxyhæmoglobin, so that the latter cannot be the source of the oxygen used in the oxidation of the aldehyde by organic extracts. It is suggested that as oxyhæmoglobin can exist in dilute solution in a vacuum for some days, the current view that the mechanism of oxygen exchange brought about by hæmoglobin is mainly physical is not strictly accurate.

T. A. H.

**Animal Peroxydases.** ERNST VON CZYHLARZ and OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1907, 10, 358—389).—An attempt to extend to animal oxydases the sharp distinction drawn by Chodat and Bach between (vegetable) direct oxydases and peroxydases, which latter only oxidise in the presence of hydrogen peroxide or of some other peroxide. The guaiacum reaction of blood is due to hæmatin and not to a true peroxydase. The difficulty of completely removing blood from the tissues makes guaiacum tincture an unsuitable reagent for the detection of peroxydases. For tissues containing blood, the liberation in the presence of hydrogen peroxide of iodine from an acidified solution of potassium iodide should be employed.

A spectro-photometric method, based on the oxidation to malachite-green of the leuco-base, has been worked out and employed in the measurement of the velocity of peroxydase action. A graphical representation of the results obtained by this method shows that the oxidation by hæmatin proceeds at a uniform rate, whereas the velocity of that due to animal peroxydase gradually falls off to zero. The peroxide reaction is much more dependent on the concentration of the leuco-base than is the hæmatin reaction.

The oxidation of ammonium sulphide by oxyhæmoglobin is not accelerated by catalase, and there is no ground for the belief that the latter enzyme has a direct oxidative action, as supposed by Ewald (this vol., ii, 184).

G. B.

**Catalase. Antagonism between Catalases and Peroxydases.** AMEDEO HERLITZKA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 473—479).—According to Ewald (this vol., ii, 184), the dissociation of oxyhæmoglobin is a phenomenon connected with the partial pressure of the oxygen of which the relation existing between oxyhæmoglobin and hæmoglobin is a function. This being so, catalase is capable of increasing the velocities of two chemical reactions of different natures, one being independent and the other dependent on the partial pressure of the oxygen, and the one irreversible and the other reversible (compare Herlitzka, this vol., i, 102). Objections are raised to Ewald's results. Further experiments by the author lead to the conclusion that there exists an antagonism between the action of catalase and that of hæmoglobin, or, in general, of the oxydases with respect to the oxidation of guaiacum resin by peroxides, that is, with respect to the formation of active oxygen. Within certain limits, the greater the concentration of the catalase, so much the greater must be the concentration of the peroxydases to produce oxidation. Thus there is direct proof of the protective action exerted by catalase towards the peroxydases destroying and rendering innocuous the peroxides in the organism. T. H. P.

**Thiophenol-5-chlorophosphines and their Derivatives.** AUGUST MICHAELIS and G. LINUS LINKE (*Ber.*, 1907, 40, 3419—3425. Compare Michaelis, *Abstr.*, 1903, i, 379; Autenrieth and Hildebrand, *ibid.*, 1898, i, 419, 476).—*Thiophenylchlorophosphine*,  $\text{SPh}\cdot\text{PCl}_2$ , obtained by heating thiophenol and phosphorus trichloride in a flask fused to a reflux condenser, forms a somewhat thick, colourless liquid, b. p.  $125^\circ/10$  mm.,  $D^{15}_4$  1.2560. It fumes in contact with the air and has a disagreeable odour. When left exposed to the air for twenty-four hours, hydrogen chloride is evolved and a crystalline mass consisting of triphenyl trithiophosphite,  $\text{P}(\text{SPh})_3$ , and phosphorous acid is obtained; but when the chlorophosphine is poured into water, a violent reaction occurs, and the products are hydrochloric and phosphorous acids and thiophenol. A thiophosphorous acid has not been obtained. With alcohol, the products are hydrogen chloride, thiophenol, and triethyl phosphite, and with sodium ethoxide, triethyl trithiophosphite, triethyl phosphite, and sodium chloride. The thiophenylchlorophosphine reacts with chlorine yielding phenyl disulphide and phosphorus trichloride. Thiophenol and phosphoryl chloride yield phosphorus trichloride, phenyl disulphide, and phosphoric acid.

*Thiophenylthionchlorophosphine*,  $\text{SPh}\cdot\text{PSCl}_2$ , obtained by heating the thiophenylchlorophosphine with sulphur at  $120^\circ$  for five hours and distilling the product under reduced pressure, forms a thick, colourless liquid with an aromatic odour, b. p.  $168$ — $170^\circ/16$  mm., and is not appreciably acted on by water.

A quantitative yield of *triphenyl trithiophosphite*,  $\text{P}(\text{SPh})_3$ , is obtained when phosphorus trichloride is heated with three equivalents of thiophenol at  $150^\circ$  in an oil-bath. It crystallises from ether in short, monoclinic prisms or from alcohol in pointed crystals, m. p.  $76$ — $77^\circ$ . With concentrated sulphuric acid, it yields thiophenol and phosphorous acid, and the same products are formed when the trithio-



phenyl derivative is heated with water or alcohol under pressure. Triphenyl trithiophosphite readily combines with oxygen, sulphur, or selenium, but is decomposed by chlorine yielding phenyl disulphide and phosphorus trichloride.

*Trithiolphenylphosphine oxide*,  $\text{O}:\text{P}(\text{SPh})_3$ , obtained by the action of hydrogen peroxide on the phosphine, crystallises from ether in strongly refracting, monoclinic prisms, m. p.  $115^\circ$ . It may also be prepared by the action of phosphorus oxychloride on sodium thiophenol, but the product described by Schwarze (*J. pr. Chem.*, 1874, [ii], 10, 234) was probably phenyl disulphide.

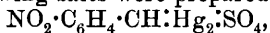
*Trithiolphenylphosphine sulphide*,  $\text{S}:\text{P}(\text{SPh})_3$ , crystallises from alcohol in plates, m. p.  $86^\circ$ . It is obtained by the direct addition of sulphur in carbon disulphide solution at  $120^\circ$ , or by the action of phosphorus sulphochloride on sodium thiophenol.

*Trithiolphenylphosphine selenide*,  $\text{Se}:\text{P}(\text{SPh})_3$ , crystallises from ether in pale yellow, monoclinic plates, m. p.  $95^\circ$ . Secondary chlorophosphines have not been prepared. J. J. S.

**Mercury Compounds from Nitrotoluenes.** ARNOLD REISSERT (*Ber.*, 1907, 40, 4209—4226. Compare this vol., i, 908).—Although aromatic amines and phenols readily admit of the entry of mercury atoms into their molecules, nitrobenzene has but slight tendency to react in this way. The author finds, however, that *o*- and *p*-nitrotoluenes are readily converted into mercury derivatives when boiled with mercuric oxide in presence of sodium hydroxide, the mercury in these cases entering the side-chain. The compounds yielded by *p*-nitrotoluene and 2 : 4-dinitrotoluene have not been obtained in a pure state, but from *o*-nitrotoluene two well-characterised chemical individuals have been prepared.

*o*-Nitromercuribenzyl chloride,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{HgCl}$ , obtained by boiling dilute sodium hydroxide solution containing *o*-nitrotoluene in suspension with precipitated mercuric oxide, is precipitated from ammoniacal solution by hydrochloric acid in bundles of colourless needles, m. p.  $145$ — $146^\circ$ .

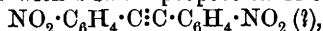
*o*-Nitrodimercuribenzylidene oxide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{Hg} \\ \text{Hg} \end{smallmatrix} \text{O}$ , obtained by protracted boiling of sodium hydroxide solution, *o*-nitrotoluene, and mercuric oxide, is precipitated from acetic acid solution by excess of sodium hydroxide in dark yellow, crystalline masses decomposing at above  $220^\circ$ . The following salts were prepared: the *sulphate*,



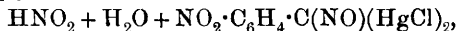
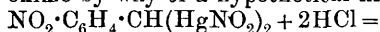
crystallising in pale yellow, broad needles or plates; *basic sulphate*,  $[\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{Hg} \cdot \text{OH})\text{Hg}]_2 \text{SO}_4$ , forming a heavy, orange-yellow powder; *chloride*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{HgCl})_2$ , a pale yellow, amorphous compound; *hydroxychloride*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{HgCl}) \cdot \text{Hg} \cdot \text{OH}$ ; *nitrate*, and *nitrite*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{Hg} \cdot \text{NO}_2)_2$ .

*o*-Nitrodimercuribenzylidene oxide is partially decomposed by hydrogen sulphide into mercuric sulphide and *o*-nitrotoluene. By zinc dust and sulphuric acid, it is reduced to *o*-toluidine and mercury. When heated with nitrous acid, it gives *o*-nitrobenzaldehyde, which is

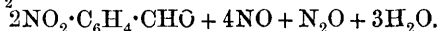
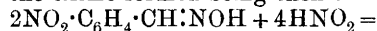
also formed together with a small proportion of *o*-dinitrotolane,



by boiling it with nitric acid. When treated in the cold with nitrous and hydrochloric acids, it is converted into approximately molecular proportions of *o*-nitrobenzaldehyde and its oxime; the dinitrite formed by the nitrous acid is converted by hydrochloric acid into the oxime by way of a hypothetical nitroso-derivative:



and the latter:  $+ 2\text{HCl} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \text{ : } \text{NOH} + 2\text{HgCl}_2$ , one half of the oxime formed being then transformed into the aldehyde as follows:



Towards acids and alkalis, *o*-nitrodimercuribenzylidene oxide is, in general, very stable, but, when boiled with 20% hydrochloric acid solution, it is transformed into anthranil,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{O}$ .

The action of chlorine, best in presence of excess of hydrochloric acid, on *o*-nitrodimercuribenzylidene oxide yields *o*-nitrobenzylidene chloride,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHCl}_2$ , which, in a slightly impure condition, is a faintly red oil, b. p. 150—151°/10 mm. Similarly, the action of bromine yields the corresponding bromide and that of iodine, *o*-nitrobenzylidene iodide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHI}_2$ , which crystallises from alcohol in yellow prisms, m. p. 70—72°.

The interaction of *p*-nitrotoluene and precipitated mercuric oxide in presence of sodium hydroxide yields *p*-nitrodimercuribenzylidene oxide, which was not obtained pure and which is converted into *p*-nitrobenzoic acid by the action of dilute nitric acid.

Similarly, 2:4-dinitrotoluene is converted almost quantitatively into 2:4-dinitrodimercuribenzylidene oxide, which is converted into mercuric sulphide and 2:4-dinitrotoluene by hydrogen sulphide, into 2:4-dinitrotoluene by 10% hydrochloric acid, and into 2:4-dinitrobenzoic acid by concentrated nitric acid.

T. H. P.

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# ERRATA.

## COLLECTIVE INDEX, 1893—1902.

Page Line  
1651 6 col. i for "iminodithio-" read "iminothio-."

## VOL. LXXXIV (ABSTR., 1903).

### PART I.

841 13\* for " $\text{CO}_2\text{Et}$ " read " $\text{CO}_2\text{H}$ ."

### PART II.—INDEX.

1019 15 col. ii for "A., ii, 224" read "A., i, 224."

## VOL. LXXXVI (ABSTR., 1904).

### PART I.

373 22 for "parasaccharic" read "parasaccharinic."  
23 "saccharic" read "saccharinic."  
25 "metasaccharate" read "metasaccharinate."  
21\* "parasaccharate" read "parasaccharinate."  
19\* "saccharate" read "saccharinate."  
19\* "isosaccharate" read "isosaccharinate."

## VOL. LXXXVIII (ABSTR., 1905).

### PART I.

508 23 for "1904, ii, 42" read "1904, i, 480."  
508 17\* "the" read "methyl."  
508 17\* "ethyl" read " $\alpha$ -dimethyl  $\beta\beta$ -diethyl."  
508 16\* " $\text{C}(\text{CO}_2\text{Et})_2[\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}]_2$ " read " $\text{C}(\text{CO}_2\text{Et})_2[\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me}]_2$ ."

## VOL. XC (ABSTR., 1906).

### PART I.

145 3 for "1905" read "1906."  
663 3\* "88°" read "70—71°."  
964 2 "acetophenone" read "phorone."

### PART II.

89 18 for "hydrogen" read "water vapour."

### INDEX.

946 26 col. i for "A., ii, 974" read "A., i, 974."

## VOL. XCII (ABSTR., 1907).

### PART I.

8 18 for "ARBASOFF" read "ARBUSOFF."  
9 19\* "ricin" read "castor oil."  
9 21\*  
10 7 } "cocoa butter" read "cocoa nut oil."  
10 8 }  
10 22 }  
11 10\* "BARTELL" read "BARTELT."  
105 16\* "benzoylconine" read "benzoylconiine."  
105 11\* "conine" read "coniine."

# ERRATA (continued).

Page	Line	
113	5	for "1881, 39" read "1906, 89."
131	17	„ "ethyl ethyl- <i>i</i> -aspartate" read "ethyl <i>i</i> -aspartate."
166	1*	„ "p-hydroxyphenylazo, &c." read "p-hydroxybenzeneazo, &c."
182	11*	„ "C <sub>9</sub> H <sub>10</sub> ·CMe·CHO" read "C <sub>9</sub> H <sub>10</sub> ·CHMe·CHO."
224	23	„ "Acyl Derivatives" read "Aryl Derivatives."
232	21	„ "MEEGEN" read "MEIGEN."
234	4	„ "NHPh·CS·S·CH <sub>2</sub> ·CO <sub>2</sub> Et" read "C <sub>10</sub> H <sub>7</sub> ·NH·CS·S·CH <sub>2</sub> ·CO <sub>2</sub> Et."
242	10	„ C <sub>6</sub> H <sub>5</sub> Me $\begin{matrix} \diagup \\ \text{C(OEt):CPh} \\ \diagdown \end{matrix}$ read C <sub>6</sub> H <sub>5</sub> Me $\begin{matrix} \diagup \\ \text{C(OH):CPh} \\ \diagdown \end{matrix}$
248	13*	after "5-Chloro-3-phenyl-1-methylpyrazole" insert "methochloride."
248	12*	for NMe $\begin{matrix} \diagup \\ \text{CCl=CH} \\ \diagdown \end{matrix}$ read NMe $\begin{matrix} \diagup \\ \text{CCl=CH} \\ \diagdown \end{matrix}$
258	20	„ "Sale" read "Salts."
259	11	„ "sodium" read "silver."
262	7	„ "1:2:4:5-tetrazine-3:6-carboxylic acid" read
262	12	„ "1:2:4:5-tetrazine-3:6-dicarboxylic acid."
326	16	„ "WILHELM" read "WALTHER."
429	17	„ "C <sub>10</sub> H <sub>7</sub> O·CO·" read "C <sub>10</sub> H <sub>17</sub> O·CO·"
429	23	„ "C <sub>10</sub> H <sub>7</sub> O·CO·" read "C <sub>10</sub> H <sub>17</sub> O·CO·"
509	5	after "forms" insert "the corresponding amide. The urethane prepared from this has b.p. 123°/12 mm., m.p. 60—61°, and on distillation with lime furnishes"
509	6 and 7	delete "the urethane has b.p. 123°/12 mm., m.p. 60—61°."
606	15*	for "2:2':5:5'-Tetramethoxybenzylideneazine" read
619	13	„ "1-Methylcyclohexyl-4-acetamide" read
726	17*	„ "O $\begin{matrix} \diagup \\ \text{C}_6\text{H}_5(\text{NEt}_2) \\ \diagdown \end{matrix}$ C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> Et" read
729	19	„ "butylene" read "buzylene"
952	11	„ "6-hydroxy-4-isopropylflavone" read
952	10*, 7*, 6*	„ "6-methoxy-4-isopropylflavanone."
953	3, 8, 11, 24	for "flavanol" read "flavonol."
952	12	„ "cumenol" read "cuminaldehyde."
952	25	„ "cumenol" read "cuminaldehyde."
952	1*	„ "cumenol" read "cuminaldehyde."
953	16	„ "Dioxycodeine" read "Deoxycodeine."
957	23*	„ "4-Bromo-3-methyl-1-ethyltriazole" read
1088	11*	„ "4-Bromo-3-methyl-1-ethylsotriazole."

## PART II.

72	3*	for "euricic" read "erucic."
108	5*	„ "lactase" read "lactose."
117	14	„ "DZIERGOWSKY" read "DZIERGOWSKY."
144	17*	„ "Tabloid"† read "Pellet."
144	15*	„ "tabloids"† read "compressed pellets."
144	1*	„ "tabloids"† read "compressed pellets."
268	19	„ "Molybdenum" read "Tungsten."

\* From bottom.

† "Tabloid" being a registered trade-mark may not be used.

# ERRATA (*continued*).

Page	Line	
268	4*	for " $\text{WO}_2\text{Cl}_2$ " read " $\text{WO}_2\text{F}_2$ ."
292	24	,, " $\text{OMe}\cdot\text{C}_{13}\text{H}_7(\text{OAc})_4\text{NOH}$ " read " $\text{OMe}\cdot\text{C}_{15}\text{H}_7(\text{OAc})_4\text{NOH}$ ."
420	5	<i>et seq.</i> should read: "Lecoq de Boisbaudran has stated (Abstr., 1887, 3) that calcium sulphate phosphoresces green under the action of the cathode rays, and similarly the author finds that the sulphide phosphoresces yellow and the phosphate red under these conditions."
520	20	for "1,254" read "1:254."
970	8*	,, " <b>46</b> " read " <b>44</b> ."
976	23	,, " <b>Filicis maris</b> " read " <b>Aspidium Filix mas</b> ."

## INDEX.

1024	col. i	insert <b>Delluc, G.</b> See <i>Thomas Roman</i> .
1097	col. ii	insert <b>Roman, Thomas</b> , and <i>G. Delluc</i> , presence of traces of zinc in alcohol, and its detection, A., ii, 397.

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\* From below.

# JOURNAL

OF

## THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

### PART II.

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#### General and Physical Chemistry.

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**The Spectra of Hydrogen.** A. DUFOUR (*Ann. Chim. Phys.*, 1906, [viii], 9, 361—432).—As the result of an exhaustive series of experiments, the author finds that the spectrum of chemically pure hydrogen consists of the two well-known spectra, the first composed of the stellar lines  $H\alpha$ ,  $H\beta$ ,  $H\gamma$  . . ., and a second, which contains a greater number of lines, chiefly in the yellow; the second spectrum is not due to the chemical nature of the electrodes or to foreign gases (water vapour, hydrocarbons) which might be occluded on the walls of the Geissler tubes, and the same results were obtained when the glass tubes were replaced by tubes of silica or boric anhydride (Dufour, *J. de phys.*, 1903, [iv], ii, 498). A complete bibliography of the subject is given, and the various theories advanced in explanation of the nature of the second spectrum are discussed. M. A. W.

**Band Spectrum of Nitrogen in a Strong Magnetic Field.** JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1906, 13, 354—355).—Experiments made with a magnetic field strength of 41,000 units confirm the earlier observation of Becquerel and Deslandres (*Compt. rend.*, 1898, 127, 20), who, working with a weaker field, could not detect any appreciable division or widening of the bands. The vibrations which



produce the nitrogen bands seem therefore to be essentially different from those produced in the spark spectra of elements the lines of which, in a similar magnetic field, are both widened and divided. J. C. P.

**Manner of Formation and Spectrum of Metallic Vapour in the Electric Spark.** BERNHARD WALTER (*Ann. Physik*, 1906, [iv], 21, 223—238).—In reference to the difference between the lines in the spark spectrum of a metal and those in the arc spectrum, the author's experiments make it probable that the light in the case of spark lines is emitted by glowing metallic particles which are still electrically charged, whilst the light of the arc lines proceeds from glowing particles which have already lost their charge. In connexion with this, it is shown that where the metal is subject to cathodic disintegration the metallic particles carry with them a negative charge, which is lost only gradually. J. C. P.

**Supposed Displacement of Lines in the Spark Spectrum.** CHRISTIAN KELLER (*Chem. Centr.*, 1906, ii, 1231—1232; from *Zeit. wiss. Phot., Photophys., Photochem.*, 4, 209—231).—A comparison of the spark and arc spectra of titanium, iron, zinc, lead, tin, aluminium, and cadmium shows that whereas the lines of the arc spectra are displaced by pressure, the lines of the spark spectra under similar conditions do not undergo displacement. P. H.

**Influence of a very strong Magnetic Field on the Spark Spectra of Palladium, Rhodium, and Ruthenium.** JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1906, 13, 325—353. Compare *Proc.*, 1905, 241; *Abstr.*, 1905, ii, 421).—The observations of the spectra of palladium, rhodium, and ruthenium are recorded in full, and the following are some of the more important results. If the lines of each separate metal are compared with one another, it is found that some of them can be grouped together as having the same general appearance of the constituents, the same polarisation, and essentially identical values of  $d\lambda/\lambda^2$ ; this agreement is well seen among the lines which become triplets. If the lines of the three metals are compared with one another, some are found to have the same appearance, the same intensity, the same polarisation, and the same value of  $d\lambda/\lambda^2$ . The displacements of the constituents of some of the divided lines are simple multiples of one another. In some cases, the value of  $d\lambda/\lambda^2$  for the constituents of some lines is a multiple of the value for the constituents of other lines. J. C. P.

**Absorption of Light in Solutions.** ERNST MÜLLER (*Ann. Physik*, 1906, [iv], 21, 515—534).—The author has determined the absorptive power over a considerable part of the spectrum of copper sulphate, nickel sulphate, potassium chromate, and cupric chloride solutions. It is not possible to explain the colour changes which accompany dilution on the basis of dissociation alone; other factors which must be taken into account are the formation and decomposition of hydrates and complex molecules or ions. The colour of a dilute solution cannot be made by rise of temperature to correspond exactly with the colour of a cold concentrated solution. J. C. P.

**Colour and Chemical Constitution.** HUGO KAUFMANN (*Zeit. Farb. Ind.*, 1906, 5, 417—421).—A summary of recent views on the connexion between colour and constitution. W. A. D.

**The Elements which Produce Phosphorescence in Minerals. Case of Chlorophane a Variety of Fluorspar.** GEORGES URBAIN (*Compt. rend.*, 1906, 143, 825—827. Compare *Abstr.*, 1906, ii, 28, 138, 359, 510, 674).—The phosphorescent spectrum of chlorophane has already been described by Becquerel (*Abstr.*, 1891, 776), and the author finds that when the oxide obtained from the fluorspar is diluted with lime, the cathode spectrum of the mixture shows the absorption bands of samarium, terbium, dysprosium, and gadolinium; and further, when the phosphorescent fluorides prepared synthetically from pure lime and the pure oxides of the above rare metals are examined in the cathode tube, the phosphorescent bands coincide with those given by the chlorophane itself in the same circumstances.

M. A. W.

**Ionisation of Gases Exposed Simultaneously to Röntgen Rays and the Radiation from Radioactive Substances.** T. NODA (*Proc. Camb. Phil. Soc.*, 1906, 13, 356—362).—The author finds that X-rays and all Becquerel rays have the same ionising power whether they act separately or simultaneously. J. C. P.

**Radioactivity of Volcanic Products of the Last Eruption of Vesuvius (April, 1906) Compared with that of Older Materials.** RAFFAELLO NASINI and MARIO GIACOMO LEVI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 391—397).—Volcanic ashes and stones, deposited during the Vesuvian eruption of April, 1906, exhibit appreciable radioactivity, whilst in the case of the lava such activity is either absent or of slight intensity. Samples of lava of remote eruptions show marked radioactivity, and the latter seems to increase with the age of the lava, that is, with the time elapsed since it occurred in the liquid state, and, doubtless, with its chemical nature also.

T. H. P.

**Energy of Radiation from Radium.** JULIUS PRECHT (*Ann. Physik*, 1906, [iv], 21, 595—601).—With the ice calorimeter the author finds that 1 gram of anhydrous radium bromide gives off 71.44 heat units per hour. This amount is increased by about 10% when the radium salt is enclosed in a lead capsule 3 mm. thick. Further increase in the thickness of the lead capsule does not lead to any increase in the amount of heat evolved. J. C. P.

**Disintegration Products of Radium in the Atmosphere.** HEINRICH MACHE and TRAVIS RIMMER (*Chem. Centr.*, 1906, ii, 1237—1238; from *Physikal. Zeit.*, 7, 617—620).—By comparing the degree of ionisation of the air with the ionising power of the disintegration products of radium, the authors have tried to determine whether these products are actually responsible for the ionisation of the air. Observations, extending over a fortnight, showed that the

amount of emanation contained in the air varies inversely as the barometric pressure, whereas the ionic charge exhibited no regularity. The radioactivity of the ground is increased after rain, owing probably to the accumulation of radium *B* and *C* as shown by the observed rapid decrease in activity. P. H.

**Decomposition of Radium *A*, *B*, and *C*.** HEINRICH W. SCHMIDT (*Ann. Physik*, 1906, [iv], 21, 609—664).—In a vessel containing emanation from radium the deposit on an uncharged metal consists of radium *A* only. Radium *B* and radium *C* are produced successively from radium *A*. The paper records the results of a detailed study of the radiation, the ionising power, and the separation of radium *A*, radium *B*, and radium *C*. J. C. P.

**Radiation of Radio-tellurium. II.** B. KUČERA and B. MAŠEK (*Chem. Centr.*, 1906, ii, 1232—1233; from *Physikal. Zeit.*, 7, 630—640).—The authors have measured the absorption by various metallic plates and by gases of the radiation emitted by radio-tellurium, and have, in the main, confirmed Bragg's results. They criticise both Mme. Curie's and Rutherford's methods of measuring absorption. P. H.

**Diffusion of Thorium *X*.** G. HOFFMANN (*Ann. Physik*, 1906, [iv], 21, 239—269).—So far as diffusion in water is concerned, thorium *X* behaves as a definite substance. The value of the diffusion coefficient at 10° is  $0.504 \pm 0.015$ . The measurements furnish a verification of Fick's law for very low concentrations. J. C. P.

**Absorption Coefficients of Uranium Compounds.** HENRY M. GOETTSCH (*J. Amer. Chem. Soc.*, 1906, 28, 1541—1555).—It has been stated by Mme. Curie that the radioactivity of uranium compounds is an atomic and not a molecular property. McCoy (*Abstr.*, 1905, ii, 366) has shown that if the absorption of the  $\alpha$ -ray activity by the active compound itself is taken into account, the radioactivity is strictly proportional to the percentage of uranium and is therefore an atomic property.

This work has now been extended to the determination of the absorption coefficients of urano-uranic oxide, uranic acid, uranyl iodate, uranyl thiosulphate, sodium uranate, and uranyl ammonium phosphate. The results are tabulated and confirm those obtained by McCoy (*loc. cit.*), showing that the value  $k_1/P$  is a constant where  $k_1$  is the total activity of unit weight of any one compound, and  $P$  the weight of uranium in 1 gram of the compound. The mean value obtained for this constant is 19.84. It is proved that the absorption is dependent neither on the sample of the compound employed nor on the form of the measuring instrument.

By means of the constant  $k_1$ , the value can be deduced of  $k_2$ , the absorption coefficient for unit weight of any one compound on unit area, and the values for a large number of compounds have thus been calculated.

The absorption is not proportional to the molecular weight, and is probably, like radioactivity, an atomic phenomenon.

E. G.

**Absorption of the  $\alpha$ -Rays of Uranium.** HERBERT N. MCCOY and HENRY M. GOETTSCH (*J. Amer. Chem. Soc.*, 1906, 28, 1555—1560).—From the data obtained by McCoy (Abstr., 1905, ii, 366) and Goettsch (preceding abstract), it is shown that the total activity of 1 gram of uranium is independent of the form in which it is combined, and is equal to 790 times the activity due to 1 sq. cm. of a film of the pure oxide,  $U_3O_8$ , sufficiently thick to be of maximum activity. From this relation, the absorption coefficient  $k_2$  of any uranium compound can be calculated from the activity  $A_1$  of a single thick film of maximum activity by means of the expression  $k_2 = 395P/A_1$ . The values of  $k_2$  have thus been determined of a large number of uranium compounds, and indicate that absorption, like radioactivity, is an atomic property independent of the form of chemical combination. It is also shown that the absorption by unit weight on unit area is for any element inversely proportional to the square root of its atomic weight. An equation has been deduced by means of which the radioactivity of a thick film of any uranium compound may be calculated from its chemical composition.

Marckwald (Abstr., 1906, ii, 143) has observed that certain fluorescent double uranium salts, particularly uranium potassium nitrate, emit light rays which he considers are due to the conversion of a part of the radioactivity into luminous energy. It is now shown that the proportion so converted must be very small.

E. G.

**Polarisation Capacity of Iron and its Bearing on Passivity.** C. MCCHEYNE GORDON and FRIEND E. CLARK (*Zeit. Elektrochem.*, 1906, 12, 769—772; *J. Amer. Chem. Soc.*, 1906, 28, 1534—1541).—In a Wheatstone bridge, using alternating current and a telephone, the polarisation of iron electrodes can usually be balanced by means of a condenser and a resistance in parallel with it.

In dilute nitric acid and (after cathodic polarisation) in ferrous sulphate and chloride solutions iron is non-polarisable.

In concentrated nitric acid, the polarisation of large electrodes can be balanced by the condenser alone.

These results are interpreted as meaning that when the iron is polarisable it is coated with a film of oxide possessing a certain conductivity. The capacity of the film is much the same whether the iron is active or passive, but its conductivity is much smaller when the iron is passive. The behaviour of large iron electrodes in concentrated nitric acid is due to the small conductivity of the film of oxide; the small currents which pass through it do not affect the telephone; with small electrodes the greater density of the current used in the measurements increases the conductivity of the film. This is quite in accordance with the views of Haber and Goldschmidt (Abstr., 1906, ii, 213).

T. E.

**Ionisation produced by Hot Platinum in different Gases.** OWEN W. RICHARDSON (*Phil. Trans.*, 1906, 207, A, 1—64. Compare Abstr., 1905, ii, 233).—The part played by the surrounding gas in the production of ions by hot platinum and in particular the process by which the positive ions originate has been examined. The ionisation in oxygen was chiefly studied, but experiments were also made with air, nitrogen, helium, and hydrogen, an electrically heated platinum wire forming the emission surface.

There is a minimum value for the number of positive ions emitted by one square centimetre of platinum surface per second, which depends on the pressure and temperature in most gases. This minimum value is much larger in an atmosphere of oxygen (at low pressures) than in the other gases examined. In oxygen at low pressures and at temperatures below  $1000^{\circ}$  it varies as the square root of the pressure, and at higher temperatures nearly directly as the pressure, whilst at higher pressures the emission of positive ions varies but little with the pressure at any temperature. In nitrogen and hydrogen, the ionisation increases more rapidly with the pressure at high pressures than in oxygen. When mixed with oxygen, nitrogen appears to exert an inhibiting effect on the emission of positive ions. The minimum value of the positive ionisation at a given pressure varies with the temperature in accordance with the relationship already deduced for the negative ionisation.

The positive ions emitted in oxygen are of the same order of magnitude as those produced by collisions. The experimental results indicate that these ions are produced from the gas adsorbed by the metal.

By allowing hydrogen to diffuse through the walls from the interior of a platinum tube heated in air, it is found that the rate of emission of positive ions is increased, and the increase is proportional to the quantity of hydrogen escaping from the surface in unit time. Under the same circumstances the negative ionisation is unaltered. The different character of the latter is also shown by the fact that the negative leak in oxygen at low pressures is independent of the pressure. Certain hysteretic effects indicate that the increased negative ionisation in hydrogen at low pressures is not caused by the hydrogen directly, but is due to some change which it produces in the surface of the platinum.

H. M. D.

**The Hydrogen-Oxygen Cell. I.** FRITZ HABER and F. FLEISCHMANN (*Zeit. anorg. Chem.*, 1906, 51, 245—288. Compare Nernst and von Wartenberg, Abstr., 1906, ii, 728, 729).—The *E.M.F.*'s of reversible hydrogen-oxygen cells and of hydrogen and oxygen concentration cells have been measured at high temperatures, glass and porcelain being used as electrolytes, and platinum and gold as electrodes, and it is shown that the observed values are in satisfactory agreement with those calculated on the basis of the thermodynamical theory.

The free energy, *A*, of the formation of water from gaseous hydrogen and oxygen, has been calculated, the data for the dissociation of water-vapour given by Nernst and von Wartenberg, and values for the specific heats of the gases obtained by two methods, being employed.

From the two expressions for  $A$ , and from a third analogous expression given by Nernst, the  $E.M.F.$  of the cell has been calculated at temperatures from  $25^{\circ}$  to  $1127^{\circ}$ , by substituting the corresponding values of the absolute temperature and dividing the values for  $A$  thus obtained by 46220. The three expressions give results which differ among themselves by a few millivolts only, the differences being due to uncertainty in the values of the specific heats; at  $25^{\circ}$ ,  $427^{\circ}$ ,  $827^{\circ}$ , and  $1127^{\circ}$  the intermediate values are 1.177, 1.068, 0.953, and 0.865 volts respectively. The three expressions give the same value for the effect of changes of concentration of the individual gases at a definite temperature.

The measurements were carried out as follows. Two hard-glass tubes of the same bore, closed at one end, were platinised in the interior at the closed ends and the latter were then fused together, so that a thin glass plate, platinised on both sides, was formed in the middle of the complete tube. Connexion was made by means of platinum wires ending in platinum brushes in contact with the respective electrodes. The platinum wires were enclosed in capillary porcelain tubes, which were also used for bringing the gases to the electrodes. The whole apparatus was enclosed in an iron tube, which could be heated in a furnace, and the temperatures were measured by means of a thermocouple. The cell with gold electrodes was constructed in a somewhat similar way.

Experiments were made at  $330^{\circ}$ ,  $470^{\circ}$ , and  $570^{\circ}$  with platinum electrodes, and at the last two temperatures with gold electrodes; the  $E.M.F.$ 's between concentrated and diluted hydrogen (nitrogen with a small proportion of hydrogen) and between concentrated and diluted oxygen (nitrogen and oxygen) as well as between hydrogen and oxygen were determined, and the results were throughout in satisfactory agreement with the calculated values. In all cases the gases contained an admixture of water-vapour. At  $330^{\circ}$  the oxygen electrode attained its final condition very slowly. Experiments with the dried gases, measured against the same gases saturated with water-vapour, gave results in qualitative, but not in quantitative, agreement with the theory. Soft glass and Jena glass gave the same results as hard glass.

At higher temperatures, measurements were made with glazed porcelain coated with platinum. The observations were somewhat disturbed by the fact that the platinum coating gradually diffused into the interior of the porcelain. At  $800^{\circ}$ , hydrogen and oxygen concentration cells and at  $1100^{\circ}$  hydrogen concentration cells, gave results in excellent agreement with the theory; at both temperatures the  $E.M.F.$  of the hydrogen-oxygen cell was rather lower than the theoretical value. With this electrolyte also the influence of water-vapour was in qualitative, but not in quantitative, agreement with theory.

G. S.

**Cathodic Evaporation of Metals in Attenuated Gases.**  
VOLKMAR KOHLSCHÜTTER (*Zeit. Elektrochem.*, 1906, 12, 869—873).—In order to obtain further confirmation of his views (*Abstr.*, 1906, ii, 418) the author has made experiments in which the discharge is allowed to fall on a cathode of fine brass gauze; a number of the

gaseous molecules carrying the current pass through the holes in the gauze and strike a small plate of metal supported at some distance behind it. These "canal rays" produce slow evaporation of the metal, proving that this evaporation is not connected with the electrical charge of the cathode. The quantity of evaporation, although much smaller than that previously observed at the cathode, was found like it to be dependent on the nature of both the metal and the gas used.

T. E.

**Electrochemical Equivalent of Silver.** G. VAN DIJK (*Ann. Physik.*, 1906, [iv], 21, 845—847. Compare Abstr., 1905, ii, 137; also Guthe, Abstr., 1906, ii, 520).—The author deals with Guthe's criticism, and records the number  $\alpha = 0.011180$  (C.G.S.) as the true electrochemical equivalent of silver.

J. C. P.

**Chemical Experiments on Flames.** A. STROMAN (*Chem. Centr.*, 1906, ii, 1470; from *Zeit. phys.-chem. Unterr.*, 19, 285—287).—A modification of Heumann's lecture demonstration apparatus for illustrating combustion.

P. H.

**Transition Temperatures and a Method for Observing Them.** KARL BECK and KURT EBBINGHAUS (*Ber.*, 1906, 39, 3870—3877).—When a substance which can exist in several solid modifications is melted in a small glass tube, then allowed to solidify, and gradually allowed to cool, characteristic phenomena are observed. At the higher temperature, the inner surface of the tube appears to be completely coated with crystals, but at the transition point these separate from the glass and a perceptible crackling is heard.

With rhombic sulphur, the solid appears quite separate from the glass for temperatures between  $25^{\circ}$  and  $95^{\circ}$ ; at  $95^{\circ}$  a slight deposit of crystals is formed on the glass, at  $96^{\circ}$  this deposit increases rapidly, and the sulphur does not melt until  $120$ — $121^{\circ}$ . Similar phenomena have been observed with ice; benzophenone,  $28.5^{\circ}$ ; *p*-dibromobenzene,  $8.5^{\circ}$ ; *p*-dichlorobenzene,  $39.5^{\circ}$ ; *p*-toluidine,  $22^{\circ}$ ;  $\alpha$ -naphthol,  $48$ — $49^{\circ}$ ;  $\alpha$ -naphthylamine,  $13.5^{\circ}$ ; phenol, between  $-2^{\circ}$  and  $-6^{\circ}$ ;  $\alpha$ -anisaldoxime,  $21$ — $22^{\circ}$ ;  $\alpha_1$ -anisaldoxime,  $12$ — $13^{\circ}$ ;  $\alpha$ -benzaldoxime,  $-25$  to  $-30^{\circ}$ .

Mixtures of *p*-dibromobenzene with *p*-dichlorobenzene and of  $\alpha$ -naphthol with *p*-toluidine have been investigated. In both cases the curves of transition points correspond to a certain extent with the melting point curves.

J. J. S.

**Behaviour of Certain Substances at their Critical Temperatures.** MORRIS W. TRAVERS and FRANCIS L. USHER (*Proc. Roy. Soc.*, 1906, A, 78, 247—261).—A distinction is sometimes drawn between the temperature at which the surface separating the liquid and vapour phases disappears (known as the temperature of Cagniard-Latour), and that at which the densities in the parts of the tube formerly occupied by the two phases become equal (known as the critical temperature). According to one theory, the former temperature is a function of the relative masses of the coexisting phases, according to another theory the results are markedly influenced by a time factor

The authors' experiments do not in any way confirm these conclusions, and in fact support the opposite view. In a study of the opalescence which may be observed at the critical temperature (compare Altschul, Abstr., 1893, ii, 446, and Wesendonck, Abstr., 1895, ii, 71), observations were made with comparatively large masses of specially purified ethyl ether and sulphur dioxide, enclosed in thin-walled glass tubes of 8—10 mm. internal diameter. Arrangements were made for maintaining a steady temperature which could be raised very slowly towards the critical point.

By using tubes containing different relative quantities of the two phases, it is found that the opalescence is confined to that phase which is decreasing in volume, as shown by the movement of the dividing surface, or, at least, is most intense in that phase. The opalescence appears, in the case of sulphur dioxide, at  $0.1^{\circ}$  below the temperature at which the surface vanishes, attains a maximum at about  $0.05^{\circ}$  above it, and finally disappears at a temperature  $0.1^{\circ}$  higher. In the case of ether, the effects persist over a range of  $2^{\circ}$ . When the surface disappears, there is observed, in the case of sulphur dioxide, evidence of optical discontinuity between the substance in the tube above and below the point at which this takes place. This discontinuity is, however, merely transient in character, and is incapable of existence at a temperature  $0.05^{\circ}$  above that of the disappearance of the surface.

It is suggested that the phenomena of opalescence are due to the presence of small non-molecular aggregates for which the interfacial tension is not zero; these accordingly can be differentiated from either the liquid or the vapour phase (compare Donnan, British Association Reports, 1904).

J. C. P.

**Opalescence in Fluids near the Critical Temperature.** SYDNEY YOUNG (*Proc. Roy. Soc.*, 1906, A, 78, 262—263. Compare Travers and Usher, preceding abstract).—In the author's experiments the substance (*n*-pentane, isopentane, hexane, or octane) was kept at the critical temperature, and the volume was altered by regular stages. It appears that the position of maximum opalescence depends on the mean specific volume of the substance, being near the bottom of the tube when the volume is large, near the top when the volume is small, and near the middle at intermediate volumes. The range of volume over which mist is visible at the critical temperature is nearly the same for the four paraffins examined, namely, about 1.18 to 0.87, taking the critical volume as unity in each case. At a temperature slightly above the critical temperature, the mist is not only much less dense, but the range of volume over which it is visible is more restricted.

J. C. P.

**Heats of Formation of Fluoro-compounds.** FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1906, 557—577).—The heats of combustion of the fluoro-compounds named below have been determined by means of a slightly modified form of Langbein's bomb calorimeter (Abstr., 1901, ii, 128). The three constants given after the name of each compound are the heat of combustion at constant volume, the heat of combustion at constant pressure and the heat of formation, each being given in major calories:  $\omega$ -Trifluorotoluene (Abstr., 1899, i, 197), 809.96,



810·25, 69·75 ;  $\omega$ -trifluoro-*m*-toluic acid (*ibid.*), 807·19, 806·9, 167·2 ; fluoroacetic acid, 171·08, 170·79, 137·11 ; ethyl fluoroacetate, 502·55, 502·84, 131·66 ;  $\beta\beta$ -difluoroethyl alcohol (Abstr., 1903, i, 222), 245·7, 245·7, 111·9 ;  $\beta\beta$ -difluoroethyl acetate (*ibid.*), 455·48, 456·06, 159·8 ; difluoroacetic acid (Abstr., 1903, i, 727), 135·14, 135·43, 152·77 ; ethyl difluoroacetate (*ibid.*), 463·26, 463·84, 152·04. Comparison of the heats of formation thus determined with those of the corresponding hydrogen compounds shows that the difference is greatest in compounds which are free from oxygen and least in those in which the fluorine is substituted in a radicle in close proximity to a carboxyl group. The change in the heat of formation, due to the substitution of a second hydrogen atom by fluorine, differs but little from that due to the substitution of a first atom. The mean difference between the heat of formation of a fluoro-compound and that of the corresponding hydrogen compound is about 20 Cal., so that the heat disengaged by the substitution of a hydrogen atom by fluorine is about 58·5 Cal. T. A. H.

#### Heats of Combustion and of Formation of some Amines.

PAUL LEMOULT (*Compt. rend.*, 1906, 143, 746—749. Compare Abstr., 1904, ii, 382 ; 1905, ii, 441 ; Berthelot, Abstr., 1880, 787 ; Girard and L'Hôte, Abstr., 1889, 562 ; Muller, Abstr., 1885, 716 ; 1886, 409 ; Petit, 1888, 773, 1239).—In the original are tabulated the heats of formation and of combustion of fifteen primary, seven secondary, and five tertiary amines, together with the theoretical values of the latter constant calculated from the formula previously established by the author (Abstr., 1904, ii, 382), and in all cases the calculated are slightly lower than the experimental values, the differences being more marked with the lower members of a homologous series than with the higher terms. M. A. W.

#### Heat of Combustion and of Formation of Nitrogen Cyclic Compounds.

PAUL LEMOULT (*Compt. rend.*, 1906, 143, 772—775. Compare Abstr., 1906, ii, 832).—The author has redetermined the heats of combustion of the following series of aromatic nitrogen compounds : hydrazobenzene, 1603·9 Cal. ; phenylhydrazine, 879·7 Cal. ; diazoaminobenzene, 1602·6 Cal. ; benzidine, 1564·1 Cal. ; azoxybenzene, 1541·7 Cal. ; *o*-azoxyphenetole, 2097·8 Cal. ; *p*-azoxyphenetole, 2108·7 Cal. ; *m*-azoxytoluidine, 1911·2 Cal. ; phenyl- $\alpha$ -naphthylamine, 2019 Cal. ; phenyl- $\beta$ -naphthylamine, 2007·6 Cal. ; *p*-aminophenol, 763·3 Cal., and *p*-acetylaminophenetole (phenacetin), 1303 Cal. From the differences between these values and the corresponding values calculated from the general formula (Abstr., 1904, ii, 382) the thermal values of the groups :  $\text{N}:\text{N}:$ ,  $\text{O} \begin{smallmatrix} \text{N} \cdot \\ \diagup \diagdown \\ \text{N} \cdot \end{smallmatrix}$ , and  $\cdot\text{N}:\text{N} \cdot$  have been deduced, and the amended calculated values agree very closely with the observed values. M. A. W.

#### Carbylamines and Nitriles.

PAUL LEMOULT (*Compt. rend.*, 1906, 143, 902—904).—The heat of combustion of methylcarbylamine is 318·7 Cal. (mean of two determinations) and the heat of for-

mation  $-26.7$  Cal.; the corresponding constants for ethylcarbylamine are  $479.20$  Cal. (mean of five determinations) and  $-23.8$  Cal. respectively; and the differences between the observed heats of combustion of the two homologues and those calculated from the author's formula (Abstr., 1904, ii, 382) are  $15.7$  Cal. and  $19.2$  Cal. respectively. Adopting, therefore,  $17$  Cal. as the thermal equivalent of the carbylamine grouping, the heat of combustion of hydrogen cyanide, calculated on the assumption that it is a carbylamine, is  $153$  Cal., which is identical with the experimental value obtained by Berthelot (Abstr., 1889, 812), whilst the corresponding value calculated on the assumption that it is a nitrile is  $146$  Cal. M. A. W.

**Compressibility of Mixtures of Gases Capable of Combining to form Solid or Liquid Compounds.** Vapour Pressures and Critical Constants of Hydrogen Chloride, Hydrogen Phosphide, and Sulphur Dioxide. E. BRINER (*J. Chim. phys.*, 1906, 4, 476—485).—The compressibility of a mixture of equal volumes of hydrogen phosphide and hydrogen chloride has been compared with that of the two components at a series of temperatures. The compressibility of the mixture is in all cases intermediate between the values for the components. According to theory, the partial pressure of the compound in the gaseous mixture is proportional to the square of the total pressure, and the fact that an increase in the total pressure from 1—50 atmospheres has no measurable influence on the relative value of the compressibility of the mixture as compared with that of the components, leads the author to conclude that the proportion of molecules of the compound  $\text{PH}_4\text{Cl}$  in the mixed gases is negligibly small. Experiments with mixtures of ammonia and carbon dioxide lead to a similar conclusion.

The vapour pressure of phosphonium chloride lies between the vapour pressures of hydrogen chloride and hydrogen phosphide in the interval of temperature investigated ( $30$ — $45^\circ$ ).

The following critical data have been obtained:  $\text{PH}_3$ ,  $p_c = 64.5$  atm.,  $t_c = 51.3^\circ$ ;  $\text{HCl}$ ,  $p_c = 83.6$  atm.,  $t_c = 51.8^\circ$ ;  $\text{PH}_4\text{Cl}$ ,  $p_c = 72.7$  atm.,  $t_c = 49.1^\circ$ ;  $\text{SO}_2$ ,  $p_c = 77.95$ ,  $t_c = 157.2^\circ$ .

Trouton's relationship, in the form  $Q/nT = K$ , where  $Q$  is the molecular heat of sublimation,  $n$  the number of gaseous molecules formed per molecule of the dissociating compound, and  $T$  the temperature at which the dissociation pressure becomes equal to  $760$  mm. mercury, gives a very nearly constant value of  $34$  for  $K$  in the case of ammonium hydrogen sulphide, phosphonium chloride, ammonium carbonate, and ammonium chloride. H. M. D.

**Viscosity of Supercooled Solutions.** CARL SHALL (*Chem. Centr.*, 1906, ii, 1375; from *Physikal. Zeit.*, 7, 645—648. Compare Abstr., 1899, ii, 640).—According to Jäger, if the internal friction  $\eta$  of a solvent is expressed as a function of the temperature  $\theta$  in the form  $\eta = f(\theta)$ , then the internal friction of a solution may be expressed by the relation  $\eta = f(\theta + \Delta)$  in which  $\Delta$  is the depression of freezing point. The author has tested this formula, using thymol as solvent, at temperatures varying from  $15$ — $50^\circ$ , and has compared the values of  $\Delta$  found

with those calculated according to Van't Hoff's formula. A satisfactory agreement is observed in the case of hydrocarbons and their halogen derivatives, especially with *cyclohexane* and *chloroform*, but the results are less satisfactory for esters. Reactive substances such as bases, aldehydes, and alcohols produce the greatest discrepancies. P. H.

**Adsorbent Properties of Different Species of Charcoal.** LEOPOLD ROSENTHALER and F. TÜRK (*Arch. Pharm.*, 1906, 244, 517—534).—The percentage of a dissolved substance absorbed from 1 per cent. solutions of it in different solvents by five times its weight of different kinds of charcoal has been investigated in the cases of codeine, caffeine, salicin, picrotoxin, gallotannic acid, gallic acid, oxalic acid, potassium oxalate, indigotin, and dextrose. The amount and rate of adsorption are greatest in the case of animal charcoal, great also with "flesh," and, in a less degree, "plant-blood" charcoals, small with "blood," "lime-wood," and "sponge" charcoals (*Tier-, Fleisch-, Pflanzenblut-, Blut-, Linden-, and Schwamm-Kohle*); they are greatest in aqueous solutions, smaller in ethyl- and methyl-alcoholic, ethyl acetate, and acetone solutions, smallest in chloroform solution. The more concentrated a solution is, the smaller is the percentage of dissolved substance adsorbed from it. The greater the readiness with which a substance is adsorbed, the greater is the difficulty of dissolving it out from the charcoal. The decolorising power of charcoal is dependent on its adsorbent power.

Charcoal to be used for decolorising should be purified carefully, either by repeated extraction with the boiling solvent or by ignition and subsequent extraction with acids and water. It should be used in as small amount as possible. There is no need to heat; several hours' contact with the solution at the ordinary temperature suffices. It is best not to use water as the solvent. The solution should be as concentrated as possible. Substances that oxidise readily must not be decolorised with animal charcoal.

In quantitative estimations, decolorisation with charcoal must not be employed unless it is known that charcoal does not adsorb the substance to be estimated. In the case of caffeine, animal or flesh charcoal may be used.

Tables of the experimental data are given in the paper.

LEOPOLD ROSENTHALER (*ibid.*, 535—536) points out that the percentage of a substance adsorbed from its solution by charcoal increases with the molecular weight of the substance. The colouring matter in a solution that is to be decolorised usually has a high molecular weight, and its concentration in the solution is usually small; both these circumstances are favourable to adsorption. C. F. B.

**Diffusion of Solutions of Copper Sulphate in Gelatin.** MICHEL YÉGOUNOW (*Compt. rend.*, 1906, 143, 882—884).—In a previous paper (*Abstr.*, 1906, ii, 338) the author has shown that the velocity of diffusion  $v = dh/dt$ , where  $h$  is the height reached by the dissolved substance in the time  $t$ . By Stephan's law,  $h = a\sqrt{t}$  where  $a$  is a specific constant for each substance. In the present paper are tabulated the experimental and theoretical values of the constant  $a$  for solutions in 10%

gelatin solution of copper sulphate of strengths varying from  $N$  to  $N/200$ .  
M. A. W.

**Estimation of Osmotic Pressure in Small Quantities of Fluid.** HARTOG J. HAMBURGER (*Biochem. Zeit.*, 1906, 1, 259—281).—A full account of methods published previously (Abstr., 1906, ii, 9).  
W. D. H.

**Origin of Osmotic Effects.** HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1906, A, 78, 264—271).—On the basis of an association hypothesis an explanation may be given of the action of enzymes and acids in promoting hydrolysis, and, more generally, association, and not dissociation, should be regarded as the condition which precedes chemical change. In formulating an association theory of osmotic phenomena, it is necessary to account for the following facts: (1) that dissolved non-electrolytes in equivalent concentration all exert a similar influence, (2) that electrolytes exert an excessive influence in comparison with non-electrolytes. In water there is an equilibrium between complex molecules and fundamental molecules (*monads*) represented by the equation  $(\text{H}_2\text{O})_n \rightleftharpoons n\text{H}_2\text{O}$ , and the dissolution of any substance in the water is supposed by the author to disturb this equilibrium and to favour the change  $(\text{H}_2\text{O})_n \rightarrow n\text{H}_2\text{O}$ . The osmotic "pressure" is then the measure of the disturbance of the equilibrium due to the formation of water monads, which are regarded as the attracting element in the region of the solution, and as conditioning a flow of similar molecules from the region of the pure solvent (or from a more dilute solution), until the two regions are in equilibrium. Any substance which dissolves in the form of its fundamental molecules and has no appreciable attractive action on the water molecules will exert a normal effect. Electrolytes, on the other hand, are supposed not only to produce a normal osmotic effect by promoting formation of water monads, but themselves to have an attractive action on the water molecules. The author accordingly regards electrolytes as substances which attract water in proportion to the efficiency of their solutions as electrolytes. From this point of view it is only right that in comparing the osmotic efficiency of different substances their influence on a *given quantity of solvent* should be measured, and the use of *weight-normal* solutions (see Morse and Frazer, Abstr., 1905, ii, 575) is thus entirely justified. It is considered that the apparent abnormalities in the depression of the freezing point may be easily explained when account is taken of the volume relations of solution and solvent.

The paper contains also various criticisms of the current views as to the behaviour of dissolved electrolytes. Special reference is made to mercuric chloride, which, from the electrolytic and osmotic point of view, behaves almost as a non-electrolyte. The author supposes that the mercuric chloride monads are really closed systems, such as  $\text{Hg} \begin{smallmatrix} \text{Cl} \\ | \\ \text{Cl} \end{smallmatrix}$  or

$\text{Hg} \begin{smallmatrix} \text{Cl}^- \\ | \\ \text{Cl}^- \end{smallmatrix}$ , which are but slightly attractive of water, whilst other

chlorides are open systems, such as  $\text{Na}-\text{Cl}=\text{}$ ,  $\text{Ca} \begin{smallmatrix} \text{Cl}=\text{} \\ \text{Cl}=\text{} \end{smallmatrix}$ . Emphasis is laid on the author's view, previously expressed, that hydrogen and the metals generally may be regarded as the analogues of the  $\text{C}_n\text{H}_{2n+1}$  hydrocarbon radicles, and that their compounds with negative elements may be likened to unsaturated hydrocarbons of the form  $\text{C}_n\text{H}_{2n+1} \cdot \text{CH}:\text{CH}_2$ . It is probable that in all its interactions the activity of a salt is primarily traceable to the negative ion. J. C. P.

**Studies of the Processes Operative in Solutions. I. The Sucroclastic Action of Acids as Influenced by Salts and Non-electrolytes.** ROBERT J. CALDWELL (*Proc. Roy. Soc.*, 1906, A, 78, 272—295).—Earlier investigations on the influence of other substances on the inversion of sucrose are to a certain extent discounted because the solutions used have generally been prepared by dissolving the various substances up to a certain volume. In this method of work, a variation in the amount of sugar means also a variation in the amount of water present, so that the results are not strictly comparable. The author has therefore employed weight-normal solutions in this investigation (compare Morse and Frazer, *Abstr.*, 1905, ii, 575).

It is well known that when volume-normal solutions are used the rate of inversion of sucrose by hydrochloric acid increases rapidly with the concentration of the sucrose. When, however, weight-normal solutions are used, and varying quantities of sucrose are taken, always with a fixed quantity of the solvent, namely 1000 grams, the rate of inversion of hydrochloric acid increases only to a slight extent with the concentration of sucrose. The electrical conductivity of hydrochloric acid is diminished by the presence of dextrose, and the higher the dextrose concentration the greater is the decrease in the conductivity; the decrease is, however, rather less marked when weight-normal solutions are used than when volume-normal solutions are used. The fact that with increasing sugar concentration the invertive power of the acid increases whilst its conductivity diminishes is regarded as a strong argument against the application of the ionic hypothesis to hydrolysis.

The influence of lactose, dextrose, glycerol, alcohol, potassium chloride, ammonium chloride, barium chloride, calcium chloride, sodium chloride, and acetic acid on the rate of inversion of sucrose by hydrochloric acid has been studied. Weight-normal solutions being used, it is found that dextrose and lactose are practically without any influence, glycerol and alcohol have a retarding, all the others an accelerating, effect. Calcium chloride, an easily soluble and hygroscopic salt, has a much greater effect than sodium chloride, and the acceleration is accordingly regarded as a concentration effect, due to the removal by the dissolved salt of a certain number of water molecules from the sphere of action of the acid. The magnitude of this concentration effect for any given so-called "neutral" salt has been found by calculating the number of gram-mols. of water which would have to be added to the original 1000 grams, in order to make the rate of change equal to that which would be observed in the absence

of the salt. Hence the "degree of hydration" of the various salts may be determined, with the following results for gram-molecular solutions:  $\text{NH}_4\text{Cl}, 10\text{H}_2\text{O}$ ;  $\text{KCl}, 10\text{H}_2\text{O}$ ;  $\text{NaCl}, 13\text{H}_2\text{O}$ ;  $\text{BaCl}_2, 19\text{H}_2\text{O}$ ;  $\text{CaCl}_2, 22\text{H}_2\text{O}$ . These values are probably rather low, but are in harmony with estimates based on other methods.

Incidentally, a simple and satisfactory device for regulation of the gas pressure is described. J. C. P.

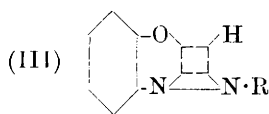
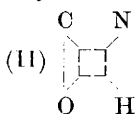
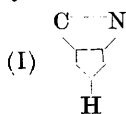
**Solubility of Substances in Water and their Physical Constants.** GEORGE G. LONGINESCU (*Chem. Centr.*, 1906, ii, 1374).—The ratio of the absolute boiling point  $T$  to the molecular weight  $M$  is an approximate indication of the magnitude of the intermolecular attraction; it varies from 20.4 for water to 1.1 for carbon disulphide; if the ratio is greater than 5, the substance is readily soluble in water, whereas when the ratio falls below 3.5 the substance is insoluble. The same relations hold for organic solids, except that the melting point must in this case be substituted for the boiling point, but the relations do not hold for inorganic substances, which are too highly associated. Those organic liquids which have the lowest molecular volume are the most soluble. When the ratio  $M/D$  is greater than 100 the substance is insoluble. The ratio  $MD/\sqrt{n}$ , in which  $n$  is the number of atoms in the molecule, increases with decreasing solubility. The product of the ratios  $T/M$  and  $M/D\sqrt{n}$  gives a quantity from which it is possible to calculate the degree of polymerisation. When  $T/D\sqrt{n} \leq 100$  the substance is insoluble. Some exceptions to this are, however, known. The author concludes from these observations that the phenomenon of solution is a purely physical one. P. H.

**Molecular Weight Determinations in Solid Solutions.** JULIUS MEYER (*Chem. Centr.*, 1906, ii, 1231; from *Verh. Ges. Deut. Naturf. Aerzte*, 77, ii, 94–96).—The lowering of vapour pressure and the coefficient of partition between two solvents can be employed as a means of determining the molecular weight of a substance in solid solution. When the solvent is enantiotropic, the change in the transformation point may be determined, thus: the *E.M.F.* of the system Sn (white),  $\text{SnCl}_2$ , Sn (grey) is zero at  $18.9^\circ$ . The heat of transformation and the molecular alteration of the transformation temperature were found to be 9.55 Cal. and  $17.8^\circ$  respectively, gold and mercury being employed as dissolved substances. P. H.

**Mesohydry.** GIUSEPPE ODDO (*Atti R. Accad. Lincei.*, 1906, [v], 15, ii, 438–447 and 500–511).—It has been recently shown by the author and Puxeddu (*Abstr.*, 1906, i, 991) that the 5-azoeugenols are neither azophenols nor quinone hydrazones, and to explain their structure the author introduces a new conception to which he gives the name "mesohydry" [*mesoidria* (*loc. cit.*), 992]. It is assumed that an atom of hydrogen, in the neighbourhood of two multivalent elements, can divide its valency between these two by assuming a mean

position of stable equilibrium; such a valency is represented by the symbol  $\angle$ .

The condition under which this phenomenon occurs is that between the two multivalent atoms there exists a double or triple linking connecting them either directly or by means of one or more other atoms. Such compounds are divided into three classes. According as the compound contains two, three or more than three multivalent atoms, these classes being represented by (I) hydrocyanic acid, (II) cyanic acid, and (III) *o*-oxyazo-compounds:



The author uses this conception to explain (1) a number of cases of pseudomeric, tautomeric, and alloisomeric compounds and the behaviour of most of them as pseudo-acids, that is, they give salts only subsequently to transposition; (2) the physicochemical behaviour exhibited by the organic acids and certain oxygenated inorganic acids as distinguished from that of the halogen hydracids.

T. H. P.

**The Shape of the Spinodal and Plait-point Curves for Binary Mixtures of Normal Substances.** IV. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 226—235. Compare Abstr., 1905, ii, 507).—The author gives a *résumé* of the results obtained in his previous papers and develops the position of the longitudinal plait. Several curves are given illustrating the method of procedure.

J. C. C.

**Growth and Solution of Crystals.** F. PÖCKELS (*Centr. Min.*, 1906, 664—667).—The theoretical conclusions, based on thermodynamical principles, of Pawloff (Abstr., 1906, ii, 552) are adversely criticised.

L. J. S.

**Isomorphism of Double Fluorides and Oxyfluorides of Bivalent Metals.** B. GOSSNER (*Zeit. Kryst. Min.*, 1906, 42, 475—488).—A criterion of the isomorphism of two substances is afforded by their capability of forming mixed crystals, but whether the intermixture may take place in all proportions or with gaps in the series is as yet undecided. Stortenbecker (Abstr., 1903, ii, 470) has asserted that no gap occurs in the mixtures of two truly isomorphous substances, whilst the present author claims to have proved that in the salts he examined such gaps exist. This conclusion is based on the determinations of the sp. gr. of a series of mixed crystals of

$\text{MoO}_2\text{F}_4\text{Zn}, 6\text{H}_2\text{O}$  (D 2.151) and  $\text{SnF}_6\text{Zn}, 6\text{H}_2\text{O}$  (D 2.445).

$\text{MoO}_2\text{F}_4\text{Co}, 6\text{H}_2\text{O}$  (D 2.093) and  $\text{SnF}_6\text{Co}, 6\text{H}_2\text{O}$  (D 2.394).

$\text{SiF}_6\text{Zn}, 6\text{H}_2\text{O}$  (D 2.139) and  $\text{SnF}_6\text{Zn}, 6\text{H}_2\text{O}$ .

$\text{SiF}_6\text{Ni}, 6\text{H}_2\text{O}$  (D 2.134) and  $\text{SiF}_6\text{Zn}, 6\text{H}_2\text{O}$ .

In complex molecules such as these, the effect of mass-isomorphism is to be considered in addition to the chemical analogy of the salts.

The isomorphous salts mentioned above differ considerably in their molecular volumes, and the greater the difference between any pair, the more likely will there be a gap in the series of mixed crystals; this seems to be conditioned by the relative sizes of the structural units (as measured by topic axes) of the two salts. L. J. S.

**Mixed Crystals in Ternary Systems.** FRANS A. H. SCHREINEMAKERS (*Arch. Néerland.*, [ii], 11, 462—501. Compare Abstr., 1906, ii, 342).—A theoretical study of the various possible cases that may arise, namely (1) where the three solid substances are miscible in all proportions, (2) where they are not miscible in all proportions, and (3) where mixed crystals of two types occur. J. C. P.

**Continuity of States of Aggregation and Fluid Crystals.** KARL FUCHS (*Ann. Physik*, 1906, [iv], 21, 393—398).—A criticism of the views recently propounded by Lehmann (Abstr., 1906, ii, 431). A substance exhibiting polymorphism may be regarded as capable of forming different molecular complexes and so existing in different crystalline forms. J. C. P.

**Intrinsic Movement of Particles in Colloidal Solutions.** THE SVEDBERG (*Zeit. Elektrochem.*, 1906, 12, 853—860).—By means of Zsigmondy's ultra-microscope, the colloidal particles are made visible as bright specks in rapid motion. By causing the solution to flow at a measured speed through the field of view, the apparent path traced out by a particle resembles a sine curve and the amplitude of the vibration and also the wave-length can be measured by means of a scale in the eye-piece of the microscope. Colloidal solutions of platinum in different organic solvents (prepared by the methods described in Abstr., 1905, ii, 817, and 1906, ii, 330) were first examined: the amplitude of vibration diminishes as the viscosity of the solvent increases, becoming zero in glycerol. The smaller particles have greater amplitudes than the larger ones. Similar results are obtained with colloidal solutions of calcium and sodium, indicating that the brightly coloured sodium solutions do not differ essentially from the others.

From the rate of flow of the solution and the wave-length of the vibration the mean velocity of the movement is easily calculated. For the platinum solutions it is found that, notwithstanding the different amplitudes of the vibrations in different solvents, the mean velocity is practically constant; for particles estimated to weigh  $2.5 \times 10^{-15}$  gram the mean velocity is  $3 \times 10^{-2}$  cm. per sec. at the ordinary temperature. T. E.

**Chemistry of Colloids.** K. WINKELBLECH (*Zeit. angew. Chem.*, 1906, 1953—1955).—When a solution of gelatin is violently shaken up for a short time with light petroleum, the gelatin separates in the form of an emulsion containing both water and petroleum. The phenomenon can be observed with a solution which contains only 0.006 gram of gelatin per litre. Slight acidity or alkalinity has but little effect on the precipitation, but in presence of larger quantities of acid, alkalis, or neutral salts the test is less sensitive. Similar



emulsions have been obtained with solutions of egg-albumin, soluble starch, soap, rosin in sodium hydroxide, tannic acid, sulphur in sodium hydroxide, and water glass. In place of light petroleum, heavier fractions of petroleum, benzene, chloroform, or carbon disulphide may be used. The action is supposed to be due to the passage of the moist colloid particles into the surface layers of the minute drops of the organic liquid, where they unite to larger aggregates which form the components of the emulsion.

H. M. D.

**Two Catalyses which can be Represented by Equations.** I. F. HOFFMANN (*Chem. Centr.*, 1906, ii, 1232; from *Woch. Brauerei.*, 23, 464—467).—The catalytic action of water in the hardening of lime is attributed to the alternate combination of a molecule of water with a molecule of lime and its displacement from combination by carbon dioxide. The oxidation of manganous salts in presence of tetramethyl-*p*-phenylenediamine as a carrier is also regarded as a catalytic action and the change can be represented by a series of equations. P. H.

**"Permanent." Apparatus for Measuring Liquids.** PAUL FUNKE & Co. (*Chem. Centr.*, 1906, ii, 1301; from *Zeit. chem. Apparatenkunde*, 1, 644—645).—The apparatus consists of a funnel to which is attached a hollow glass stop-cock, which is divided into two compartments, each of 10 c.c. capacity. By a suitable turn of the cock one compartment is put in connexion with the funnel above and is thereby filled with liquid, whilst the other compartment is put in communication with the stem of the funnel and discharges 10 c.c. of liquid into it. By another half turn of the cock the positions are reversed.

P. H.

**Two Lecture Experiments in Illustration of the Theory of Ionisation.** WILLIAM W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1906, 26, 325—326).—A solution of egg-albumin added to a solution of nitric acid, which is so dilute that no coagulation of albumin occurs, is immediately caused to coagulate by the addition of a saturated solution of potassium nitrate. The potassium nitrate solution itself does not induce coagulation, and the observed effect is attributed to an increase in the concentration of un-ionised nitric acid which is the active agent.

A saturated potassium nitrate solution and a solution of acetic acid when added together to a solution of albumin cause coagulation, although the two solutions separately are inactive. A solution of potassium acetate is also inactive, and the activity of the mixed solutions is due to un-ionised nitric acid formed by displacement by the weaker acetic acid.

H. M. D.

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### Inorganic Chemistry.

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**Ignition Temperatures of Hydrogen-Oxygen Mixtures.**  
KAUFMAN G. FALK (*J. Amer. Chem. Soc.*, 1906, 28, 1517—1534).—  
Previous determinations of the ignition temperature of detonating gas

have been made either by plunging a sealed bulb of the gas into a bath of known temperature, or by passing the gas through a tube heated to a definite temperature. The results obtained by these methods show considerable variation which is due to the fact that the whole of the gas does not reach the ignition temperature at the same instant. The heat would reach the outer layers of the gas first, and in the time necessary for the whole of the gas to attain the required temperature, an indefinite amount of combination would have occurred.

In order to overcome these objections, a method has been devised for generating the necessary heat by the adiabatic compression of the gas itself in a steel cylinder fitted with a steel piston. The apparatus and method are fully described with the aid of diagrams. Mixtures of hydrogen and oxygen were employed in the volumetric proportions of 4:1, 2:1, 1:1, 1:2, and 1:4. The whole of the heat involved in the experiments was produced by the adiabatic compression, which was so rapid that radiation to the walls of the vessel was impossible. Two forms of apparatus were employed, one of which was larger than the other and probably gave more accurate results. The ignition temperature was calculated by a method based on the equation for adiabatic changes, and the following average results were obtained which are expressed as absolute temperatures. In the smaller apparatus,  $4\text{H}_2 + \text{O}_2$ ,  $874^\circ$ ;  $2\text{H}_2 + \text{O}_2$ ,  $811^\circ$ ;  $\text{H}_2 + \text{O}_2$ ,  $786^\circ$ . In the larger apparatus,  $4\text{H}_2 + \text{O}_2$ ,  $893^\circ$ ;  $2\text{H}_2 + \text{O}_2$ ,  $819^\circ$ ;  $\text{H}_2 + \text{O}_2$ ,  $796^\circ$ ;  $\text{H}_2 + 2\text{O}_2$ ,  $808^\circ$ ;  $\text{H}_2 + 4\text{O}_2$ ,  $849^\circ$ .

The results show that the ignition temperature is independent of the final pressure of the gas for pressures greater than 39 atmospheres (the lowest pressure at which the ignition temperature was determined) and, under the conditions of the experiments, is also independent of the initial temperature of the gas. The ignition temperature of the mixture,  $\text{H}_2 + \text{O}_2$ , is lower than that of any of the other mixtures, and this minimum temperature corresponds with a maximum affinity. The probable explanation is that hydrogen peroxide is formed first in the combination of hydrogen and oxygen, and is subsequently decomposed, the degree of completeness of this decomposition depending on the conditions.

According to the theory of the explosion wave, the ratio of the pressure of the gas at the ignition point to the initial pressure should be constant for any one mixture, and this has been found to be approximately the case. The ratio found in the case of detonating gas is 36.6, which agrees fairly closely with the value deduced by Jouquet (*J. math.*, 1906, 80).

E. G.

**The Equilibrium of the Deacon Process.** VOGEL VON FALCKENSTEIN (*Zeit. Elektrochem.*, 1906, 12, 763—764).—Asbestos soaked in copper chloride was used as the catalyst at  $450^\circ$  and platinum tetrachloride at temperatures above  $500^\circ$ . The equilibrium, represented by the equation  $2\text{Cl}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{HCl}$ , was attained from both sides. The values of the equilibrium constant,  $K = (p_{\text{H}_2\text{O}})^2 \cdot (p_{\text{Cl}_2})^2 / (p_{\text{O}_2}) (p_{\text{HCl}})^4$ , are given below; they are the mean values of fifty-eight experiments at  $450^\circ$ , forty-eight at  $650^\circ$ , and five at  $600^\circ$ .

Temperature.	From chlorine side,	From hydrogen chloride side,	Log $K$ (cal.).
	log $K$ .	log $K$ .	
450°	1.50	1.49	1.52
650	-0.407	-0.390	-0.43
600	-0.046	-0.050	-0.02

From Dolezalek's experiments on the chlorine-hydrogen gas cell, Nernst has calculated  $\log[\text{Cl}_2]^2 \cdot [\text{H}_2]^2 / [\text{HCl}]^4 = -88000/4.571T - 1.6$ . Nernst and Wartenberg calculate from their experiments on the dissociation of steam,  $\log[\text{H}_2\text{O}]^2 / [\text{H}_2]^2 [\text{O}_2] = 25050/T - 1.75 \log T - 0.00013T + 0.2$ . From these expressions the value of  $\log K$  in the process studied is found to be  $5790/T - 1.75 \log T - 0.00013T - 1.4$ . The calculated values in the above table are obtained from this expression.

T. E.

**Sublimation of Sulphur at the Ordinary Temperature.** RICHARD J. MOSS (*Sci. Proc. Roy. Dubl. Soc.*, 1906, ii, 105—106).—Some fragments of ordinary roll sulphur were sealed up in an exhausted tube twenty-four years ago. After twenty years, during which time the tube was placed in a horizontal position in a drawer, a minute, crystalline sublimate was observed.

H. M. D.

**The Two Forms of Liquid Sulphur as Dynamic Isomerides.** ALEXANDER SMITH and CHARLES M. CARSON (*Proc. Roy. Soc. Edin.*, 1906, 26, 352—356. Compare Abstr., 1906, ii, 157).—The liquid obtained by melting sulphur, which after recrystallisation has not been in contact with air, contains the two liquid forms  $S_\lambda$  and  $S_\mu$  in equilibrium proportions, the equilibrium condition being attained in a few moments. Ammonia bubbled through the melted sulphur also facilitates the rapid establishment of equilibrium. The conversion of  $S_\mu$  into  $S_\lambda$  on cooling is equally rapid, so that by plunging into water, ordinary monoclinic sulphur is obtained.

On the other hand, equilibrium is only slowly reached in the fused mass obtained from sulphur which has been exposed to the air. This inert condition is also induced by passing hydrogen chloride or sulphur dioxide through the fused mass obtained from sulphur not exposed to air after recrystallisation. These gases act as simple catalytic agents, and the two liquid forms,  $S_\lambda$  and  $S_\mu$ , are to be classed as dynamic isomerides. The equilibrium proportions at any temperature may be rapidly measured by passing in ammonia to accelerate the attainment of equilibrium and afterwards sulphur dioxide before cooling to prevent further change. Iodine retards the adjustment of equilibrium, but displaces the equilibrium to a considerable extent.

The solidification of molten sulphur is considered with reference to a temperature concentration diagram. The freezing point of  $S_\lambda$  is  $119.25^\circ$ , the "natural freezing point" at which the two liquid forms are in equilibrium with solid monoclinic sulphur is  $114.5^\circ$ , and the liquid contains 96.3%  $S_\lambda$  and 3.7%  $S_\mu$ . The proportion of  $S_\mu$  in the liquid increases with rise of temperature, and the rate of increase is much greater above  $160^\circ$  than it is below this temperature, as the following numbers show:

Temperature .....	121°	154°	156°	162°	165°	167°
% S <sub>μ</sub> in equilibrium condition .....	3.75	7.5	8.0	13.5	15.5	16.7

The marked absorption of heat and fall in temperature at or just above 160°, which are observed when liquid sulphur is heated continuously at a constant rate, is shown to be due to the fact that the proportion of S<sub>μ</sub> in the liquid lags behind that corresponding to the equilibrium condition. The observed fact that the liquid becomes viscous at a lower temperature when the rate of heating is diminished is due to the same circumstance.

H. M. D.

**Conditions under which Metallic Sulphides are Precipitated and Redissolved.** HENRI BAUBIGNY (*Compt. rend.*, 1906, 143, 678—679).—A claim for *priority* against Bruni and Padoa (*Abstr.*, 1906, ii, 157); compare *Abstr.*, 1882, 805, 928, 1031, 1032, 1172; 1883, 22, 24, 25; 1888, 113, 423; 1889, 118, 346, 652, 653).

M. A. W.

**Selenium.** WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1906, 143, 682).—The brick-red, amorphous variety of selenium obtained when selenious acid is reduced by glucose (? lævulose), dissolves in concentrated sulphuric acid to form selenium sulphoxide, SeSO<sub>3</sub> [compare Divers and Shimosé, *Trans.*, 1883, 43, 329; 1884, 45, 194, 201; Divers and Shimidzu, *Trans.*, 1886, 49, 583]. This slowly decomposes according to the equation  $\text{SeSO}_3 + \text{H}_2\text{O} = \text{Se} + \text{H}_2\text{SO}_4$ , yielding a different variety of selenium to that originally employed. The new variety is pale or deep brown in colour, does not become fluorescent when exposed to diffused light, or undergo any change in contact with carbon disulphide, in which it is very sparingly soluble. On prolonged exposure to sunlight, it is slowly converted into the amorphous, black variety of selenium.

M. A. W.

**Vapour Pressure of Carbon Dioxide at Low Temperatures.** JOHN ZELENY and ROY H. SMITH (*Chem. Centr.*, 1906, 1486; from *Physikal. Zeit.*, 7, 667—671).—The vapour pressure of carbon dioxide was measured at temperatures varying from 7° to -134°. Solid carbon dioxide was placed in a glass tube closed at the top and connected by a side tube to a mercury gauge. The tube was immersed in a bath of pentane, the temperature of which was measured by means of a nickel-iron couple, the pentane bath being itself surrounded by liquid air. The following values were obtained for the vapour pressure in atmospheres: 27.8 at -7°, 19.52 at -20°, 9.88 at -40°, 4.35 at -60°, 1 atmosphere at -78.2°; 28.8 mm. at -90°, 11.9 at -100°, 1.4 at -120°, and 0.1 mm. mercury at -134°. The addition of alcohol or ether has very little influence on the vapour pressure. The critical point lies at -56.4° and 5.11 atmospheres. The value of  $dp/dT$  was found to be 6.35 cm. per degree and the latent heat of vaporisation *L* was found to be -140 Cal.

P. H.

**Behaviour of Carbon Disulphide towards Nascent Hydrogen.** A. GAWALOWSKI (*Chem. Centr.*, 1906, ii, 1248; from *Zeit. Oesterr. Apoth. Ver.*, 44, 460—461).—Carbon disulphide, when treated with zinc and sulphuric acid, yields a gas which produces a pure black pre-

precipitate in a solution of lead nitrate and blackens a filter paper moistened with the same solution. The gas evolved on heating carbon disulphide with zinc and strong potassium hydroxide, however, yields a bright orange-red precipitate with lead nitrate solution. The colour of the stain produced on filter paper moistened with lead nitrate is orange, and fades rapidly. P. H.

**Fractionation of Rare Gases from Mineral Waters. Proportion of Helium.** CHARLES MOUREU and ROBERT BIQUARD (*Compt. rend.*, 1906, 143, 795—797. Compare Abstr., 1905, ii, 5; 1906, ii, 442).—By submitting the rare gases obtained from certain mineral waters to the selective absorption of wood charcoal at  $-185^{\circ}$  (compare Dewar, Abstr., 1904, ii, 652, 728), the authors have separated the helium and part of the neon from the other gases, but further treatment with charcoal at  $-100^{\circ}$  or at the temperature of liquid air boiling under 40—60 mm. pressure, failed to effect the separation of the neon and helium. The former gas, therefore, is present in quantities too small to be estimated. The proportion of helium in the gaseous constituents of the waters of forty-three thermal springs is given in the original, and varies from 0.00063 per cent. in Châtel-Guyon spring to 5.34 per cent. in that of Maizières; the gases from the latter source also contain krypton. M. A. W.

**Causticising of Sodium and Potassium Carbonates with Lime.** MAX LE BLANC and KARL NOVOTNÝ (*Zeit. anorg. Chem.*, 1906, 51, 181—201. Compare Lunge and Schmid, Abstr., 1886, 203; Bodländer and Lucas, Abstr., 1905, ii, 634).—In the reversible reaction,  $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3$ , when the solution is in equilibrium with solid calcium hydroxide and carbonate, the value of the equilibrium constant  $k = (\text{OH}')^2 / \text{CO}_3''$  can be calculated when the solubilities of the two solid substances are known. In aqueous solution, calcium carbonate is partially hydrolysed, and to obtain the solubility of the non-hydrolysed salt, necessary for the calculation of the constant, determinations have been made in excess of sodium hydroxide (by which the hydrolysis is depressed: compare Gardner and Gerassimoff, Abstr., 1904, ii, 544) directly at  $18^{\circ}$  and  $95$ — $100^{\circ}$ , and by conductivity measurements at the former temperature. By comparison of the solubility in water with that in sodium hydroxide, the degree of hydrolysis has been determined; according to the conductivity measurements 67% and by direct measurement 80% of the salt is hydrolysed at  $18^{\circ}$ . From the solubility of the non-hydrolysed salt thus obtained, the value  $k = 16040$  at  $18^{\circ}$  has been calculated.

The equilibrium has also been reached directly from both sides with 1, 2, and 3*N*-sodium and potassium hydroxides and lime at intervals of temperature from  $15$ — $150^{\circ}$  in iron bombs, the relative proportions of hydroxide and carbonate being determined by titration. The reaction is most complete with small concentration of carbonate; not only is the yield decreased by increase of carbonate, 1, 2, and 3*N*-sodium carbonate, and excess of lime, giving 99, 97, and 93.6% of hydroxide respectively at  $100^{\circ}$ , but the equilibrium is somewhat displaced in favour of the carbonate. The yield is not appreciably increased by rise of temperature.

The technical bearing of these results is discussed. It is pointed out that the patents for increasing the yield by working under pressure are useless; efforts should be directed to facilitating the attainment of equilibrium, which is favoured by high temperature, thorough stirring, and presence of excess of lime. The possible loss of part of the soda as an insoluble double salt is also discussed.

The above results are in satisfactory agreement with those of Lunge and Schmid, but not in all respects with those of Lucas (*loc. cit.*).

G. S.

**Solubility of Lithium Sulphate in Mixtures of Water and Alcohol.** FRANS A. H. SCHREINEMAKERS and WILLEM A. VAN DORP, junr. (*Chem. Centr.*, 1906, ii, 1235; from *Chem. Weekblad.*, 3, 557—561).—The following conclusions are arrived at: (1) hydrated lithium sulphate is not altered by mixtures of water and alcohol containing less alcohol than a limiting value, whereas the anhydrous salt under these conditions becomes hydrated; (2) in solutions of alcohol and water containing more alcohol than the upper limiting value the anhydrous salt is not affected, whilst the hydrated form loses its water; (3) in solutions intermediate between these two, both salts remain unchanged. The solubility of lithium sulphate diminishes rapidly with increase in the amount of alcohol; it is practically insoluble in 80% alcohol.

P. H.

**Influence of Lithium Sulphate on the Formation of Layers in the System Water-Alcohol-Ammonium Sulphate.** FRANS A. H. SCHREINEMAKERS and J. TH. BORNWATER (*Chem. Centr.*, 1906, ii, 1306; from *Chem. Weekblad.*, 3, 569—575. Compare preceding abstract; *Abstr.*, 1906, ii, 855).—In continuation of their earlier work, the authors have found that whereas there are two liquid phases in the system water-alcohol-ammonium sulphate, there is only one phase in the system water-alcohol-lithium sulphate or water-alcohol-lithium-ammonium sulphate. The effect of lithium sulphate on the formation of two layers in the system water-alcohol-ammonium sulphate has been studied, and the results are recorded in tabular form. At first the addition of lithium sulphate increases the amount of alcohol in the alcoholic layer and diminishes the amount in the aqueous layer; then the reverse phenomenon takes place and the composition of the two layers becomes more and more alike.

P. H.

**Silver Chromate. II.** BENJAMIN M. MARGOSCHES (*Zeit. anorg. Chem.*, 1906, 51, 231—235. Compare *Abstr.*, 1904, ii, 731).—The behaviour of silver chromate towards certain inorganic acids has been described in the previous paper, and the investigation has now been extended to some weak acids, more particularly acetic acid, with regard to which there are contradictory statements in the literature.

Silver chromate is practically insoluble in water and in glacial acetic acid, but dissolves to a considerable extent in dilute acetic acid. It behaves in a similar manner with propionic, lactic, and other organic acids. Chromates can be detected most readily by conversion into the

lead salt, which is insoluble in acetic acid. When the red modification of the silver salt is dissolved in dilute acetic acid and the solution concentrated, the greenish-black modification separates. G. S.

**Action of Alkali Chlorides on the Double Silicates of Calcium and Aluminium.** F. H. CAMPBELL (*Landw. Versuchs.-Stat.*, 1906, 65, 247—252).—The object of the experiments was to ascertain the amounts of calcium liberated from calcium aluminium silicate (prepared by precipitating a solution of the chlorides with sodium silicate) by shaking for some days with solutions ( $N/5$  to  $8N$ ) of lithium, sodium, potassium, and ammonium chlorides.

Lemberg (*Zeit. deut. geol. Ges.*, 28, 579) and Dittrich (Abstr., 1903, ii, 176) have shown that the power of parting with calcium is greatly reduced, or even lost altogether, after ignition. It is now shown that even drying at  $100^{\circ}$  considerably reduces the amount of calcium displaced by  $N$ -sodium chloride. The action is very slow at  $25^{\circ}$ , but the amount of calcium replaced is very little less than at  $32.5^{\circ}$ , the temperature finally adopted.

The amount of calcium displaced rises, in each case, with the increase in concentration of the alkali salt; but less with higher than with lower concentrations. With sodium, potassium, and ammonium chlorides, the maximum is reached with  $3N$ -solutions, whilst in the case of lithium chloride the maximum is with a  $6N$ -solution.

With low concentrations the displacing power of lithium, sodium, and potassium chlorides increases with the atomic weight; it is greatest in the case of ammonium chloride. At higher concentrations, sodium and potassium chlorides have nearly the same maximum; lithium chloride has a higher, and ammonium chloride a much higher, maximum. N. H. J. M.

**Molecular Weights of Inorganic Compounds in Boiling Quinoline.** ERNST BECKMANN [with WERNER GABEL] (*Zeit. anorg. Chem.*, 1906, 51, 236—244).—The quinoline was dried over phosphoric oxide or potassium hydroxide and fractionated from "active" aluminium. The mean value of the molecular elevation of the boiling point, determined with benzil, benzoin, and other organic compounds, is  $56.1$ .

The chlorides, bromides, and iodides of zinc and cadmium, and the chlorides and bromides of cobalt and nickel, have the normal molecular weights in this solvent, whilst cuprous chloride gives results which indicate that the  $\text{CuCl}$  molecules present in dilute solution associate to  $\text{Cu}_2\text{Cl}_2$  molecules in more concentrated solution. G. S.

**Isomorphous Crystals of Lead and Barium Nitrates.** P. GAUBERT (*Compt. rend.*, 1906, 143, 776—777).—The investigation of selective absorption exhibited by the cubic and octahedral faces of lead nitrate crystals towards organic colouring matter (Abstr., 1906, ii, 152, 343) is extended also towards isomorphous nitrates such as barium nitrate. The so-called mixed crystals of lead and barium nitrates are not homogeneous, but vary in composition with the nature of the face to which they correspond.



The experiments were conducted as follows: from the crystals deposited at 18—25° by a saturated solution of 500 grams of barium nitrate and 10 grams of lead nitrate, 1 gram each of the crystals below the octahedral faces and the cubic faces respectively were separated, and the amount of lead in each determined by means of a colorimetric method; the results showed that the parts of the crystals corresponding with the octahedral faces contained more lead than those under the cube faces, and similar results were obtained with crystals of lead nitrate which had been grown in a solution containing a little baryta and nitric acid.

M. A. W.

**Influence of Small Quantities of Elements in Copper on its Reactions with Nitric Acid.** JOHN H. STANSBIE (*J. Soc. Chem. Ind.*, 1906, 25, 1071—1075).—The investigation is a continuation of experiments described in a former paper (*Abstr.*, 1906, ii, 166), the apparatus having been modified somewhat to facilitate the determination of the amount of nitrous acid formed in the reactions. For this purpose, the solution was not allowed to come into contact with air until the free acid had been neutralised by addition of a measured quantity of sodium carbonate in excess. The nitrous acid was then estimated by means of ferrous ammonium sulphate and potassium permanganate solutions, and the unneutralised sodium carbonate gave the amount of acid used in the reaction.

Experiments with pure copper at temperatures from 15—85° indicate that the secondary change by which nitric oxide is produced is practically uninfluenced by a rise of temperature, whereas the amount of nitrous acid formed decreases considerably. The nitrous acid is supposed to result from the oxidation of nitric oxide according to the equation  $2\text{NO} + \text{H}_2\text{O} + \text{HNO}_3 = 3\text{HNO}_2$ . At all temperatures a certain amount of nitric acid disappears in changes other than the formation of nitric oxide and nitrous acid. This may be ascribed in part to the formation of ammonia, but the quantities of ammonia observed are not large enough to explain the entire loss.

Pure bismuth dissolves according to the equation  $2\text{Bi} + 8\text{HNO}_3 = 2\text{Bi}(\text{NO}_3)_3 + 4\text{H}_2\text{O} + 2\text{NO}$ , and the whole of the nitric acid used is accounted for by the nitric oxide and nitrous acid formed. Arsenic also reacts in a simple manner, and the nitric acid used corresponds with the equation  $6\text{As} + 10\text{HNO}_3 = 3\text{As}_2\text{O}_5 + 5\text{H}_2\text{O} + 10\text{NO}$ . Experiments with copper alloys containing 0—3% of arsenic or antimony at 65° show that the decrease and increase in the amount of nitrous acid, formed as the amount of the second element increases follow pretty closely the decrease and increase in the volume of the liberated nitric oxide (*loc. cit.*). In the case of copper-bismuth alloys, the amount of nitrous acid formed increases slightly until the percentage of bismuth reaches about 0.25 and then decreases exactly as was observed for the volume of nitric oxide liberated. The author considers that the conclusions drawn in the first paper are supported by these further experiments.

H. M. D.

**Mercury Chromates.** A. GAWALOWSKI (*Chem. Centr.*, 1906, ii, 1307; from *Pharm. Post*, 39, 602).—*Mercuric perchromate* is obtained

as a scarlet-red, granular precipitate on adding a solution of potassium dichromate and some 25% sulphuric acid to a solution of a mercuric salt. The dried substance on ignition evolves water, oxygen, and mercury vapour, and leaves a brownish-black modification of chromic oxide. If sulphuric acid is not present, a brick-red, earthy precipitate of mercury dichromate is obtained, which on ignition yields a finch-green modification of chromic oxide. When metallic mercury is left for several days covered with a cold solution of potassium dichromate and an excess of concentrated sulphuric acid, a bright red variety of mercuric chromate is formed, which is probably a polychromate; this substance on ignition leaves about 42% of a leaf-green variety of chromic oxide. P. H.

**Chemistry of the Rare Earths. II.** GRÉGOIRE N. WYROUBOFF and AUGUSTE VERNEUIL (*Ann. Chim. Phys.*, 1906, [viii], 9, 289—361. Compare Abstr., 1906, ii, 88).—This paper is chiefly a detailed account of work already published relating to the nature of the oxides of cerium and the separation and purification of cerium compounds (compare Abstr., 1897, ii, 452; 1898, ii, 222; 1899, ii, 224, 423, 598, 613); also polemical against Brauner regarding the atomic weight of the element (compare Abstr., 1897, ii, 492; 1898, ii, 294; and Brauner, Abstr., 1903, ii, 295). The red sulphate of cerium (compare Rammelsberg, Abstr., 1873, 601; Muthmann and Stützel, Abstr., 1900, ii, 544; Meyer and Aufrecht, Abstr., 1904, ii, 175) forms hexagonal crystals which are strongly dichroic, appearing a beautiful red when viewed across the base and deep orange or yellow in a perpendicular direction; the composition of the salt is represented by the formula  $\text{Ce}_3\text{O}_4 \cdot 3\text{CeO} \cdot 8\text{SO}_3 \cdot \text{SO}_4\text{H}_2 \cdot 28\text{H}_2\text{O}$ , and it is to be regarded as the sulphate of the violet oxide  $\text{Ce}_7\text{O}_8$  ( $\text{Ce}_3\text{O}_4 \cdot 4\text{CeO}$ ). M. A. W.

**Elements of the Ytterbium Group.** CARL AUER VON WELSBACH (*Monatsh.*, 1906, 27, 935—945).—Most of the supposed elements of the ytterbium group which have been described are compounds. The present paper contains a description of a part of the author's work on the isolation of the true elements of this group. The material for the investigation, consisting of crude ytterbium oxalate obtained from monazite and containing cerite earths, thorium, and phosphoric acid, was treated in the manner previously described for the working up of crude earths (Abstr., 1884, 717; 1885, 350, 1113), and the elements of the ytterbium group separated finally as the basic nitrates. These were purified by recrystallisation as follows: one-half of the substance was stirred with water and neutralised with nitric acid; the other half was then recrystallised from the neutral solution of the nitrate and a series of fractions of the basic nitrate obtained, the final liquid giving only a weak erbium spectrum. This process was repeated twenty-one times, when the fractions, which were free from yttrium, all contained erbium, ytterbium, holmium, and dysprosium.

To separate the elements of the ytterbium group, advantage is taken of the differences in the solubility in a saturated solution of ammonium oxalate of the double oxalates which are formed by precipitation of the moderately concentrated solution of the nitrates with a hot

saturated solution of ammonium oxalate. The solubility of ytterbium ammonium oxalate in a saturated solution of ammonium oxalate is ten times that of holmium ammonium oxalate. The method of fractional crystallisation is described in detail.

Of the series of about one hundred fractions obtained, the first is almost colourless, about the next fifteen are light yellow, then orange-yellow, passing through the rose-coloured erbium to the colourless ytterbium salts at the other end. Observed directly by transmitted light the first fractions show a changed dysprosium with traces of the neodymium spectrum; the light yellow fractions give the normal dysprosium, the orange-yellow the holmium, and the intensely rose-coloured the characteristic erbium spectrum. As the rose-colour weakens, the erbium spectrum changes into a modified spectrum which is termed Ery, after which the thulium lines appear, to disappear in the colourless ytterbium fractions.

The spark spectra of the first fractions are complicated and contain lines which do not coincide with those of any known element. The orange-yellow fractions which give the most intense holmium absorption spectrum, give a yttrium spark spectrum in which the holmium lines are absent, but in which other groups of lines appear. The rose-coloured fractions give the erbium, the colourless soluble fractions the ytterbium spark spectra.

The mother liquors from the crystallisation of the ammonium oxalates were further investigated and found to contain ytterbium, traces of scandium, thorium, uranium, iron, and substances such as alumina and silicic acid, which are derived partly from the water and partly from the ammonium oxalate. The fraction which should have contained pure ytterbium gave a spark spectrum which shows marked differences from the ytterbium spectrum; this is considered to be the first certain indication of the degradation of ytterbium. G. Y.

**Catalytic Action of Aluminium Chloride.** PAUL ROHLAND (*Chem. Zeit.*, 1906, 30, 1173—1174).—The addition of 0.2 molecule of aluminium chloride per litre to a mixture of quicklime and water considerably accelerates the setting of the lime. The rate of hydration of the two sulphates of calcium, containing respectively  $1\frac{1}{2}\text{H}_2\text{O}$  and  $2\text{H}_2\text{O}$ , is also increased, whereas that of the anhydrous sulphate is decreased. The setting of Portland cement is accelerated by small quantities of aluminium chloride, but is retarded by quantities above 7%. The accelerating effect of aluminium chloride is increased by the presence of sodium carbonate or of aluminium sulphate. A summary is given of the other reactions in which aluminium chloride acts as a catalytic agent. P. H.

**Crystallised Aluminium Sulphate.** A. GAWALOWSKI (*Chem. Centr.*, 1906, ii, 1236; from *Zeit. Oesterr. Apoth. Verein.*, 44, 460).—Crystallised aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , is obtained by dissolving "aluminium carbonate" in sulphuric acid, adding nitric acid, and evaporating until no more nitric oxide is evolved; it crystallises in smooth tetrahedra with truncated edges. The salt obtained by heating the carbonate with sulphuric acid alone differs from aluminium sul-

phate in evolving nitric oxide, when treated with nitric acid; the author considers that the aluminium in the "carbonate" is combined in the form  $\text{AlO}\cdot\text{OH}$ .  
P. H.

**Revision of the Atomic Weight of Manganese.** GREGORY P. BAXTER and MURRAY A. HINES (*J. Amer. Chem. Soc.*, 1906, **28**, 1560—1580).—From a computation of the values of the atomic weight of manganese obtained by previous workers, Clarke has found the most probable value to be 54.987.

The present investigation was carried out with manganous chloride and bromide. These salts have been analysed previously by Dewar and Scott (*Abstr.*, 1883, 856), who obtained for the atomic weight the values, 54.91 from the chloride and 54.97 from the bromide.

Four specimens of manganous bromide were employed. Two of these (*A* and *B*) were prepared from pure potassium permanganate in the following manner. The solution was treated with sulphur dioxide, ammonium carbonate was added to the resulting solution of manganous sulphate, and the precipitate was well washed and then dissolved in nitric acid. The manganous nitrate thus obtained was crystallised repeatedly from a solution acidified with nitric acid, was afterwards treated with ammonium carbonate, and the precipitate was thoroughly washed and dissolved in hydrobromic acid in a quartz dish. The solution of the bromide was heated to expel bromine and the salt was repeatedly crystallised and finally dried in a vacuum over potassium hydroxide.

The third sample (*C*) was prepared from pyrolusite by dissolving it in hydrochloric acid, boiling the solution to expel chlorine, passing hydrogen sulphide into the solution, and fractionally precipitating with sodium hydroxide until the precipitate was obtained free from iron. The manganese was then precipitated with ammonium carbonate and the manganous carbonate was treated as in the preparation of the previous samples.

The fourth sample (*D*) was prepared from manganous sulphate by treating the solution with hydrogen sulphide, converting the sulphide into carbonate, and heating the latter as in the former cases.

Two samples of manganous chloride were prepared, one from the carbonate obtained in the preparation of sample *B*, and the other from the mother liquors of the manganous nitrate resulting from the preparation of samples *B* and *D*.

The hydrobromic, hydrochloric, and nitric acids, and the silver employed, were carefully purified by methods which are described.

The analysis of the bromide and chloride was effected by titrating weighed portions of the salts, after fusion in hydrogen bromide or chloride, against weighed portions of pure silver; the precipitated silver salts were collected and weighed. In some experiments the silver nitrate was added to the manganous salt, whilst in other cases the operation was carried out in the reverse manner. Various precautions were taken to ensure accuracy and vacuum corrections were applied. Manganous bromide has  $D_4^{25}$  4.385 and manganous chloride  $D_4^{25}$  2.977.

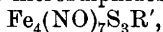
Thirty-one analyses were made of the bromide and fourteen of the chloride, and the results are tabulated. The average of the results obtained with the bromide gives  $Mn = 54.957$ , and the average of those obtained with the chloride gives  $Mn = 54.958$  [ $Ag = 107.930$ ;  $Br = 79.953$ ;  $Cl = 35.473$ ]. E. G.

**Corrosion of Iron by Acids.** C. F. BURGESS and S. G. ENGLE (*Trans. Amer. Electrochem. Soc.*, 1906, 9, 199—206).—The rate of solution of different kinds of iron in normal solutions of sulphuric and hydrochloric acid has been measured. Electrolytic iron deposited from a solution containing sulphate and chloride, the same iron which had been heated to about  $1000^\circ$  and allowed to cool slowly, soft sheet-iron containing little carbon, tempered steel, and ordinary cast-iron were used in the experiments. The electrolytic iron before heating dissolved about four times as rapidly as the steel, six times as rapidly as the cast-iron, and about forty times as rapidly as the soft sheet-iron. After heating, the rate of solution of the electrolytic iron diminished to about one-fortieth of its original value. The authors suppose that this is indirectly due to the removal of hydrogen by the thermal treatment, but suggest that change of the crystalline structure is the primary cause. A coarsely crystalline sample of electrolytic iron was found to dissolve more rapidly than a more dense deposit. Electrolytic iron is suggested as a means of obtaining pure hydrogen by the action of acids.

Traces of arsenic exhibit a very marked influence in protecting iron from the corroding action of acids.

No definite relationship between the difference of potential exhibited by the various samples of iron in acid solution and the rate of corrosion could be detected. H. M. D.

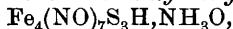
**Roussin's Salts.** ITALO BELLUCCI and C. CECCHETTI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 467—474. Compare *Abstr.*, 1905, ii, 253).—Roussin's salts or nitrosulphides of the first series,



when treated with alkali hydroxide, pass into nitrosulphides of the second series,  $Fe(NO)_2SR'$ .

When the sodium salt,  $Fe_4(NO)_7S_3Na \cdot 2H_2O$ , is treated with hydrazine or hydroxylamine in either acid or alkaline solution, it yields the corresponding hydrazine or hydroxylamine compound, whilst with phenylhydrazine hydrochloride it gives the phenylhydrazine derivative (compare Hofmann and Wiede, *Abstr.*, 1896, i, 291).

The *hydrazine* salt,  $Fe_4(NO)_7S_3H \cdot N_2H_4$ , dissolves slightly in water and readily in alcohol or ether. The *hydroxylamine* derivative,



is readily soluble in water, alcohol, or ether. The *phenylhydrazine* compound,  $Fe_4(NO)_7S_3H \cdot N_2H_3Ph$ , melts under hot water, in which, and in benzene, it is sparingly soluble, and dissolves in alcohol or ether. The *semicarbazide* salt,  $Fe_4(NO)_7S_3H \cdot N_2H_3 \cdot CO \cdot NH_2$ , dissolves in water, alcohol, or ether.

All these new compounds form shining, black crystals and are

markedly stable. They can be crystallised from water and remain unaltered for a long time in the absence of light. T. H. P.

**Behaviour of Chromium towards Sulphuric Acid.** ALFRED BURGER (*Ber.*, 1906, 39, 4068—4072. Compare Döring, *Abstr.*, 1902, ii, 660; 1906, ii, 451; Mazzucchelli, *Abstr.*, 1905, ii, 570).—The author has attempted, without success, to estimate chromium by measurement of the hydrogen evolved on solution of the metal in an acid. A sketch is given of the apparatus employed.

When dissolved in boiling sulphuric acid, a sample of chromium, prepared by Goldschmidt's process, and containing 99% of chromium, forms a blue, or at lower temperatures a greenish-blue, solution. In both experiments more hydrogen is evolved than corresponds with the formation of the chromous salt, a pure solution of which cannot be obtained. On concentration of the solution, a further evolution of hydrogen takes place, but is not complete on addition of dilute sulphuric acid and re-evaporation until fumes of sulphuric acid are given off. The rate of oxidation of the chromous to the chromic sulphate is found to be greatest in a 48% solution. The oxidation takes place more rapidly in hydrochloric acid solution.

The chromous salt present in the solution is estimated best by addition of an excess of ferric sulphate and titration of the resulting ferrous sulphate with potassium permanganate, and the total chromic salt by oxidation to chromic acid by means of persulphate and titration with ferrous ammonium sulphate and potassium permanganate.

G. Y.

**Reduction of Chromium Oxide by Boron.** ARMAND BINET DU JASSONEIX (*Compt. rend.*, 1906, 143, 897—899).—Moissan (*Abstr.*, 1894, ii, 454) first prepared a crystalline chromium boride by heating the two elements in a carbon crucible in an electric furnace; Tucker and Moody (*Trans.*, 1902, 31, 14) showed that the compound has the composition represented by the formula  $\text{CrB}$ ; and Wedekind and Fetzner (*Chem. Zeit.*, 1905, 29, No. 98) obtained the same compound by the aluminothermic process; the author, however, finds that when chromium oxide is reduced by boron in magnesia crucibles heated in an electrical furnace the fused masses thus obtained contain 5 to 17% of combined boron, the boride  $\text{CrB}$  ( $\text{B} = 17.4\%$ ) representing the limit of saturation of chromium by boron. These borides are very hard and scratch glass or quartz; those containing about 7% of boron have a well-marked, crystalline structure which disappears as the proportion of boron increases, and the boride  $\text{CrB}$  is not crystalline. The densities vary from 6.8 (7% boron) to 6.1 (16% boron), and all the compounds are attacked by hydrofluoric, hydrochloric, or sulphuric acid even in the cold, with the formation of boric acid. Nitric acid or alkaline solutions have no action on them; chlorine attacks them with incandescence, but incompletely below a red heat, forming a mixture of chromous and chromic chlorides; hydrogen chloride attacks them under similar conditions, liberating hydrogen and forming chromous

chloride, and they are oxidised with incandescence by the action of fused alkali carbonates or hydroxides.

When the reduction of chromium oxide by boron is carried out in carbon crucibles, the fused products have a crystalline structure but always contain carbon.

M. A. W.

**Derivatives of Quinquevalent Chromium. II.** RUDOLF F. WEINLAND and M. FIEDERER (*Ber.*, 1906, **39**, 4042—4047. Compare Weinland and Fridrich, *Abstr.*, 1906, **i**, 37).—Chromium oxychloride forms double salts with chlorides of the alkali metals. The *potassium* salt,  $\text{CrOCl}_2 \cdot 2\text{KCl}$ , forms rhombic prisms of a dark garnet-red colour. Its oxidising power gradually diminishes when it is kept in a desiccator. Corresponding *rubidium*, *cæsium*, and *ammonium* salts have been prepared and analysed. Their crystalline forms are similar to those of the corresponding double salts derived from molybdenum oxychloride (Klason, *Abstr.*, 1901, **ii**, 162; Nordenskjöld, *ibid.*, 454) and from columbium oxychloride (Weinland and Storz, *Abstr.*, 1906, **ii**, 764). The *cæsium* compound has been shown to be isomorphous with the compound  $\text{CbOCl}_2 \cdot 2\text{CsCl}$ .

J. J. S.

**Reduction of Metallic Sulphides.** OLIVER W. BROWN (*Trans. Amer. Electrochem. Soc.*, 1906, **9**, 109—115).—The product obtained by heating molybdenite in graphite crucibles at a high temperature contains considerable quantities of sulphur. Complete reduction can, however, be effected by heating the sulphide with a mixture of lime and coke. An excess of lime is advantageous, but an excess of carbon leads to the formation of carbide, which retains a considerable quantity of molybdenum. This method of reduction is superior to the ordinary method of roasting and subsequent reduction with carbon in that it prevents loss of metal by volatilisation of the oxide. When galena is similarly heated in the electric furnace with lime and coke, very little lead is obtained, and this is probably due to the formation of a stable double sulphide of lead and calcium. The reduction of stibnite is also very incomplete.

H. M. D.

**New Molybdenum Silicide.** OLIVER P. WATTS (*Trans. Amer. Electrochem. Soc.*, 1906, **9**, 105—107. Compare Vigouroux, *Abstr.*, 1900, **ii**, 144).—A molybdenum silicide of the probable formula  $\text{MoSi}_2$  has been obtained by heating a mixture of the oxides of molybdenum, silicon, and boron with metallic copper and aluminium in an arc furnace with the addition of cryolite as a flux and lime as a retarder to prevent the reaction from becoming too violent. By successive treatment of the product with nitric acid and dilute hydrofluoric acid, dark coloured crystals with a metallic lustre were obtained. These correspond closely with the formula  $\text{MoSi}_2$ , but contain small quantities of boron and iron. The silicide is not acted on by boiling nitric acid, boiling aqua regia, or boiling hydrofluoric acid, but reacts with incandescence with fused sodium carbonate and slowly with fused sodium nitrate, D<sup>20.5</sup> 6.31.

H. M. D.

**Reduction of Molybdic Acid in Solution by Molybdenum, and the Titration of the Reduced Solution by Permanganate.**

MARCEL GUICHARD (*Compt. rend.*, 1906, 143, 744—746. Compare Abstr., 1901, ii, 659).—When a solution of the compound  $\text{MoO}_3\text{SO}_3$  containing not less than 560 grams  $\text{H}_2\text{SO}_4$  per litre is placed in contact with a large excess of powdered molybdenum in a closed vessel for a period of several months, a brown solution is obtained which contains a salt of the oxide  $\text{Mo}_2\text{O}_5$  and not of the oxide  $\text{MoO}_2$  as stated by Rammelsberg (*Ann. Phys. Chem.*, 1864, 127, 281). This fact, taken in conjunction with the results obtained by Bailhache (Abstr., 1902, ii, 243) and Klason (Abstr., 1901, ii, 162), render it probable that the oxide  $\text{MoO}_2$  does not form salts. The titration of the reduced solution was conducted in an atmosphere of hydrogen by means of a permanganate solution which had been standardised against iron reduced in hydrogen.

M. A. W.

**Preparation of Hydrated Hypovanadic Acid.** GUSTAVE GAIN (*Compt. rend.*, 1906, 143, 823—825).—The *sulphite*,  $2\text{V}_2\text{O}_4 \cdot 3\text{SO}_2 \cdot 10\text{H}_2\text{O}$ , prepared by dissolving in a saturated solution of sulphur dioxide in air-free water the mixture of oxides,  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_4$ , obtained by calcining ammonium metavanadate at a dull red heat, forms fine, silky, clear blue needles, and when an aqueous solution of the salt is boiled, sulphur dioxide is evolved and crystals are deposited which, after drying on porous tile, form a pale red, crystalline powder of hydrated hypovanadic acid,  $\text{V}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

M. A. W.

**Alloys of Palladium and Copper.** RUDOLF RUER (*Zeit. anorg. Chem.*, 1906, 51, 223—230).—The freezing-point curve of the palladium-copper alloys falls regularly from the melting point of palladium (which, in accordance with the most recent determinations, is taken as  $1541^\circ$ ) to the melting point of copper,  $1084^\circ$ , the part representing alloys rich in copper being nearly horizontal. Although the course of certain parts of the curve is somewhat uncertain owing to a tendency to super-cooling, there is no evidence of chemical combination, the metals forming a complete series of mixed crystals.

On etching alloys containing 30—70% of palladium with dilute aqua regia, slender, needle-shaped crystals were observed. The proportion of these crystals was not appreciably altered by heating for two hours at  $1500^\circ$  or for the same period at  $1180^\circ$ , just above the melting point of the mixture, and did not attain a maximum with a definite composition of the alloy, so that they do not indicate the formation of a chemical compound.

Even up to 90% of palladium the alloys retain the structure of copper. Those containing 10% of palladium are red in colour; when more than 20% of the same element is present they are white.

The alloys are rather harder than the metals themselves and this property attains its maximum when the components are present in equal parts by weight.

G. S.



**Solid Solutions in the Dissociation of Palladous Oxide and Cupric Oxide.** LOTHAR WÖHLER (*Zeit. Elektrochem.*, 1906, 12, 781—786).—Further experiments have been made on the dissociation of palladous oxide (compare Abstr., 1906, ii, 94). The principal results are that the pressure observed depends on the relative quantities of oxide and metal present and also on the time of heating. The greater the relative amount of metal the lower is the pressure. The results are best explained by supposing that palladium slowly dissolves in the oxide, forming a solid solution the dissociation pressure of which is lower than that of the pure oxide. The dissolution takes place very slowly, so that the pressure observed depends on the time of heating.

The dissociation pressures of cupric oxide were measured at temperatures between  $960^{\circ}$  and  $1084^{\circ}$ ; its m. p. was found to be  $1064^{\circ}$ . That solid solutions are formed in this case was shown by heating 2 grams of the oxide in a vacuum quartz tube (volume 20 c.c.) at  $1000^{\circ}$ , equilibrium is reached in a few minutes at 111 mm. The tube was again evacuated and equilibrium re-established; the repetition of these operations gave pressures of 106, 104, 101, 95, and 91 mm. Similar results were obtained at other temperatures. An experiment with 7.3 grams of the oxide gave a dissociation pressure of 50 mm. at  $960^{\circ}$ ; taking this as the dissociation pressure of the pure oxide and using the heat of dissociation of copper oxide,  $2\text{CuO} = \text{Cu}_2\text{O} + \text{O} - 33.5$  Cals., the dissociation curve of the pure oxide is calculated from van't Hoff's equation. The curve so obtained gives higher pressures than any of those measured with mixtures of copper and copper oxide, but the experimental curves approach it more nearly the purer the copper oxide used.

T. E.

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## Mineralogical Chemistry.

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**Researches on Vulcanism.** ALBERT BRUN (*Arch. Sci. phys. nat.*, 1906, [iv], 22, 425—448).—It is suggested that the gases produced by the dissociation of ammonium chloride and ammonium nitrate, which salts are of deep-seated origin, are the main causes of volcanic explosions, and that aqueous vapour is of little importance in this connexion.

L. J. S.

**Lead and Arsenic Minerals as Fumarole products in the Recent Eruption of Vesuvius.** ALFRED LACROIX (*Compt. rend.*, 1906, 143, 727—730).—During the recent eruption of Vesuvius numerous fumaroles were opened along fissures near the crater. On May 3 these were in an acid stage, evolving water vapour charged with hydrochloric and sulphuric acids; the temperature was 350°. Specimens of the solid material deposited by the fumaroles were collected on this date, and also subsequently in July and September. The

most abundant consists, like that of earlier eruptions, of chlorides of iron, potassium, sodium, calcium, magnesium, &c., but, with the exception of erythrosiderite, the mineral species are not well individualised. The chlorides are coated in places with realgar, either as fused, glassy, isotropic crusts or as minute crystals. Galena was also noticed as small cubes (compare Abstr., 1906, ii, 766) in association with crystals of magnetite (or magnesioferrite), hæmatite, pyrrhotite, and pyrites. The galena would have been formed by the action of hydrogen sulphide on vapours of lead chloride. In some cases it has been altered to lead chloride by the action of hydrochloric acid, as shown by the existence of pseudomorphs of cotunnite after galena. Lead chloride is also present in the scoria, and may be extracted by boiling water. This occurrence of lead is commented on in connexion with the formation of mineral-veins.

L. J. S.

**Formation of Quartz in Silicate Fusions.** P. D. QUENSEL (*Centr. Min.*, 1906, 657—664).—A mixture of oligoclase (74 parts) and silica (26 parts) was heated with 1—6% tungstic oxide for several hours at temperatures of 800—1000° while superheated steam was forced through the mass. The microscopical examination of the glassy products proved the presence of minute crystals of quartz. The tungstic oxide acts as a "mineraliser" by reducing the viscosity of the mass and lowering its temperature of fusion. Tridymite was formed when silica was fused with a large excess of sodium tungstate at 950—1000°.

L. J. S.

**Dioxides of Elements of the Fourth Group of the Periodic System.** JACOB BECKENKAMP (*Zeit. Kryst. Min.*, 1906, 42, 448—474).—Constants are deduced for a theoretical tetragonal modification of silica, and are compared with those of the known crystallised modifications of silica; and the latter are compared with the pseudo-rhombohedral forms produced by the twinning of rutile. The relations between atomic weights and crystallographic constants in the several oxides are discussed.

L. J. S.

[Cassiterite, Jamesonite, Tapiolite, &c., from South Dakota.] WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1906, 8, 167—182).—*Cassiterite*.—Analyses I—IV are of material from various mines in the Black Hills district of South Dakota; also anal. V of cassiterite from Mecklenberg, North Carolina. Tantalite is associated with some of the specimens, but appears to have no connexion with the presence or absence of tantalic acid in the cassiterite:

	SuO <sub>2</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	Insol.	Ign.	Total.	Sp. gr.
I.	94.36	2.42	1.80	1.00	—	—	99.58	6.622
II.	96.08	—	1.90	0.88	—	0.12	99.68	6.680
III.	98.22	—	0.72	—	0.64	0.34	99.92	7.019
IV.	98.13	—	0.43	—	1.40	—	99.96*	
V.	95.18	3.82	{ 1.11 (FeO)	—	—	—	100.11	6.767

\* Also trace of CaO.

*Jamesonite*.—Columnar masses occur in quartz-veins at Sheridan,

Pennington Co., S.D.; analysis VI agrees fairly closely with the formula  $2\text{PbS}, \text{Sb}_2\text{S}_3$ .

*Meneghinite*.—Analysis VII of fibrous material from Rochford, Pennington Co., S.D., agrees with  $4\text{PbS}, \text{Sb}_2\text{S}_3$ :

	S.	Sb.	Pb.	Fe.	Cu.	Zn.	Co.	Insol.	Total.	Sp. gr.
VI.	18.90	26.99	51.15	1.30	0.24	0.05	trace	1.13	99.76	5.81
VII.	17.51	18.20	62.85	trace	0.86	—	—	0.49	99.91	* 6.21

\* Also traces of As, Bi, Cd.

*Hübnerite*.—Crystallised material from Comstock mine, Lawrence Co., S.D., gave anal. VIII; massive material from Sunday Gulch, Pennington Co., S.D., anal. IX:

	WO <sub>3</sub> .	SnO <sub>2</sub> .	Cb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	MnO.	FeO.	CaO.	Total.
VIII.	75.12	—	—	—	20.54	3.01	1.04	99.71
IX.	74.46	—	—	—	19.90	3.29	1.05	99.87 *
X.	0.11	0.07	4.29	78.61	—	16.85	—	100.24 †
XI.	0.59		3.90	78.58	—	15.60	—	99.96 ‡

\* Including: Insol., 0.42; Ignition, 0.75.

† Including: Cassiterite, 0.31; TiO<sub>2</sub>, trace.

‡ Including: Insol., 1.29.

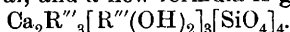
*Tapiolite*.—Indistinct crystals from granite at Custer City, S.D., were determined by Penfield to be tetragonal, D. 7.218; analyses X and XI on the same sample of material. The method employed for the determination of tantalic and niobic acids is discussed.

Analyses are also given of some zinc-blendes which phosphoresce when scratched; the material is mixed with other minerals, and the analyses suggest no cause for the phosphorescence. L. J. S.

**The Gas Observed when Tantalite is Attacked by Potassium Hydroxide.** CAMILLE CHABRIÉ and F. LEVALLOIS (*Compt. rend.*, 1906, 143, 680—681).—When tantalite is heated to redness in a vacuum there is a slight evolution of gas containing 84% carbon dioxide, 12.4% nitrogen, and 3.1% oxygen. If the mineral is subsequently fused in a vacuum in a Jena glass tube lined with silver with potassium hydroxide dried by prolonged fusion in a current of hydrogen, water vapour is formed and a gas is evolved at the rate of 11.5 to 14.5 c.c. per gram of tantalite, which consists of 93.2% hydrogen, 4.6% nitrogen, and 1.2% oxygen. The nitrogen and oxygen are due to air occluded in the mineral, the water and hydrogen are formed by the replacement of the ferrous oxide of the mineral by potassium oxide and its subsequent oxidation at the expense of the potassium hydroxide with the formation of hydrogen, water, and iron sesquioxide according to the equation:  $2\text{TaO}_5, \text{FeO} + 4\text{KOH} = 4\text{KTaO}_3 + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + \text{H}_2$  (compare Moissan, *Abstr.*, 1881, 74).

Ilmenite (titaniferous iron) is similarly decomposed when fused with potassium hydroxide, hydrogen and water being evolved:  $2\text{TiO}_2, \text{FeO} + 4\text{KOH} = 2\text{K}_2\text{TiO}_3 + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + \text{H}_2$ . M. A. W.

**Hellandite from Kragerö, Norway.** WALDEMAR C. BRÖGGER (*Zeit. Kryst. Min.*, 1906, 42, 417—439).—In the granitic pegmatite-veins, which are quarried for felspar in the neighbourhood of Kragerö, the following minerals are found: microcline-perthite, quartz, tourmaline, orthite, titanite (yttrotitanite), thorite, euxenite, apatite, phenacite, and hellandite; brief descriptions are given of each of these, and a detailed description of hellandite (*Abstr.*, 1903, ii, 657). Hellandite when fresh is nut-brown with a resinous lustre on the conchoidal fracture; some of the optical characters are now given; usually, however, the mineral is much altered and is then optically isotropic. The following are new analyses by L. Andersen-Aars, both made on altered material; the more altered material of analysis II was white and earthy. In analysis I, 6% of the water is lost gradually up to 500°, and the remaining 5% is expelled only at a red heat. The latter appears, therefore, to enter into the constitution of the mineral, and a new formula is given as



	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Mn <sub>2</sub> O <sub>3</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	Er <sub>2</sub> O <sub>3</sub> .	ThO <sub>2</sub> .
I.	23·66	10·12	2·56	5·91	1·01	19·29	15·43	0·62
II.	27·88	9·67	2·01	3·13	0·37	19·71	13·26	0·30
	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.		
I.	9·81	0·10	0·23	0·06	11·75	100·55		
II.	9·97	0·13	0·41		13·09	99·93		

A relation is traced between the crystallographic and chemical characters of hellandite, guarinite, danburite, and topaz. Hellandite is near to, but distinct from, gadolinite, kinosite, rowlandite, thalénite, and yttrialite.

L. J. S.

**Manganese-Garnet containing Yttrium.** CARL BENEDICKS (*Bull. Geol. Inst. Upsala*, 1906, 7, 271—277).—Spessartite occurs at Kårarfvet, near Falun, in Sweden, as rounded masses, rarely as distinct crystals, embedded in quartz and albite. Analyses by O. Tenow, of pale red material (I and II) and of dark brown (III), gave:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	Total.	Sp. gr.
I.	35·67	22·50	1·19	19·17	21·91	trace	100·44	4·197
II.	36·23	19·15	1·18	18·76	23·44	0·56	99·38	
III.	35·36	22·34	1·23	22·01	18·80	trace	99·74	4·068
IV.	5·5	n. d.	0·7	3·1	1·4	n. d.	—	—

Under IV is given the composition of the portion which went into solution when the pale red material was digested with dilute hydrochloric acid. The few previous analyses of garnets containing yttrium, and those of Swedish spessartite, are quoted.

L. J. S.

**Alkali Quartz-Porphyrries in Corsica. Remarkable Occurrence of Orthoclase.** J. DEPRAT (*Compt. rend.*, 1906, 143, 753—756).—Dykes of quartz-porphyry containing phenocrysts of quartz and anorthoclase and microliths of ægirite and riebeckite occur in connexion with the soda-granites of Corsica. A description is also given of simple and twinned crystals of orthoclase from a weathered microgranulite from Corsica.

L. J. S.

## Physiological Chemistry.

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**Reaction of the Blood in Rarefied Air as Determined by Titration and by the Electrometric Method.** ALBERTO AGGAZZOTTI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 474—483).—The author has measured (1) the concentration of the hydrogen ions, and (2) the acidity towards sodium hydroxide of the blood of small dogs after these have been subjected to a moderately rapid diminution of pressure under the bell jar of an air-pump. It is found that the alkalinity of the blood undergoes diminution under these conditions, but not to so great an extent as when the diminution in pressure is attained by ascent of a mountain, in which case the action is of longer duration (compare Galeotti, *ibid.*, 1903, [v], 12, ii, 646). T. H. P.

**The Stroma of the Red Corpuscles.** M. PIETTRE and ANTONY VILA (*Compt. rend.*, 1906, 143, 787—790. Compare Abstr., 1905, i, 399, 500; 1906, ii, 373).—The stroma obtained from the red corpuscles by hæmolytic and extraction with ether forms a soft, viscous substance, greyish-red or yellowish-white in colour, soluble in water and readily fermented. The amount obtained from a litre of defibrinated blood varies with the nature of the blood; the blood of the horse yields 2·65—2·54; the pig, 2·90; the dog, 3·65; the guinea-pig, 3·74, and the pigeon, 21·55. The percentage numbers obtained by analysing the dried product were C, 53·32; H, 7·47; N, 11·70 in the stroma from horse's blood, and C, 54·22; H, 8·20; N, 13·21 in the stroma from dog's blood. The amount of ash in stroma, isolated as above, is much higher than that obtained by previous workers (compare Pascucci, Abstr., 1905, ii, 729), the percentage amount being as follows: horse, 2·32—3·0; dog, 2·9; duck, 8·25; pigeon, 8·96. The ash contains manganese, is free from chlorine, and contains 0·31—0·33; 2·6 or 2·3 per cent. of phosphorus, according as it is derived from the blood of horse, fowl, or duck respectively. M. A. W.

**Action of Photodynamic Substances on Colourless Corpuscles.** HUGO SALVENDI (*Chem. Centr.*, 1906, ii, 1511; from *Arch. klin. Med.*, 87, 356—364).—In diffuse daylight, eosin shows a harmful action on frog's leucocytes in six hours, in sunlight in two to three hours. The action on lymphocytes is more rapid. Other substances, fluorescein, Bengal red, &c., act in the same way but not so rapidly. The action of these material on *Paramæcium* is similar.

W. D. H

**Photodynamic Action in Alkaline, Neutral, and Acid Media.** R. DAX (*Chem. Centr.*, 1906, ii, 1511—1512; from *Arch. klin. Med.*, 87, 365—372).—If the photodynamic action of eosin and similar substances is due to the amount of acid liberated, the action should be greater in an alkaline than in a neutral or acid medium. But the action on *Paramæcium* is not greater in an alkaline than in a

neutral or acid medium. The reaction also does not influence the rate at which they destroy invertase. W. D. H.

**The Chemical Nature of Fertilisation.** JACQUES LOEB (*Biochem. Zeit.*, 1906, 1, 183—206).—A somewhat condensed account of the author's work and theories; artificial parthenogenesis is regarded as an acceleration of oxidation processes directed into certain channels. The influence of agents and reagents on these is discussed.

W. D. H.

**The Physiologico-pathological Meaning of Hyperacidity of the Gastric Juice.** ADOLF BICKEL (*Biochem. Zeit.*, 1906, 1, 153—160).—A discussion from the medical point of view of hyperchlorhydria. The symptom is probably an indication of a complex condition, in which nerves are concerned, and opinions regarding its meaning require revision.

W. D. H.

**Action of Trypsin. II and III.** KARL MAYS (*Zeit. physiol. Chem.*, 1906, 49, 124—187; 188—201).—Pancreatic juice has an ereptic action. This may be due to the continued action of trypsin or to the presence of a second enzyme (pancreatic erepsin). Vernon's positive statement that the second enzyme exists is criticised, but with the present methods for the separation of ferments, the question must still be an open one.

Bayliss and Starling state that the fresh pancreatic juice of the dog contains no trypsin until it is activated by the succus entericus. They attribute the feeble proteoclastic power of the fresh juice to the action of pancreatic erepsin. The view taken by the present author is that it is due to the presence of a small amount of trypsin, for ereptic action in Cohnheim's sense is absent. Extracts of pancreas have only a feeble ereptic action.

W. D. H.

**Digestion and Rennet-action.** MARTIN JACOBY (*Biochem. Zeit.*, 1906, 1, 53—74).—This research arose out of Pawloff's theory that peptic and rennetic actions are both due to one enzyme. Although it is admitted that preparations can be obtained which in certain concentrations exhibit one action only, Pawloff's view is favoured on the whole on account of the resemblances in the action of certain factors which influence the two activities. No specificity was found in the behaviour of anti-substances.

W. D. H.

**Metabolism Experiments in a Woman with a Permanent Biliary Fistula.** PHILIP SHAFFER (*Amer. J. Physiol.*, 1906, 17, 362—391).—The patient's metabolism was normal, except for poor absorption of fats, high excretion of indican (due to increase of intestinal putrefaction), a low excretion of creatinine (to be discussed in a future paper), and a high excretion of ammonia, the cause of which is not understood. The taurine of the bile is not to any extent the source of the neutral sulphur of the urine. The latter was not lower than normal, and was not increased when bile was given by the mouth or through the fistula. In jaundice, it is suggested that the increase in neutral

sulphur may be derived from taurine absorbed from the bile passages into the circulating blood and thus diverted from the normal bile circulation. Absorption of fat was not increased by bile medication or bile injection; absorption of proteids was good. No relation between the composition of the bile and the amount of proteid in the food was found. Excretion of bile is increased by bile medication or bile injection; the bile given is probably not a hepatic stimulant, but merely furnishes the liver with ready-made bile constituents which it excretes by the usual channel.

W. D. H.

**Nutritive Value of Glycerol.** BERNHARD KNAPP (*Chem. Centr.*, 1906, ii, 1510; from *Arch. klin. Med.*, 87, 340).—Glycerol has "proteid-sparing" action and is thus of nutritive value. At the commencement of the glycerol periods, sugar appears in the urine, and a portion of the glycerol given leaves the body as such.

W. D. H.

**The Behaviour of Moss Carbohydrates in the Human Body, and their use in Diabetes Mellitus.** E. POULSSON (*Chem. Centr.*, 1906, ii, 1511; from *Hammarsten's Festschrift*, xiv).—The carbohydrates of two mosses, *Cetraria islandica* and *C. nivalis*, were investigated. In the former plant, about half of the water-soluble carbohydrate consists of lichenin, which on acid hydrolysis yields amorphous products and dextrose. The insoluble carbohydrates are hemicelluloses of which dextran, mannan, and galactan were identified; about 3% of pentosans and a small amount of true cellulose are present. Given in bread, about half the carbohydrates present are absorbed and burnt in the body. *C. nivalis* has a similar composition, except that lichenin is less and hemicelluloses more abundant. A bread prepared from it causes disturbances of health, due to the presence of usnic acid.

W. D. H.

**Proteid Synthesis in Animals.** VALDEMAR HENRIQUES and C. HANSEN (*Zeit. Physiol. Chem.*, 1906, 49, 113—123. Compare Abstr., 1905, ii, 180).—The experiments were made on white rats to determine whether the hydrolytic products of casein obtained by the action of acids act as "proteid-sparers" and whether protamines given in addition assist in lessening the loss of nitrogen. The answer to both questions is in the affirmative; the loss of nitrogen in the body was diminished especially when protamines were given also, as compared with periods during which the animals received no nitrogenous food.

W. D. H.

**Behaviour of Ovo-mucoid in the Organism.** K. WILLANEN (*Biochem. Zeit.*, 1906, 1, 108—128).—This gluco-proteid occurs in considerable amount preformed in eggs (10% in hen's egg-white); it is not altered by boiling. If given by the stomach to men and animals, it is destroyed and behaves like other proteids. If injected intravenously, from 14 to 28% of it reappears in the urine. This does not occur if it is injected subcutaneously. In gastric digestion and during putrefaction, its carbohydrate group (glucosamine) is split off. This does not occur during tryptic digestion, or in autolysis produced by



splenic tissue. In the later stages of putrefaction, the glucosamine is broken up. Ovo-mucoid gives a feeble Adamkiewicz reaction.

W. D. H.

**Effect of Alcohol on Secretion of Bile.** WILLIAM SALANT (*Amer. J. Physiol.*, 1906, 17, 408—428).—Physiological doses of alcohol, however introduced into the body, exert little or no direct secretory action on the digestive glands. This conclusion was confirmed by the present experiments, which were conducted on dogs, the alcohol being given intravenously. An increased flow of bile, sometimes noticed, may, as in the case of other digestive glands, be nervous in origin or due to the formation of secretin, which stimulates the liver as well as the pancreas.

W. D. H.

**Maintenance of Cerebral Activity in Mammals by Artificial Circulation.** CHARLES C. GUTHRIE, F. H. PIKE, and GEORGE N. STEWART (*Amer. J. Physiol.*, 1906, 17, 344—349).—Saline solutions are quite inadequate to sustain the reflex or voluntary functions of the brain in a freshly decapitated animal. Defibrinated blood is effective for eight or nine minutes only; oxygenated active blood from the circulation of another animal of the same species prolongs the period to nineteen minutes.

W. D. H.

**Influence of Temperature on Rate of Heart in the Light of the Law for Chemical Reaction Velocity.** CHARLES D. SNYDER (*Amer. J. Physiol.*, 1906, 17, 350—361).—Experiments on the hearts of various animals, invertebrate and vertebrate (including mammalian), show that the velocity is the same as that for known chemical reactions as influenced by temperature. This is expressed by the formula (Arrhenius),  $\log k = -A/T + \text{constant}$ , in which  $A$  is a constant, and  $k$  is the heart rate at any temperature  $T$ , which falls within certain limits.

W. D. H.

**The Action of Carbon Dioxide and Alcohol on Muscle.** FR. W. FRÖHLICH (*Chem. Centr.*, 1906, ii, 1443—1444; from *Verh. Ges. Deut. Naturf. Ärzte*, 1905, ii, 405—406).—Before paralysis sets in as an action of the two agents investigated, the contractions of muscle and the action currents of nerve increase. This is not regarded as due to an increase in vital processes, but as an accompaniment of the destruction of life, especially on the anabolic side.

W. D. H.

**The Influence of Muscular Work on the Weight and Composition of the Organs.** FELIX ROGOZINSKI (*Biochem. Zeit.*, 1906, 1, 207—228).—In dogs, muscular work causes no change in the physical or chemical characters of the blood. The muscle substance becomes poorer in water, which will account for the loss of weight.

W. D. H.

**The Contents of a Chylous Cyst.** OTTO SCHUMM (*Zeit. physiol. Chem.*, 1906, 49, 266).—The cyst was situated in the mesentery and its contents measured about 1500 c.c. It contained total solids,

39·76; fat (ether extract), 35·76; fatty acids (from soaps), 0·43; proteids, 1·97; ash, 0·9%. On microscopic examination, it was found to contain fat globules and crystals of a mixture of calcium palmitate and stearate. The proteids were globulin, albumin, and a small amount of proteoses. The ash was specially rich in calcium and sodium chloride; it also contained phosphoric acid and potassium. Leucine, tyrosine, and sugar were absent. The fluid contained a peroxidase and probably a fat-decomposing ferment, but no proteo-clastic enzyme. The fat present had the same characters as in human adipose tissue.

W. D. H.

**A Heptose in Human Urine.** F. ROSENBERGER (*Zeit. physiol. Chem.*, 1906, 49, 202—209).—In a case of diabetes, in addition to the ordinary fermentable sugar, a second lœvorotatory carbohydrate was found, which was identified as a heptose. Crystals of *l*-mannoheptosazone (m. p. 203°) were prepared from it.

W. D. H.

**Methylguanidine in Normal Human Urine.** W. ACHELIS (*Chem. Centr.*, 1906, ii, 1445; from *Centr. Physiol.*, 20, 455).—The statement of Kutscher and Lohmann on this subject is confirmed. Thirty litres of urine yielded about 0·7 gram of the picrolonate.

W. D. H.

**Ehrlich's Diazo-reaction and Russo's Methylene-blue Reaction in Urine.** REINHOLD DUNGER (*Chem. Centr.*, 1906, ii, 1518; from *Deut. med. Woch.*, 32, 1582—1583).—Russo's reaction (*Riforma med.*, 1905, 507) consists in shaking 4 or 5 c.c. of urine with four drops of a 1% solution of methylene-blue. A positive reaction is the appearance of an emerald-green colour; a bluish-green or blue colour is negative. Positive results were obtained by him in typhoid, measles, small-pox, and other diseases. In the present research, 1100 urines were examined, but the reaction is of no value. It is given by many urines which do not give Ehrlich's diazo-reaction and *vice versa*. It is not a chemical reaction at all, but is simply due to a mixture of colours, and if the urine contains more than 0·6% of urochrome the result is the green which Russo describes as his positive reaction.

W. D. H.

**Acetonuria in Dogs.** A. BAUMGARTEN and H. POPPER (*Chem. Centr.*, 1906, ii, 1452; from *Centr. Physiol.*, 20, 377—381).—In extra-uterine pregnancy, hæmorrhage into the peritoneum leads to intense and lasting acetonuria, which disappears when the blood is removed. In the present research, isovaleric and butyric acids, after neutralisation by ammonia, were injected (1) into the peritoneal cavity of dogs, or (2) under the skin in amounts of 1 to 2 grams per kilo. of body weight. In the first case, acetonuria ensued; in the second it did not.

W. D. H.

**Phloridzin Diabetes.** KARL GLAESSNER (and ERNST P. PICK) (*Chem. Centr.*, 1906, ii, 1451; from *Verh. Ges. Deut. Naturf. Ärzte*, 1905, ii, 411—412).—The influence of various amino-acids on the ex-

cretion of sugar in diabetes caused by phloridzin in rabbits was investigated. In well-fed animals, alanine and glutamic acid produced the strongest effect, leucine and glycine less, and asparagine none at all. Acetamide, sodium lactate, caffeine, and chloral hydrate also gave negative results. If the animals were fasting, no amino-acid gave a positive result. If, however, the liver of phloridzinised rabbits was administered subcutaneously, glycosuria ensued. If the rabbits' kidneys were removed, phloridzin given, and the animals killed twenty-four hours later, their blood or liver substance given subcutaneously to dogs produced no glycosuria. Phloridzin appears to be destroyed in the blood or rendered inactive. W. D. H.

**The Cause of Death in Acute Diseases of the Pancreas.** N. GULEKE (*Chem. Centr.*, 1906, ii, 1451; from *Verh. Ges. Deut. Naturf. Ärzte*, 1905, ii, 116—119).—The pancreatic secretion causes in many cases fatal poisoning, and in destruction of the pancreatic tissue passes into the blood or lymph stream, by which means it is distributed to the tissues which it destroys. The poisonous substance is trypsin.

W. D. H.

**Action of Magnesium Salts. IV.** SAMUEL J. MELTZER and JOHN AUER (*Amer. J. Physiol.*, 1906, 17, 313—320; compare Abstr., 1906, ii, 473).—Subcutaneous and intravenous injections of magnesium salts produce neither purgation nor intestinal peristalsis. Peristalsis produced in other ways can be completely inhibited by an intravenous injection of magnesium sulphate or chloride in doses insufficient to embarrass the respiration. Intravenous injection of these salts also inhibits the muscular tremor produced by intravenous injection of physostigmine.

W. D. H.

**Behaviour of Nutrose given Subcutaneously and its Relation to the Excretion of Kynurenic Acid and Allantoin.** A. BAUMGARTEN and ERNST P. PICK (*Chem. Centr.*, 1906, ii, 1449; from *Verh. Ges. Deut. Naturf. Ärzte*, 1905, ii, 413—414).—In dogs, the hypodermic administration of 7—8 grams of nutrose increased the excretion of kynurenic acid, whereas the excretion after administration by the mouth is very small. The proteid given is considered to be the source of the acid. No definite conclusion is drawn regarding allantoin. In rabbits, Ellinger's statement is confirmed that hypodermic injection of tryptophan leads to the occurrence of kynurenic acid in their urine, but the similar injection of nutrose or proteoses led to a negative result.

W. D. H.

**The Action of Morphine. I.** RUDOLF MAGNUS (*Pflüger's Archiv*, 1906, 115, 316—330).—In cats, a prolonged milk diet causes chronic diarrhoea, which is stopped by the subcutaneous injection of 4 or 5 centigrams of morphine hydrochloride. Morphine has the same action after the whole of the sympathetic nerve supply from stomach to anus has been cut through and undergone degeneration. The presence of inhibitory nerve fibres is therefore not necessary for morphine action in this direction. After small doses of morphine, the peris-

taltic sodium chloride reflexes of the small intestine cannot be observed with certainty. W. D. H.

**The Liver in Phosphorus Poisoning.** JULIUS WOHLGEMUTH (*Biochem. Zeit.*, 1906, 1, 161—165).—The main outcome of the examination of the livers in cases of phosphorus poisoning in rabbits is that the nuclear material is much less, and much more slowly broken down, than the cell-protoplasm. W. D. H.

**Toxity of some Rare Earths. Their Action on Certain Ferments.** ALEXANDRE HÉBERT (*Compt. rend.*, 1906, 143, 690—693).—The sulphates of thorium, cerium, lanthanum, and zirconium have no toxic action on guinea-pigs or frogs when injected subcutaneously in quantities of 160 mg. per kilo. of body weight. Fishes (minnows) die in solutions of the sulphates containing 0·5 gram per litre, the zirconium and thorium salts are the most poisonous, then follow those of cerium and lanthanum. Germinating seeds of the pea, wheat, or rape are killed when transplanted to a solution containing 5 grams of the rare earth sulphates per litre, whilst experiments conducted on *Aspergillus niger*, beer yeast, diastase, and emulsin show that thorium and zirconium sulphates are poisonous towards the lower organisms and ferments, solutions containing 0·5 or 1 gram of salt per litre being in this respect comparable with solutions of mercuric chloride. Cerium and lanthanum sulphates have no toxic action on the cultures, even in such quantities as 5 or 10 grams per litre. M. A. W.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Oxidation of Hydrogen by Bacteria.** A. J. NABOKICH and A. F. LEBEDEF (Centr. Bakt. Par., 1906, ii, 17, 350—355).—The results of several experiments with Russian black soils (Odessa) and Polish soil showed that hydrogen is oxidised by autotrophic rod bacteria (compare Kaserer, Abstr., 1906, ii, 113; and Immendorff, *ibid.*, 1892, 374).  
N. H. J. M.

**Formation of Arabin by Bacteria and their Relation to the Gum of the Amygdaleae.** W. RUHLAND (*Chem. Centr.*, 1906, ii, 1348; from *Ber. deut. bot. Ges.*, 24, 393—401).—Cultivations of *Bacillus spongiosus* on sucrose give rise to production of mucus; a similar result was obtained with raffinose, but the time required was longer. With mannitol, the production of mucus was very slight, whilst with dextrose and lævulose there was none at all. The gum of the mucus was pure arabin without galactin, hemicellulose, or nitrogenous matter.

It was shown previously that the bacillus (obtained from diseased

cherry shoots) causes a flow of gum when cherry trees are inoculated with it and that the gum is a mixture of arabin and galactin.

N. H. J. M.

**Formation of Free Oxalic Acid by *Aspergillus Niger*.** CARL WEHMER (*Chem. Centr.*, 1906, ii, 1348; from *Ber. deut. bot. Ges.*, **24**, 381—384).—In former experiments an abundant production of oxalic acid by *Aspergillus niger* was always observed, whilst subsequent experiments gave negative results. New experiments have confirmed the results first obtained; the later, negative results were perhaps due to impurities in the calcium carbonate.

N. H. J. M.

**Causes of the Formation of Aldehyde in Wines and the Amounts in some Tuscan Wines.** NAPOLEONE PASSERINI (*Chem. Centr.*, 1906, ii, 1280—1281; from *Staz. sper. agrar. ital.*, **39**, 221—240).—Tuscan wines (62) were found to contain from 1 to 60 mg. of aldehyde per litre. The amount is generally higher in wines containing much alcohol than in those with low amounts of alcohol, and white wines generally contain more than red wines. The amount seems to increase with the age of the wine.

Aldehyde is produced by aerobic ferments (*Mycoderma vini* and *Fermentum aceticum*), but not by anaërobic microbes.

N. H. J. M.

**Formation of Fusel Oil by Yeast.** FELIX EHRLICH (*Ber.*, 1906, **39**, 4072—4075. Compare Pringsheim, *Abstr.*, 1906, ii, 880).—Fusel oil is not formed by the action of acetone-yeast (Albert, Buchner, and Rapp, *Abstr.*, 1902, ii, 521) on sugar alone or in presence of *d*-leucine, which remains unchanged.

G. Y.

**Influence of the Chemical Constitution of the Nitrogenous Food Material on the Fermenting Power of Yeast.** HANS PRINGSHEIM (*Ber.*, 1906, **39**, 4048—4055).—Yeast which has been grown in a medium free from sugar, but containing other carbon compounds and suitable nitrogenous food, will induce alcoholic fermentation when brought into a solution containing sugar. Suitable nitrogenous compounds are those containing the grouping



such as glycine, alanine, leucine, tyrosine, and aspartic acid, also phenylglycine, allantoin, phenylalanine, and hippuric acid. The compounds with the longer side chains, for example, propionic acid derivatives, react more readily than acetic acid derivatives. Guanine and uric acid, which contain the grouping  $\cdot\text{NH}\cdot\text{C}\cdot\text{CO}\cdot$ , may be used, and also ammonia.

Yeast will grow in a 10% sucrose solution containing small amounts of potassium hydrogen phosphate, magnesium sulphate, traces of common salt and ferrous sulphate, and certain nitrogenous substances, without inducing alcoholic fermentation. Such nitrogen compounds are sulphanilic acid, metanilic acid, naphthionic acid, aniline and its salts, benzamide, benzylamine, acetamide, acetanilide, methylaniline, diphenylamine, dimethylaniline hydrochloride, and

pyridine. The addition of a compound containing the group  $\cdot\text{NH}\cdot\text{CH}\cdot\text{CO}\cdot$  to such an inactive solution readily starts alcoholic fermentation.  
J. J. S.

**Mutual Effect of *Nicotiana Tabacum* and *N. affinis* in Grafting.** VIKTOR GRAFE and K. LINSBAUER (*Chem. Centr.*, 1906, ii, 1276; from *Ber. deut. bot. Ges.*, 24, 366—371).—When a variety of tobacco containing nicotine is grafted on to one containing little or no nicotine (*Nicotiana affinis*) or *vice versa*, the leaves of the variety which in ordinary circumstances contains very little nicotine will be found to contain relatively large amounts.  
N. H. J. M.

**[Cyanogenesis] in Plants Growing in Belgium.** P. FITSCHY (*Bull. Acad. roy. Belg.*, 1906, 613—617).—Small quantities of hydrocyanic acid have been obtained by macerating the following plants, previously ground, in water: *Ranunculus repens*, *R. arvensis*, *Gynerium argenteum*, *Melica altissima*, *M. nutans*, *M. uniflora*, *M. ciliata*. In *R. repens*, *G. argenteum*, *M. altissima* a cyanogenetic glucoside appears to be present, which is decomposed by sweet almond emulsion.  
T. A. H.

**Occurrence of Vanillin.** EDMUND O. VON LIPPMANN (*Ber.*, 1906, 39, 4147).—Vanillin may be obtained from dahlia bulbs.  
A. McK.

**Chemistry of the Scleroderms. II. *Scleroderma aurantium* (*S. vulgare*).** MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1906, 27, 963—967. Compare *Abstr.*, 1905, ii, 852).—Ripe specimens of *Scleroderma aurantium* from the neighbourhood of Graz were dried and the peridium and hymenium investigated separately. The light petroleum extract of the peridium yields two crystalline substances. The substance,  $\text{C}_{22}\text{H}_{36}\text{O}_2$ , crystallises from chloroform on cooling, or from a mixture of chloroform and acetone in transparent, rectangular plates, m. p.  $183\cdot5^\circ$  in an open, or  $188^\circ$  in a closed, capillary tube; with Liebermann-Burchard's reaction, the aqueous emulsion is orange-yellow and becomes green, red, and finally yellow, whilst the chloroform solution is orange-yellow and changes through rose and lilac to blue; Liebermann's reaction gives similar colour changes.

The substance,  $\text{C}_{21}\text{H}_{34}\text{O}_2$ , obtained from the chloroform filtrate from the preceding substance, crystallises from a mixture of acetone and alcohol in stout, hexagonal plates, or from ether in thin needles, m. p.  $196\text{—}197^\circ$  in a closed capillary tube; this gives with Liebermann's and Liebermann-Burchard's reactions, colour changes similar to those described above.

The peridium contains also large amounts of mannitol, which is found only in small quantities in the hymenium.

The hymenium yields small amounts of substances which give colour changes resembling those of ergosterol.  
G. Y.

**Investigations on the Properties of Wheat Proteids.** JOSEPH S. CHAMBERLAIN (*J. Amer. Chem. Soc.*, 1906, 28, 1657—1667).—Osborne and Voorhees (*Abstr.*, 1893, i, 741) have stated that wheat contains five proteids, namely, gliadin, glutenin, an albumin, a globulin, and a proteose. The gliadin and glutenin together constitute about 80—85% of the total proteids; the former is soluble in 70% alcohol whilst the latter is insoluble. The three other proteids are soluble in dilute salt solutions.

It is now found that on extracting air-dry wheat or flour with cold 70% alcohol, the gliadin is removed together with a large part of the proteids which are soluble in salt solutions, and it is therefore necessary that a correction should be made for the latter when quantitative separations are attempted. Potassium sulphate solution (5%) effects the same extraction as sodium chloride solution (10%), and has the advantage that the evolution of hydrogen chloride in the Kjeldahl operation is obviated.

Dry gluten from wheat flour consists of about 75% of proteids and 25% of non-proteids. Of the total proteids present in the wheat itself, about 60—65% are retained in the gluten whilst 35—40% are lost in the washings, this loss being at the expense of gliadin or glutenin. For these reasons, it is considered that the estimation of gluten is incapable of yielding any information which cannot be obtained by the estimation either of the total proteids or of those which are soluble in alcohol and those which are insoluble. E. G.

**Nature of the Phosphoric Acid Compounds in Barley and their Changes during Brewing Processes.** WILHELM WINDISCH and W. VOGELSANG (*Chem. Centr.*, 1906, ii, 1573; from *Woch. Brau.*, 23, 516—519).—Barley does not contain any inorganic phosphate. During germination the organic phosphoric acid compounds are decomposed. The breaking up of the phosphoric acid compounds in malt is attributed to enzyme action. N. H. J. M.

**Proteids of Barley in the Grain and During the Brewing Process.** HENRIK SCHJERNING (*Chem. Centr.*, 1906, ii, 1209—1210; from *Compt. rend. Lab. Carlsberg*, 6, 229—307).—The amount of proteids in barley grain does not always indicate the quality. The size of the grain seems to some extent to depend on the duration of the growing and ripening period. The transformation of soluble nitrogenous compounds into insoluble substances is more rapid, when the period of development is short, than the assimilation of nitrogen, and the production of soluble proteids from amides is intensified.

Proteoses are exclusively products of the hydrolytic breaking down of higher proteids, and any marked amount of proteoses in barley grain is evidence of a very unfavourable crop. Loss of dry matter during storage is unlikely when the conditions of storage are suitable and when the grain has reached the right degree of ripeness before cropping.

The composition of the dry matter of the grain, as regards the various groups of nitrogenous substances, mineral matter, and acid compounds soluble in water, is independent of the variety and type of



barley. Climatic conditions affect the amounts of ash constituents, total nitrogen, and amides, but have less influence on the other nitrogenous constituents, the amounts of which depend rather on the degree of ripeness and time of storage.

N. H. J. M.

**Influence of the Ash Constituents of the Lower Portions of Oat Stems on the Falling of the Stems.** D. LIENAU and ALBERT STUTZER (*Landw. Versuchs-Stat.*, 1906, 65, 253—263. Compare Lienau, *Inaug. Diss. Königsberg*, 1903).—According to Wieler (*Bot. Zeit.*, 1889, 32) and Wolff (*Prakt. Düngerlehre*, 1886, 158), phosphoric acid has the effect of strengthening straw, whilst much nitrogen and potassium cause softening; Guffroy (*J. d'Agric. prat.*, 1901, i, 65) found that the cell-walls become thin under the influence of nitrogen, whilst phosphoric acid has the opposite effect.

The results of anatomical and chemical investigations with oat straw grown on variously manured plots showed that phosphoric acid is the manure which most promotes the thickening of the cell-wall, and that its effect is greatly lessened when much potassium or calcium is applied along with it. Large amounts of potassium or nitrogen reduce the thickness of the cell-walls, nitrates having more effect than ammonium salts.

The amounts of total ash and potassium are increased by manuring with large amounts of potassium, nitrogen, and calcium, whilst phosphoric acid in many cases reduced the total ash and potassium. The amount of phosphoric acid in the straw does not depend on the amount applied as manure, but is increased by large applications of potassium, calcium, and nitrogen. The calcium in the straw is increased by ammonium salts and diminished by phosphoric acid. The amounts of sodium, iron, and silicon seem to have no relation to the manuring.

The thickening of cell-walls is greatest the less the amounts of total ash and potassium. The relations as regards calcium and phosphoric acid remain to be ascertained.

N. H. J. M.

**Amounts of Potassium and other Important Constituents in Various Grasses.** ALBERT STUTZER (*Landw. Versuchs-Stat.*, 1906, 65, 264—274).—Determinations of dry matter, nitrogen, potassium, calcium, phosphoric acid, and silica in a number of grasses grown in soil, in pots, without manure, with phosphoric acid both alone and in conjunction with potassium, and with potassium and nitrogen.

The effect of phosphoric acid on the yield was very slight, except in the case of *Alopecurus pratensis*, *Avena flavescens*, and *Anthoxanthum odoratum*.

The grasses were able to assimilate considerable amounts of potassium, although the soil contained very little soluble in cold hydrochloric acid. The greatest amount was taken up by *Dactylis glomerata*, which with *Phalaris arundinacea* also acquired the greatest amount of nitrogen (from the unmanured plot).

The amounts of calcium are small as compared with potassium and nitrogen.

N. H. J. M.

**Pot Experiments with Soils Containing Copper.** ALBERT STUTZER (*Landw. Versuchs-Stat.*, 1906, 65, 285—288).—*Trifolium*

*pannonicum* was grown in pots containing 10 kilos. of a mixture of sand and garden soil with addition, of calcium carbonate (100 grams) and mineral manures. Two pots received finely-powdered copper (10 grams and 1 gram), two the same amounts of powdered copper oxide, and two no copper. No injury was observed except in the case of the pot which had 10 grams of copper oxide; the plants of this pot failed in part and those which grew at all remained small.

No copper could be detected in any of the plants or roots. It is therefore doubtful whether *Trifolium pannonicum* is a plant which takes up relatively large amounts of copper as has been stated. Soil which contains much copper is to be regarded as permanently sterile.

N. H. J. M.

**Nitrogenous Nutrition of Agricultural Plants.** E. WEIN (*Chem. Centr.*, 1906, ii, 1454; from *Verh. Ges. Deut. Naturf. Ärzte*, 1905, ii, 119—123).—The results of field experiments showed that calcium cyanamide is at least equal in value to ammonium sulphate. On peat soil containing much calcium carbonate both calcium cyanamide and sodium nitrate gave good results, whilst ammonium sulphate caused a diminished yield.

N. H. J. M.

**Pot Experiments on the Action of Calcium Cyanamide.** ALBERT STUTZER (*Landw. Versuchs-Stat.*, 1906, 65, 275—282).—Pot experiments are described in which rye was manured with calcium cyanamide, ammonium sulphate, and sodium nitrate respectively. Subsequently, mustard was grown three times in the same pots without further manuring.

When the amount of nitrogen applied was 0.5 gram per pot (16 kilos. of soil), 68.4% of the ammonia nitrogen was recovered in the plants, 65.9% of the calcium cyanamide, and 55.2% of the nitrate. The last result is attributed to loss of nitrogen in the winter, the sodium nitrate having been applied in the autumn.

N. H. J. M.

**Employment of Thiocyanates as Manure.** RENATO PEROTTI (*Chem. Centr.*, 1906, ii, 1282; from *Staz. sper. agrar. ital.*, 39, 193—212).—The manure "sulphocyanide" contains: total N, 5.06; N as ammonia, 1.66; K, 2.28; Ca, 1.73;  $P_2O_5$ , 0.8;  $SO_3$ , 2.01; total S, 23.89%. It contains about 4.5% of ammonium thiocyanate, but no potassium thiocyanate. It is nearly completely and fairly quickly decomposed in the soil without loss.

N. H. J. M.

**Action of Wolter's Phosphate.** ALBERT STUTZER (*Landw. Versuchs-Stat.*, 1906, 65, 283—284).—Pot experiments with hemp manured with equal amounts of phosphoric acid in the forms of superphosphate and Wolter's phosphate showed that the two manures are about equal.

N. H. J. M.

**Amount of Chlorine in Rain Water.** WILLEM P. JORISSEN (*Chem. Centr.*, 1906, ii, 1579; from *Chem. Weekblad*, 3, 647—649. Compare Abstr., 1906, ii, 486).—As the result of 154 more analyses

of rain water it is found that the average amount of chlorine is 32.5 mg. per litre. The author also quotes analyses of 121 samples of rain water collected in casks.

P. H.

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## Analytical Chemistry.

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**Improved Eudiometer; its Application to Measuring Fire-damp. Detection and Estimation of Methane and Carbon Monoxide.** NESTOR GRÉHANT (*Compt. rend.*, 1906, 143, 813—815).—A modification of the eudiometer consists in the employment of a fine platinum wire heated by an electric current to fire the gases; the wire is supported on two copper terminals which pass through a rubber stopper closing the eudiometer tube. The presence of 1% of methane in air can be measured with an accuracy of 92% in an eudiometer of this form by passing the current 400 to 600 times.

Comparative experiments conducted on rabbits, on the poisonous action of small quantities (1:5000 or 1:10,000) of carbon monoxide in air, show that the amount of carbon monoxide absorbed by the blood becomes constant after five hours (compare Abstr., 1900, ii, 95).

M. A. W.

**Standardisation of Normal Solutions [Acids and Alkalis]; Note on the Zeiss Immersion Refractometer.** B. WAGNER, A. RINCK, and F. SCHULTZE (*Chem. Zeit.*, 1906, 30, 1181—1183).—The acid, hydrochloric acid, for instance, is first tested by Lunge's sp. gr. process. It is then titrated by means of standard potassium hydroxide, free from impurities, and the liquid is evaporated to dryness with the usual precautions. The residual potassium chloride is weighed and the result represents the amount of hydrogen chloride. The sp. gr. and the titration results serve as a useful check.

A further check may be made by testing the acid or alkali, or the resulting potassium salt in the Zeiss immersion refractometer. The authors have constructed a new table for nitric acid at 17.5°, and other tables are in course of construction. When using this instrument it is of fundamental importance that the temperature should be 17.5° exactly, and a new warming arrangement and special thermometers should therefore be used, for a description of which the original paper and drawings must be consulted.

L. DE K.

**Use of Alkaline Mercuric Iodide Solution as an Oxidising Agent in Volumetric Analysis.** GYSBERT ROMIJN (*Ber.*, 1906, 39, 4133).—A claim for priority (compare Rupp, Abstr., 1906, ii, 902).

A. McK.

**Detection of Traces of Water.** F. SCRIBA (*Chem. Centr.*, 1906, ii, 1458; from *Zeit. phys. chem. Unterr.*, 19, 298).—A test paper is made by soaking strips of filter paper in a 5% solution of ferrous ammonium sulphate; the dried paper is then sprinkled over with finely-powdered potassium ferricyanide. The most minute drop of water produces a blue spot.  
L. DE K.

**Estimation of Halogens in Carbon Compounds by Means of Sodium and Ethyl Alcohol.** A. STEPANOFF (*Ber.*, 1906, 39, 4056—4057).—See Abstr., 1905, i, 335.

**Estimation of Sulphur in Pyrites.** GEORG LUNGE (*Zeit. angew. Chem.*, 1906, 19, 1854—1855).—Polemical. A reply to Drenstedt and Hassler (Abstr., 1906, ii, 896).  
L. DE K.

**Estimation of Sulphur Existing as Zinc Sulphate in Roasted Blendes.** V. HASSREIDTER (*Bull. Soc. chim. Belg.*, 1906, 20, 163—164).—Zinc sulphate contained in roasted zinc ores may be extracted with water and the zinc titrated as usual, 1 part of zinc = 0.492 part of sulphur. Insoluble basic zinc sulphate is also present in the roasted ore, but in negligible quantity.  
L. DE K.

[Kjeldahl] **Ammonia Distillations with or without Cooling Arrangement.** ERNST PESCHECK (*J. Landw.*, 54, [iv], 367—384).—Equally satisfactory results may be obtained in the Kjeldahl process either with or without the use of a cooling arrangement, if only care be taken to have the condenser made of glass poor in alkali (Jena glass).

Loss of ammonia may be prevented as follows: the liquid in the distilling flask should occupy about 300 c.c., the amount of sodium hydroxide added should not be excessive, the acid in the receiver should be diluted to 100—150 c.c., and the delivery tube which at the lower end should have a diameter of 0.5 cm. should reach almost to the bottom of the acid. If no cooling arrangement is used, the acid in the receiver is considerably heated and must be allowed to cool before it can be titrated; this, however, depends on the nature of the indicator used.  
L. DE K.

**Estimation of Nitric Acid in Soils.** ERNST GUTZEIT (*Landw. Versuchs-Stat.*, 1906, 65, 217—219).—Precipitation of the humus present in soil extracts before estimating nitrates by reduction does not cause high results as stated by Buhlert and Fickendey (Abstr., 1906, ii, 125). It was found that results obtained with solutions from which the humus had been precipitated were considerably lower (37%) than those obtained with the original solutions containing humus.

N. H. J. M.

**Estimation of Phosphoric Acid by Woy's Method.** G. B. VAN KAMPEN (*Chem. Centr.*, 1906, ii, 1357; from *Chem. Weekblad*, 3, 376—379).—The author confirms the accuracy of Woy's gravimetric

process (weighing as  $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$ ), but equally good results are obtained by the volumetric molybdate method. L. DE K.

**Moisture in Coal.** E. E. SOMERMEIER (*J. Amer. Chem. Soc.*, 1906, 28, 1630—1638).—This apparently simple determination only gives trustworthy and concordant results when careful attention is paid to the following points. It is absolutely necessary that care be taken to prevent changes in moisture in the coarse sample during transit. The fine sample for chemical analysis should be in nearly an air-dry condition. The air of the drying-oven should be of a uniform dry condition, and the dried sample should be cooled in a desiccator over sulphuric acid. L. DE K.

**Estimation of Moisture and Volatile Matters in Coals.** HENRI PELLET and ALBERT ARNAUD (*Ann. Chim. anal.*, 1906, 11, 428—431).—*Moisture.*—Having made a series of experiments, the authors conclude that the moisture in coals may be determined equally well by heating 2 grams of the powder for fifteen minutes at  $100\text{--}105^\circ$  and drying for an hour at  $90^\circ$ , or by placing the sample in a desiccator over sulphuric acid for forty-eight hours at  $25\text{--}28^\circ$ .

*Volatile Matters.*—Two grams of the sample are heated rapidly in a small platinum crucible provided with a suitable lid; when the flame ceases, the heating is continued for another three minutes. A correction should be applied for carbon oxidised by the air inside the crucible, generally 2 or 3 mg. This may be determined readily once for all by reweighing the coke several times after a six minutes' re-ignition, thus obtaining the average loss due to oxidation. L. DE K.

**Estimation of Carbon Dioxide alone or in Admixture with Hydrogen Sulphide or Chlorine.** GEORG LUNGE and AUGUST RITTENER (*Zeit. angew. Chem.*, 1906, 19, 1849—1852).—Combined carbon dioxide is liberated as usual with hydrochloric acid over brine in presence of a little aluminium, the gas is collected in a gas burette, and the volume of carbon dioxide estimated as usual by means of aqueous sodium hydroxide. Waste gases are passed through the burette and treated similarly. If hydrogen sulphide should be present, the gas is distributed in two burettes; in one of these the joint volume of carbon dioxide and hydrogen sulphide is found by absorption, and in the second one a known volume of standard iodine is introduced, which is then titrated with sodium thiosulphate as usual; the weight of the hydrogen sulphide thus found is then reduced to volume.

In presence of chlorine, the last traces of carbon dioxide are expelled from the liquid by boiling with a little hydrogen peroxide. The joint carbon dioxide and chlorine are then found by absorption, and the chlorine in the alkaline liquid is estimated by the arsenic titration process. L. DE K.

**Detection of Barium, Strontium, and Calcium.** STANLEY R. BENEDICT (*J. Amer. Chem. Soc.*, 1906, 28, 1596—1598).—The method is based on the fact that barium and strontium solutions are precipitated completely by excess of potassium iodate; the latter precipitate, however, is soluble in dilute hydrochloric acid.

A few c.c. of the neutral solution are mixed with half the volume of 5*N*-hydrochloric acid, and to the mixture is added an equal volume of saturated solution of potassium iodate. An immediate precipitate indicates barium; a precipitate forming but very slowly may be due to strontium, and in such a case the presence or absence of barium should be confirmed in a portion of the original solution with potassium dichromate. The filtrate is then tested for strontium by boiling the last portion of it with an equal volume of saturated ammonium sulphate solution.

Another portion of the original neutral solution is then mixed with twice its volume of potassium iodate, and after a minute or so the filtrate is tested for calcium with ammonium oxalate and a drop of ammonia.

L. DE K.

**Separation of Barium, Strontium, and Calcium.** CARON and RAQUET (*Bull. Soc. chim.*, 1906, [iii], 35, 1061—1069).—The mixed carbonates, separated in the usual way by the group reagent, are dissolved in excess of acetic acid, the solution boiled, and from this the barium is precipitated by the addition of a solution containing 10% of ammonium chromate and 5% of acetic acid. To the filtrate ammonia solution is added until the liquid assumes a pale yellow colour and has a distinctly ammoniacal odour; strontium chromate is then precipitated unless only small quantities are present, when it is necessary to add alcohol (60—70°). To the filtrate from this, potassium ferrocyanide is added, when potassium calcium ferrocyanide is precipitated; at once, if a considerable quantity of calcium is present, but only on warming if the amount present is small.

By this method, 0.001 gram of barium chloride can be detected in presence of 0.5 gram of strontium chloride or calcium chloride, the two metals being precipitated in the first instance as carbonates. If the reagents are applied directly to a solution containing both chlorides, one part of barium chloride can be detected in presence of 8000 parts of strontium chloride.

A critical *résumé* of other methods in use for the separation of these three elements is given.

T. A. H.

**Separation and Estimation of Glucinum.** CHARLES L. PARSONS and S. K. BARNES (*J. Amer. Chem. Soc.*, 1906, 28, 1589—1595).—The authors have found that glucinum may be separated quantitatively from iron and aluminium by heating the neutralised solution to boiling with excess of sodium hydrogen carbonate; 10% of the solid salt should be added, which causes the precipitation of the iron and aluminium and leaves the glucinum in solution. The precipitate

must be freed from any glucinum hydroxide by redissolving in hydrochloric acid, neutralising with ammonia, and reprecipitating with sodium hydrogen carbonate.

From the mixed filtrate the glucinum is recovered by adding excess of hydrochloric acid, boiling, and precipitating with ammonia. The precipitate is washed with a solution of ammonium acetate, ignited, and weighed.

L. DE K.

#### Quantitative Separation of Glucinum and Aluminium.

CARL FRIEDHEIM (*Ber.*, 1906, 39, 3868—3869).—The method described by Glassmann (*Abstr.*, 1906, ii, 902) has been used previously by Joy (*J. pr. Chem.*, 1864, [i], 92, 235) and also by Zimmermann (*Abstr.*, 1888, 323).

J. J. S.

#### A Highly Sensitive Method of Precipitating Zinc.

GABRIEL BERTRAND and MAURICE JAVILLIER (*Compt. rend.*, 1906, 143, 900—902).—Zinc is precipitated in the form of sparingly soluble, highly refractive, crystalline, hydrated calcium zinc oxide,  $\text{Ca}(\text{O} \cdot \text{Zn} \cdot \text{OH})_2 \cdot 4\text{H}_2\text{O}$  (Bertrand, *Abstr.*, 1893, ii, 118), when a very dilute solution of a zinc salt containing calcium hydroxide is boiled with excess of ammonia, and this reaction can be employed for the estimation of one part of zinc in 500,000 parts of water. For this purpose 500 c.c. of the solution is mixed with a few c.c. of dilute milk of lime or 50 c.c. of lime water, and 10 to 15% of concentrated ammonia solution, filtered, and then boiled until alkaline vapours are no longer evolved; the precipitate of calcium zinc oxide and calcium carbonate is collected on a small filter, dissolved in hydrochloric acid, the solution evaporated to dryness, the residue taken up with a little water, and the calcium precipitated as the oxalate in the presence of excess of ammonia. By evaporating and igniting the filtrate in the presence of sulphuric acid the zinc is obtained and can be weighed in the form of the sulphate, or in cases where the amount of zinc is too small to admit of estimation, its presence can be detected by dissolving the residual sulphate in water and adding hydrogen sulphide or potassium ferrocyanide solution.

It is essential that all the reagents employed shall be free from zinc, and the result of each experiment must be corrected for errors introduced by the slight solubility of calcium oxalate and of glass in water, by subtracting from the weight of the zinc sulphate the weight of the residue obtained in a control experiment.

M. A. W.

#### Influence of Ammonia and Ammonium Salts in the

Schaffner Zinc Titration. ALPHONSE DECKERS (*Bull. Soc. chim. Belg.*, 1906, 20, 164—166).—Experiments showing that the accuracy of the Schaffner process (titration with sodium sulphide) is seriously affected by the amount of free ammonia and ammoniacal salts present in the liquid. In order to obtain trustworthy results, the comparison liquid should therefore contain the same amount of ammonium



compounds. Owing to the action of these salts on the zinc sulphide, they should not be introduced too liberally. L. DE K.

**Quantitative Estimations of Metals by Electrolysis.** FRITZ FOERSTER (*Zeit. angew. Chem.*, 1906, 19, 1842—1849, 1889—1895).—A lengthy review of the subject, dealing principally with the electrolytic estimation of nickel, zinc, cadmium, and copper. A large number of tables and formulæ are given.

The use of wire gauze electrodes is strongly recommended.

L. DE K.

**Volumetric Estimation of Copper by means of Potassium Iodide.** H. CANTONI and M. ROSENSTEIN (*Bull. Soc. chim.*, 1906, [iii], 35, 1069—1073).—It is shown that the results obtained by this method are not influenced by the quantity of potassium iodide added, and are but little affected by the presence of potassium, sodium, ammonium, zinc, or magnesium sulphate, whilst the results are considerably modified by the presence of varying amounts of water or acetic acid. The method gives excellent results when carried out under certain well-defined conditions, and it is indispensable that the solution of sodium thiosulphate employed should be standardised under conditions similar to those, which will hold when the actual determination is being made, and that the solution of iodine should be standardised with reference to the particular type of copper salt which it is proposed to estimate with it. T. A. H.

**Solubility of Iron in Vinegar.** W. HOFFMANN (*Chem. Centr.*, 1906, 11, 1368—1369; from *Deut. Essigind.*, 10, 306).—Iron is decidedly soluble in vinegar, communicating a green colour to malt vinegar and a yellow or red colour to distilled vinegar. This iron interferes with the ordinary titration of samples, which should therefore be submitted to distillation. L. DE K.

**[Estimation of] Chrome and Acid in Chrome-tanning Liquors.** F. W. ALDEN (*Chem. Centr.*, 1906, 11, 1460; from *J. Amer. Leather Chem. Assoc.*, 1, 174).—A quantity of the liquor supposed to contain 2—3 grams of chromic oxide is diluted with water to 500 c.c. Ten c.c. are then diluted with 15 c.c. of water and 2 grams of sodium peroxide are added. After boiling for a very short time, excess of hydrochloric acid is added, and the chromate formed is then titrated as usual with potassium iodide and sodium thiosulphate. The combined acid is estimated by adding 50 c.c. of the liquor to a boiling solution of 50 c.c. of *N*/2 sodium carbonate diluted with 150 c.c. of water, and diluting, when cold, to 500 c.c. Two hundred c.c. of the filtrate are then titrated back with *N*/2 hydrochloric acid. L. DE K.

**Conditions of Quantitative Precipitation of Uranium Peroxide.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 429—438 and 494—500. Compare Fairley, *Trans.*, 1877, 127; Melikoff and Pissarjewsky, *Abstr.*, 1898, ii, 165).—The author has

studied the conditions under which uranium peroxide,  $\text{UO}_4$ , is precipitated quantitatively from solutions of uranyl salts by means of hydrogen peroxide.

The solubility of uranium peroxide, expressed in grams of  $\text{UO}_3$  per litre of solution, is (1) in water, 0.0061 at  $20^\circ$  and 0.0084 at  $90^\circ$ , and (2) in  $N/10$  ammonium chloride, 0.0053 at  $20^\circ$  and 0.0088 at  $90^\circ$ .

In presence of free acetic, hydrochloric, or nitric acid, the precipitation of uranium peroxide from solutions of uranyl salts by hydrogen peroxide is incomplete, the amount remaining in solution depending on the extent of dissociation of the acid. When free sulphuric acid is present, the precipitation is slight in amount and slow, probably owing to abnormal ionisation of the uranyl sulphate. Hence the acidity of the solution should only be slight and sulphuric acid should be absent. If the solution contains ammonium chloride (best in about  $N$ -concentration), the precipitated uranium peroxide is easily filtered and washed; the washing liquid should be  $N/10$  ammonium chloride. A temperature of not above  $70^\circ$  and an excess of the hydrogen peroxide accelerate the precipitation.

Moderate amounts of the chlorides, sulphates, and nitrates of the alkali metals or ammonium do not interfere appreciably with the precipitation of uranium peroxide, but acetates, fluorides, oxalates, or tartrates hinder it to a greater or less extent. Large proportions of the chlorides of the alkaline earth metals prevent the precipitation in some degree, which is, however, diminished by the addition of ammonium chloride.

The anion present in uranyl salts may be estimated by adding a slight excess of hydrogen peroxide and titrating, in presence of the precipitate, with sodium hydroxide or ammonia solution, using phenolphthalein as indicator; the liquid assumes an orange colour when alkaline.

T. H. P.

**Nitrogenous Compounds and Silica in Sea-water.** WILHELM E. RINGER (*Chem. Centr.*, 1906, ii, 1459; from *Chem. Weekblad*, 3, 585—608).—Raben's process is recommended. The sample must be examined without delay; otherwise it should be preserved by addition of 0.1% of mercuric chloride. One hundred c.c. are distilled with a few drops of acetic acid and the distillate is examined colorimetrically for nitrous acid (phenylenediamine test). One gram of magnesium oxide is then added and the free ammonia collected and determined by the Nessler test. The residue may then be tested for nitrate by reducing it with aluminium foil and sodium amalgam and Nesslerising the ammonia formed.

Silica is estimated in the usual manner by evaporating 3 litres of the sample with hydrochloric acid in a platinum dish and taking up the residue with dilute acid.

L. DE K.

**Estimation of Manganese in Drinking Waters.** JOHANNES PRESCHER (*Chem. Centr.*, 1906, ii, 1458; from *Pharm. Centr.-Halle*, 799—802).—The residue obtained from 1 litre of water is treated

with nitric acid and potassium chlorate (Hampe's process for estimating manganese in iron), and the resulting manganese dioxide is titrated as usual with standard oxalic acid and potassium permanganate.

L. DE K.

**Detection of Small Quantities of Dextrose in Urine.** CH. PORCHER (*Chem. Centr.*, 1906, ii, 1362; from *Bull. Assoc. Chim. Sucr. Dist.*, 24, 155—159).—The sample is precipitated with mercuric nitrate, then neutralised, and diluted to ten times its volume. The excess of mercury is removed by zinc dust or hydrogen sulphide, the filtrate is evaporated in a vacuum to a small bulk, the residue is mixed with excess of alcohol, and the filtrate evaporated in a vacuum. The residue is then tested for dextrose by the usual phenylhydrazine method (osazone reaction). An excess of this reagent should be avoided.

L. DE K.

**Lævulosuria. Detection of Lævulose in Urine.** ADOLF JOLLES (*Arch. Pharm.*, 1906, 244, 542—549).—Lævulose may occur in urine alone, as well as in conjunction with dextrose.

Lævulose is detected by adding to 10 c.c. of the urine a little resorcinol and about 3 c.c. of 10% hydrochloric acid, and heating to boiling; an *immediate* red coloration indicates lævulose (Seliwanoff's reaction).

For the estimation of lævulose, Ost's method (*Abstr.*, 1891, 125) is the best. The urine is boiled with a solution of copper sulphate in aqueous potassium carbonate and potassium hydrogen carbonate, and the precipitate is reduced to metallic copper and weighed. If dextrose is present, a polarimetric determination is made also, the urine being first clarified with normal lead acetate; from the results of the two experiments the amounts of dextrose and lævulose can be calculated.

The method of calculation is exemplified in the paper, and some test analyses are given.

C. F. B.

**Separation of Starch and Glycogen.** EMIL BAUR and EDUARD POLENSKE (*Chem. Centr.*, 1906, ii, 1360—1361; from *Arbb. Kais. Ges. A.*, 24, 576—580).—*Estimation of the Starch.*—A few decigrams of the mixture of starch and glycogen obtained from sausages are dissolved in 30 c.c. of water and 11 grams of powdered ammonium sulphate are added. This precipitates the starch, which is washed first with a solution of ammonium sulphate of the same strength and then with proof spirit. The aqueous filtrate (60 c.c.) contains the glycogen, which may be recovered by adding 300 c.c. of water and 500 c.c. of alcohol.

*Estimation of Glycogen in Meat.*—A modification of Mayrhofer's process. Sixty grams of meat are treated with alcoholic potassium hydroxide, the hot liquid is mixed with 100 c.c. of proof spirit, and the crude glycogen is collected. It is washed, first with alcoholic potassium hydroxide (80 grams in 1 litre 90% alcohol) and then with 90% alcohol until the filtrate is no longer rendered turbid by hydro-

chloric acid. The precipitate is then dissolved in 50 c.c. of *N*-aqueous potassium hydroxide and when cold acidified with acetic acid and diluted to 110 c.c. From the filtrate, the glycogen is precipitated by addition of alcohol, collected in a Gooch crucible, and washed, first with 70% alcohol, then with absolute alcohol, and finally with ether. After weighing, any mineral impurity is found by incineration.

L. DE K.

**Methods of Determining Esters, Aldehydes, and Furfuraldehyde in Whisky.** LUCIUS M. TOLMAN and T. C. TRESCOT (*J. Amer. Chem. Soc.*, 1906, **28**, 1619—1630).—A lengthy investigation as to the merits of the various processes recommended for the estimation of esters, aldehydes, and furfuraldehyde in whisky.

All these processes give unsatisfactory results, unless applied to the distillates, when the whisky is coloured with caramel. For further particulars the original paper and tables should be consulted.

L. DE K.

**Estimation of Soluble and Insoluble Volatile Fatty Acids [in Butter].** J. DELAITE and J. LEGRAND (*Bull. Soc. chim. Belg.*, 1906, **20**, 230—233).—The glycerol-soda saponification process is not safe in practice, as the soluble volatile fatty acids decrease on slightly prolonged heating, whilst the insoluble volatile acids increase. When saponifying with alcoholic potassium hydroxide, the boiling should not be prolonged to more than half an hour, as shown by the following experiment. After boiling for fifteen minutes the Reichert-Meissl figure of a butter was found to be 30·03; after thirty minutes, 30·14; after forty-five minutes, 30·58; after an hour, 31·98; after two hours, 34·89, and after five hours, 46·53.

L. DE K.

**Rapid Method for Estimating Citric Acid in Lemon Juice.** CELSO ULPANI and A. PARROZZANI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 517—518).—This method is based on the fact that in a cold solution of citric acid containing calcium chloride, sodium hydroxide produces a precipitate when the total acidity is neutralised, whilst if the liquid is hot, precipitation takes place when only one-third of the acidity is neutralised.

After the total acidity of the juice has been estimated approximately by titration with *N*-sodium hydroxide, 50 c.c. of the juice are placed in a 200 c.c. flask, together with sufficient *N*-sodium hydroxide solution to neutralise about one-tenth of the acidity; the latter value represents the maximum proportion of tartaric and oxalic acids, which are hence precipitated after the liquid is boiled (*vide infra*). About 17 grams of calcium chloride and 5 grams of animal charcoal are added to the solution, which is then boiled, cooled, made up to volume, and filtered. The following estimations are made in the filtrate: (1) to 50 c.c., *N*-sodium hydroxide solution is added in the cold until a faint, permanent turbidity appears; (2) another 50 c.c. is boiled and

*N*-sodium hydroxide solution is run in until a permanent turbidity appears. The difference between the volumes of sodium hydroxide solution used in (1) and (2) represents two-thirds of the citric acid, free and combined, present in the juice.  
T. H. P.

**Estimation of Salicylic Acid in Canned Tomatoes, Cat-sups, &c.** WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1906, 28, 1616—1619).—The following method has been adopted finally by the author: fifty grams of the pulped tomatoes are transferred to a 200 c.c. flask containing 50 c.c. of water, the mixture is neutralised with ammonia, and 15 c.c. of milk of lime (1:10) are added. The whole is diluted to the mark, well shaken, and filtered. 150—160 c.c. of the filtrate are acidified with hydrochloric acid and extracted four times in succession with 75—100 c.c. of ether. After washing the mixed ethereal extracts twice with 25 c.c. of water, the ether is recovered by distilling slowly until about 20—25 c.c. are left, which are then left to evaporate spontaneously. The residue is dissolved in hot water and when cold diluted to a definite bulk. The salicylic acid is then estimated colorimetrically in the usual manner with ferric alum solution.  
L. DE K.

**[Assay of] Sodium Salicylate.** FRANK H. ALCOCK (*Pharm. J.*, 1906, 597).—0.5 gram of the sample and 0.5 gram of ammonium chloride are dissolved in 10 c.c. of water and evaporated to dryness in a platinum dish. During this operation ammonia is evolved and also salicylic acid, together with any phenol, if present. The residue is now gently ignited, and the mass which consists of sodium chloride is then dissolved in water and titrated with *N*/10 silver nitrate, of which 31.2 c.c. should be required. An allowance should, of course, be made for any chloride pre-existing in the sample.  
L. DE K.

**Estimation of Humus Acids in Soils by Tacke's Method.** C. K. VAN DAALEN (*Chem. Centr.*, 1906, ii, 1458. Compare Tacke, *Abstr.*, 1898, ii, 103).—The difficulty of the method is attributed to the slow evolution of carbon dioxide and to the complexity of the reactions which cannot be represented as the result of a single reaction.  
N. H. J. M.

**Estimation of Fatty Matter in Butter.** A. FROEHNER (*Chem. Zeit.*, 1906, 30, 1250—1251).—0.63 gram of the sample is melted, preferably in a graduated tube with 10 c.c. of water to remove the salt, 10 c.c. of alcohol are added, then 25 c.c. of ether, and the whole is well shaken. The shaking is now repeated after addition of 25 c.c. of benzene. When the aqueous layer has separated, 25 c.c. of the ethereal layer are withdrawn and evaporated in a weighed dish. In calculating the amount of fat, the total volume of the ethereal solution may be taken as 52.8 c.c. (52.3 c.c. + a correction of 0.5).

The salt may be titrated in the aqueous solution in the usual manner.  
L. DE K.

**The Examination of Wool-fat.** W. HERBIG (*Chem. Rev. Fett. Harz. Ind.*, 1906, 13, 303—304).—Concordant results may be obtained in the estimation of the saponification number of wool-fat by dissolving the latter in light petroleum before boiling with the alkali. The figures obtained tend to be higher than those yielded by the ordinary process, but are constant between themselves for each particular sample. The increase in the saponification number observed on boiling the fat and alkali mixture for a long time is not due to the action of the alkali on the higher alcohols present. W. P. S.

**Constants of Carnaüba Wax.** LIONEL G. RADCLIFFE (*Pharm. J.*, 1906, 596—597).—A sample of the pure unbleached wax gave the following result: m. p.  $84^{\circ}$ ; acid number, 2.9; saponification number, 88.3; ether number, 85.4; iodine number, 13.17.

The free acidity was found as usual by boiling with absolute alcohol and titrating with *N*/20 aqueous potassium hydroxide. The saponification number was found by boiling with a mixture of redistilled amyl alcohol and alcoholic potassium hydroxide for several hours and titrating the excess of the latter. The iodine number was obtained by dissolving the sample in chloroform and treating with Wijs's reagent (iodine monochloride in glacial acetic acid); the original Hübl solution was almost inactive. L. DE K.

**Estimation of Camphor [in Celluloid].** ALOIS ARNOST (*Zeit. Nahr. Genussm.*, 1906, 12, 532—539).—In the method described, the camphor is obtained in alcoholic solution which is shaken with light petroleum and acidified water; the increase of the volume of the light petroleum is equivalent, with certain corrections, to the quantity of camphor present. Ten grams of the finely-rasped celluloid are agitated for one hour in a flask with 100 grams of 25% sodium hydroxide solution. The flask is then connected with a condenser, and its contents heated to a temperature of about  $80^{\circ}$  until homogeneous. By increasing the heat, the camphor is volatilised into the condenser, and is carried over into the receiver (a 100 c.c. flask) by adding several successive small quantities of alcohol to the distillation flask. The distillate is diluted to 100 c.c. with alcohol and the camphor estimated as follows: 90 c.c. of water acidified with sulphuric acid are placed in a bulb-shaped vessel the neck of which is graduated, showing each 0.05 c.c. from 98 c.c. to 100 c.c.; the bulb holds exactly 90 c.c., and the part of the neck between the 90 c.c. and 98 c.c. marks is widened out into a small bulb. Above the graduated neck is an upper pear-shaped bulb provided with a short neck which may be closed with a stopper. Ten c.c. of the alcoholic camphor solution are next introduced into the apparatus and then 50 c.c. of light petroleum, D 0.64—0.67. After closing the apparatus with an indiarubber stopper, the contents are shaken for two minutes, allowed to separate for half an hour, and the increase of the volume of the petroleum read off, all the readings being taken at  $15^{\circ}$ . This increase is due to the extracted camphor and to the contraction caused by the mixing of the alcohol and aqueous layers. The quantity of alcohol actually present

is ascertained by transferring 50 c.c. of the aqueous portion to a flask, adding an excess of sodium hydroxide, and distilling the alcohol. The sp. gr. of the distillate when the latter has been diluted to 50 c.c. indicates the percentage of alcohol, and the contraction due to its presence is then found by reference to tables. The corrected increase of the volume of the light petroleum gives the *volume* of the camphor in the 10 c.c. of solution taken for the estimation. Camphor has  $D_{15}^{25}$  0.993:

*Contraction Table.*

Alcohol. c.c.	Water c.c.										
	89.	90.	91.	92.	93.	94.	95.	96.	97.	98.	99.
3.00	176	176	175	175	175	175	174	174	174	174	173
4.00	242	242	242	241	241	241	241	240	240	240	240
5.00	311	311	311	310	310	310	310	309	309	308	308
6.00	384	384	383	382	381	381	380	379	379	378	378
7.00	459	459	458	458	457	456	455	454	453	451	450
8.00	540	539	538	537	536	534	533	532	531	530	529
9.00	628	626	624	621	618	616	614	613	612	611	610
10.00	717	715	713	711	709	706	704	702	700	698	696

The contractions are expressed in cubic millimetres. W. P. S.

**Direct Estimation of [Quebracho] Tannin.** H. FRANKE (*Chem. Centr.*, 1906, ii, 916—917; from *Pharm. Centr.-Halle*, 47, 599—604).—One hundred c.c. of an aqueous decoction of Quebracho wood or a solution of 0.2 gram of the tannin obtained from it by Körner's process (*Ledermarkt*, 1897, No. 37) in 100 c.c. of water are heated to boiling with 50 c.c. of formalin; 25 c.c. of 25 per cent. hydrochloric acid are added, and the whole is heated for ten minutes longer. After half an hour, the precipitate is collected, washed with water, alcohol, and ether, and dried at 110°. Its weight  $\times 0.9834$  = quebrachotannic acid.  
L. DE K.

**Separation of Proteoses and Peptones from the Simpler Amino-compounds.** WILLARD D. BIGELOW and F. C. COOK (*J. Amer. Chem. Soc.*, 1906, 28, 1485—1499).—A comparison has been made of the action of the proteid precipitants, tannin-salt solution, and phosphotungstic acid on amino-compounds such as glycine, alanine, creatine, phenylenediamine, and sarcosine, both singly and in mixtures. It has been found that a satisfactory separation of proteoses and peptones from the simpler amino-compounds can be effected by means of a solution containing 4 to 5 grams of sodium chloride and 15 grams of tannin in 100 c.c. The precipitation is best carried out at 12°. The reagent should be kept in a cool place, and should not be left more than a few days before being used. An error is occasioned by the precipitation of a portion of the creatine by the reagent, but this may be corrected by estimating the creatine in a portion of the solution before applying the reagent and in the filtrate from the precipitate given by that reagent.  
E. G.

## General and Physical Chemistry.

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**Spectroscopic Observations at Very High Temperatures.** RAFFAELLO NASINI and FRANCESCO ANDERLINI (*Gazzetta*, 1906, 36, ii, 561—570).—With the help of Helbig's carbon tube heated in an electric furnace, the authors have examined the spectra of iodine and nitrogen at high temperatures. The former shows bands of a luminous spectrum distinctly at a temperature somewhat higher than 1000°, and, with nitrogen, a luminous line and band spectrum is obtained at about 3000°. T. H. P.

**The Ultra-violet Phosphorescence Spectrum of Fluorspar.** Variations in the Phosphorescence Spectrum of the same Element in the same Diluent. GEORGES URBAIN and C. SCAL (*Compt. rend.*, 1907, 144, 30—32. Compare this vol., ii, 3).—In fifteen specimens of fluorspar the presence of rare earths has been recognised by the appearance in their cathodic phosphorescence spectra of ultra-violet bands characteristic of gadolinium. On comparison of the gadolinium spectra of natural and synthetical fluorspar, striking differences were observed in the intensity of bands of the same wavelength. These are due to the greater diminution in intensity of one group of bands as compared with that of the other group when the proportion of gadolinium is decreased. This was shown by preparing the fluoride from pure chalk and less than one-thousandth part of gadolinite; its spectrum is identical with that of natural fluorspar. This phenomenon is observed with other phosphorescent systems (compare Abstr., 1906, ii, 138), and is termed the *phenomenon of dilution*. E. H.

**Photochemistry and the Phase Rule.** WILDER D. BANCROFT (*J. Physical Chem.*, 1906, 10, 721—728).—The displacement of the equilibrium in systems under the influence of light is considered from the standpoint of the phase rule. The variability of the intensity of the light introduces another degree of freedom. Strictly speaking, there are as many degrees of freedom as there are kinds of active light, but for most purposes a beam of light may be treated as though it were homogeneous. If the independent variables of a system are the  $n$  components, the pressure, the temperature, and one kind of active light, the coexistence of  $n + 3$  phases will constitute an invariant system. Reference is made to the equilibrium between oxygen and ozone. For a given initial quantity of oxygen at a given pressure and temperature, the equilibrium percentage of ozone is fixed if these are the only variables; it is not fixed, however, if ultra-violet light is introduced as an independent variable. The case of the displacement of the equilibrium between two modifications of a light-sensitive substance in solution is also discussed. H. M. D.



**Radium.** ALBERTO MAYORAL OLIVER (*Anal. Fis. Quim.*, 1906, 4, 132—135).—Actinographs obtained by means of the rays from an incandescent lamp of 5-candle power were found to have blurred outlines, whilst those produced by the agency of 5 mg. of radium bromide had sharply-defined contours. The blurring is regarded as an effect due to the secondary rays.  
G. T. M.

**Production of Radium by Actinium.** BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1906, [iv], 22, 537—538).—The fact that the experimentally determined rate of production of radium from uranium is very much smaller than that indicated by theory is supposed to be due to the existence of a relatively slow-changing intermediate product, and the author suggests that this is actinium. Measurement of the rate of production of radium emanation in the actinium separated from a kilogram of carnotite has furnished numbers from which the time required for the decay of the activity of radium to one-half its initial value is about 3300 years. This is of the same order of magnitude as the most recent estimate made by Rutherford, and this result is supposed to afford evidence in favour of the view that actinium is the intermediate disintegration product between uranium and radium.  
H. M. D.

**Radioactinium.** OSKAR HAHN (*Phil. Mag.*, 1907, [vi], 13, 165—180. Compare Abstr., 1906, ii, 323).—Radioactinium is a direct disintegration product of actinium and is the direct parent of actinium X. The transformation of actinium into radioactinium is rayless. The latter product emits only  $\alpha$ -rays, and is half transformed in about 19.5 days. The methods of separation employed for the isolation of radioactinium throw no definite light on its properties.  
J. C. P.

**The Supposed Derivation of Radium from Uranium.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1905, 3, 60—64).—The experimental results, obtained in the examination of the radioactive pyromorphite of Issy l'Évêque, the radioactive barytes of Carlsbad, and the radioactive deposits of the thermal springs of Battaglia, Baden-Baden, and Nauheim (all of which materials are quite free from uranium) favour the view that radium, thorium, and uranium are three independent radioactive chemical elements.  
G. T. M.

**Relative Activity of Radium and Thorium, Measured by the  $\gamma$ -Radiation.** A. S. EVE (*Amer. J. Sci.*, 1906, [iv], 22, 477—480. Compare Abstr., 1906, ii, 593).—It is found that radium is  $6.9 \times 10^6$  times as active as thorium when both are in radioactive equilibrium, when the activity is measured by the  $\gamma$ -rays. In the preparation of the commercial salts of thorium, about one-half of the radiothorium in the radioactive minerals is abstracted. By measurement of the  $\gamma$ -activity, it is found that the thorium and its products in thorianite is about 2.5 times as active as the thorium and its products in thorium nitrate. This result is in good agreement with those obtained by the  $\alpha$ -ray method and by the emanation method.

In consequence of the continued increase in the proportion of radiothorium, commercial thorium nitrate cannot be used as a standard for  $\gamma$ -ray measurement as was suggested previously.

H. M. D.

**Velocity and Energy of the  $\alpha$ -Particles from Radioactive Substances.** ERNEST RUTHERFORD (*Phil. Mag.*, 1907, [vi], 13, 110—117. Compare Abstr., 1906, ii, 719; Rutherford and Hahn, *ibid.*).—The initial velocities of expulsion of the  $\alpha$ -particles from the products of the radio-elements all lie between  $1.56 \times 10^9$  and  $2.25 \times 10^9$  cm. per second. The  $\alpha$ -particles emitted from thorium C have the greatest velocity, and those from uranium and radium have the least velocity. The average velocity and average energy of the  $\alpha$ -particles from the thorium and actinium families are nearly equal, and are greater than the corresponding values for the radium family. The total energy liberated in consequence of the successive disintegrations of a radium atom is less than the corresponding value for the thorium atom, but is greater than that for actinium. It is noteworthy that for a large number of the radioactive products the velocity of expulsion of the  $\alpha$ -particle for each of the radioactive families increases progressively as the period of transformation decreases. Hence it is probable that the velocity of expulsion of the particle is least for the most stable atoms.

J. C. P.

**The Radioactivity of Spanish Medicinal Springs.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 119—120, 147—149).—The waters from fourteen medicinal springs, obtained from nine hydropathic establishments, have been examined with the result that several samples formerly supposed to possess no radioactive properties have now been found to exhibit a slight degree of radioactivity. Another series of investigations, carried out with Engler and Sieveking's apparatus, showed that specimens from fourteen different springs were all, with one exception, more or less radioactive. As these samples lose their radioactivity very appreciably on keeping, the tests were made as soon as possible after collection. In the case of the water from Burgas de Orense the dissolved gases were also very radioactive.

G. T. M.

**The Radioactivity of Medicinal Springs containing Nitrogen.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 189—192).—Those Spanish mineral waters containing nitrogen, which are reputed to have a valuable therapeutic action, owe this property to the presence of a radioactive emanation. Samples from ten different sources all exhibited radioactivity; these specimens contained some carbon dioxide, but oxygen was more or less displaced by nitrogen.

G. T. M.

**Probable Relationship Subsisting between the Radioactivity of Minerals and Cold Springs in the Sierra de Guadarrama.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 263—269).—A study of the radioactive minerals and springs found in the vicinity of Guadarrama leads to the view that the water owes its

activity to the fact that it has percolated through layers of radioactive minerals.

These minerals belong to many different species all of which are rare; titanium and iron are the predominant elements, accompanied in certain instances by manganese, bismuth, copper, and other common elements. The most radioactive specimens show traces of uranium. These very active substances were found on the highest points of the Sierra, so that the melted snow at once comes into contact with them.

G. T. M.

**Radioactivity of Thermal Mud deposited from the Bagni di Lucca (Tuscany).** GIUSEPPE MAGRI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 699—704).—The author has separated the constituents of the mud deposited by the thermal springs of Bagni di Lucca by means of the ordinary group precipitants, and has tested the radioactivities of equal weights of the various precipitates by means of the electroscopic method. In this way he has demonstrated the presence of several radioactive substances, and the physical examination of the emanations are in accord with the chemical properties of the groups in indicating the presence of radium and thorium. The sulphide precipitate of Group II exhibits strong dispersion, which is possibly due to polonium or one of the radium products. No conclusion can be drawn as regards the presence of actinium.

T. H. P.

**The Radioactivity of Ashes from the Last Eruption of Vesuvius [April 1906].** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 124).—A specimen of Vesuvian ash, collected from the deck of a steamer stationed at Naples at the time of the eruption, was found to be a light grey powder, which when sifted had D 1.20, and when examined by Elster and Geitel's method indicated less than 18.57 volts per 100 grams of material per hour.

G. T. M.

**Radioactive Minerals from Motril (Granada).** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 46—48).—Samples of minerals containing iron and copper from Motril (Granada) were generally found to be more or less radioactive, as was also in a slight degree a sample of spring water from the same locality.

G. T. M.

**Radioactive Cinnabar from Granada [Spain].** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 58—59).—In examining the radioactivity of the non-uraniferous Spanish minerals, a small specimen of cinnabar from Albuñol, Granada, was studied and found to produce an appreciable effect on a photographic plate after twenty to thirty-two days.

G. T. M.

**Radioactivity from the Human Body.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 202—205).—The rate of decay of the radioactivity exhibited by the medicinal water of Caldas de Oviedo was determined at frequent intervals (four to seven days), and it was found that it had practically disappeared in one-and-a-half months. Fresh samples of this water were administered to a human subject

with the result that a slight amount of radioactivity could be detected by Engler and Sieveking's apparatus in the urine and also in the expired air.

G. T. M.

**Electrical Conductivity of Alloys. I. Relation between Conductivity and Constitution.** W. GUERTLER (*Zeit. anorg. Chem.*, 1906, 51, 397—433).—From a comparison of the curves representing the relation between the electrical conductivity and composition of numerous binary alloys with the constitution of the latter as determined more particularly by thermal and microscopic methods, a number of rules showing how the constitution of alloys can be deduced from their electrical conductivity have been established. The available data on conductivity and on constitution are discussed in detail, and it is shown that the rules in question give results which are trustworthy and in good agreement with those obtained by other methods when account is taken of the very different temperatures at which the conductivity and thermal observations have been carried out.

The conductivity data are taken from papers by Matthiessen, Le Chatelier, and others, and are compared with the results of thermal and microscopic observations by Tammann and his pupils, by Heycock and Neville, and others.

The more important rules connecting conductivity and constitution of binary alloys are as follows: (1) Alloys the electrical conductivity of which is a linear function of the volume concentration of the components are not mutually miscible to any appreciable extent in the solid state, and conversely; (2) the conductivity curve (the values of the conductivity being plotted as ordinates against the volume concentration) of alloys which form a complete series of mixed crystals is continuous, but falls rapidly on both sides from the points representing the conductivity of the pure metals and shows a flat minimum; (3) if the components show only limited miscibility, the first law holds for the parts of the curve between the concentrations of the saturated mixed crystals, the second law for the parts between the pure metals and the saturated mixed crystals; (4) if two metals form  $m$  compounds, the complete diagram can be divided up into  $m + 1$  single binary diagrams, and, conversely, from the shape of the curve information as to the existence of compounds can be obtained.

It is pointed out that a sharp point on the conductivity curve always indicates the presence of a chemical compound, but, contrary to the view of Liebenoff, the converse does not always hold.

In the course of the paper, the effect of small quantities of other metals on the properties of iron are discussed, and it is shown, in accordance with the above laws, that the conductivity of the iron is only seriously affected when the admixture is present in solution.

From an investigation of the system copper-zinc, Shepherd (*Abstr.*, 1904, ii, 662) had drawn the conclusion that the elements do not enter into chemical combination, whilst the conductivity curve, as determined by Matthiessen, indicates formation of a compound. The author points out that Shepherd's observations may be interpreted as indicating the existence of a compound of the formula  $\text{Cu}_2\text{Zn}_3$ .

A bibliography of the subject is appended.

G. S.

**Variation of Electrical Conductivity with Change of Temperature in Solutions of Sodium and Potassium Chlorides.**

AURELIO SUÁREZ INCLÁN (*Anal. Fis. Quim.*, 1906, 4, 94—98).—The electrical conductivities of solutions of 1 mol. of sodium chloride in 17.73, 26.52, and 35.36 mols. of water were determined over a range of temperatures from 2—96°; the results when plotted showed points of inflexion for the first solution at 20° and for the other two at 35°. Solutions containing 1 mol. of potassium chloride in 11.85, 23.70, 35.55, and 47.40 mols. of water were similarly examined at 3—94°; the first solution seemed to have a point of inflexion below 0°, whilst with the other three the inflexion occurred at 50°, 60°, and 75° respectively.  
G. T. M.

**Relation of Solution Pressure to Surface Condition in Metals.**

CHARLES E. FAWSITT (*J. Soc. Chem. Ind.*, 1906, 25, 1133—1134).—The surface condition of rods of iron, silver, and gold has been examined by measuring the difference of potential between these and solutions of the corresponding salts. By rotating the rods at about six revolutions per second, constant results were readily obtained. With a series of steels containing different amounts of carbon, it was found that the potential difference in 0.5 molar ferrous sulphate solution is practically constant and equal to that of ferrite.

The solution pressure of brightly polished silver is diminished by annealing at a red heat, but attains its initial value after the silver has been hammered until hard. In the case of gold, after annealing and hardening, the solution pressure is greater than that of the polished metal. A roughening of the surface of iron or steel by etching or blasting also produces an increase of the solution pressure. This is attributed to the greater surface of contact of the metal with the solution.  
H. M. D.

**The Hydrogen-Oxygen Cell. II.**

FRITZ HABER and GLYN W. A. FOSTER (*Zeit. anorg. Chem.*, 1906, 51, 289—314. Compare this vol., ii, 6).—In a former paper it was shown that, whilst the *E.M.F.*'s of hydrogen and oxygen concentration cells and of hydrogen-oxygen cells at high temperatures, gold and platinum being used as electrodes and glass and porcelain as electrolytes, are in satisfactory quantitative agreement with the thermodynamical theory, the influence of varying pressures of water vapour on the *E.M.F.* of hydrogen concentration cells is in qualitative, but not in quantitative agreement with the theory. It is now shown that this divergence is, to some extent at least, due to the absorption and retention of water vapour by the material of the electrolytes, even at 1000°.

In the experiments with porcelain, the middle part of a tube of this material was coated outside and inside with platinum or gold; the outer electrode was in contact with a slow stream of air and served as normal electrode, whilst the inner electrode was in contact with the gases under investigation. The experiments at 860° and 1000° confirmed the results of Haber and Fleischmann (*loc. cit.*).

As regards the influence of water vapour, the thermodynamic theory requires that, if the material of the electrolyte is not indifferent to it,

the effect of increased vapour pressure of water on the *E.M.F.* of the oxygen concentration cell must be in the opposite direction to that in the hydrogen concentration cell, and for the same change of vapour pressure the magnitude of the effect should be equal in the two cases. Experiments with porcelain show that the changes of *E.M.F.* are in opposite directions, as is to be expected, but a slight divergence is found from the values required by theory, probably due to experimental error.

Measurements with glass were made at 450°, and it is shown that the deviations from the simple formula for the *E.M.F.* are due to the action of water vapour on the electrolyte. G. S.

**The Hydrogen-Oxygen Cell. III. FRITZ HABER** (*Zeit. anorg. Chem.*, 1906, 51, 356—368. Compare preceding abstract).—The paper deals with the development of a suggestion which is now finding fairly general acceptance (compare Nernst and von Wartenberg, *Abstr.*, 1906, ii, 729; Lorenz and Hauser, *Abstr.*, 1906, ii, 825), that a platinum electrode saturated with oxygen is not completely reversible, an oxide of platinum being formed which is electrically active, but has a smaller oxygen pressure than the gas itself. From Bose's value for the *E.M.F.* of the hydrogen-oxygen cell (1.14 volts) as compared with the thermodynamical value at the ordinary temperature, 1.23 volts, it is calculated that the oxygen pressure of the compound in question is  $10^{-6}$  atmospheres.

In a previous paper, the reduction potential of hydrogen peroxide was estimated at 0.8 volt, and from this, employing the former value for the *E.M.F.* of the hydrogen-oxygen cell, 1.4 volts was obtained as the oxidation potential of the peroxide. With the new value, 1.23 volts, the oxidation potential of hydrogen peroxide is 1.66 volts, and is therefore identical with the potential at which water is decomposed between platinum electrodes. On this basis it is suggested that in the latter process two OH' ions unite to form hydrogen peroxide which is immediately decomposed in contact with the oxidised platinum surface.

If a platinum electrode is dipped into hydrochloric acid containing chlorine and then washed thoroughly with water and hot alkali, it gives a blue coloration with potassium iodide and starch, much more intense than that produced by the catalytic action of the metal on the oxygen of the air. Since this effect is retained when the potential falls to that of platinum in contact with a solution containing  $\text{Pt}^{+++}$  ions, it is considered that the metal has been attacked with formation of a solid platinum compound. An electrode which has undergone anodic polarisation in sulphuric acid shows similar behaviour. These observations also support the view that passivity is connected with the formation of a superficial layer of oxide.

In addition to the investigations at high temperatures with glass and porcelain as electrolytes (preceding abstract), similar measurements have now been carried out with potassium and sodium hydroxides as electrolytes, and it is shown that in this case also the results are in excellent accord with the thermodynamical theory. G. S.

**Electrolysis of Dilute Solutions of Acids and Alkalis at Low Potentials: Dissolving of Platinum at the Anode by a Direct Current.** GEORGE SENTER (*Trans. Faraday Soc.*, 1906, 2, 142—149).—Dilute solutions of sulphuric acid and sodium hydroxide have been submitted to the action of a current between platinum electrodes at a potential below that at which gaseous oxygen is evolved. The current density at the anode was  $1-2 \times 10^{-7}$  amperes per square centimetre and the anode potential  $-1.4$  to  $-1.55$  volts, the electrolysis being continued for three or four days. In these circumstances an oxidising substance is formed in very small quantity at the anode. It is very stable, especially in alkaline solutions, and is not destroyed by boiling. It liberates iodine from hydriodic acid, but does not react with titanous acid like hydrogen peroxide. Under the same conditions small quantities of platinum are dissolved from the anode in acid solutions, this action taking place to a greater extent with electrodes which have been used for some time than with fresh electrodes. The solvent action is not observed in the electrolysis of alkalis and the author supposes that the platinum is superficially oxidised, the oxide dissolving in acid but not in alkaline solutions.

H. M. D.

**Electrolysis of the Alkali Chlorides. Conductivity, Density, and Specific Heat of Simple and Mixed Solutions of Sodium Chloride and Sodium Hydroxide.** LOUIS DEMOLIS (*J. Chim. Phys.*, 1906, 4, 528—546).—Numerous data have been obtained for the electrical conductivity, density, and specific heat of solutions containing sodium chloride and hydroxide at a series of different concentrations and temperatures.

The density of pure sodium chloride solutions and of mixed solutions can be expressed by the equation  $D_t = [0.999871 + 0.037298N - 0.062455N^2 + 0.00103R - 0.06688R^2]/1 + 0.00039t$ , in which  $N$  and  $R$  are the numbers of grams of sodium chloride and sodium hydroxide per litre respectively, and  $t$  is the temperature. The specific heat values for sodium chloride solutions are found to satisfy the formula proposed by Mathias.

H. M. D.

**Electrolysis of the Alkali Chlorides. Refractive Index, Viscosity and Ionic Transport Ratio of Simple and Mixed Solutions of Sodium Chloride and Hydroxide.** E. BRINER (*J. Chim. Phys.*, 1906, 4, 547—564).—From the experimental data for the refractive index at  $18^\circ$  and for the sodium line the following equations are deduced. For solutions of sodium chloride,  $n_D = 1.3334 + 0.031683C - 0.0669C^2$ ; for sodium hydroxide,  $n_D = 1.3334 + 0.02694C - 0.06289C^2$ ; for potassium hydroxide,  $n_D = 1.3342 + 0.031866C - 0.06112C^2$ , in which  $C$  denotes the concentration in grams per litre. The refractive index of a solution containing sodium chloride and hydroxide cannot be represented accurately by an equation of this type.

The data for the coefficient of viscosity at  $20^\circ$  can be represented by similar equations. Sodium chloride,  $\eta = 0.010015 + 0.041004C + 0.0764C^2$ ; sodium hydroxide,  $\eta = 0.010015 + 0.04457C + 0.06321C^2$ ; potassium hydroxide,  $\eta = 0.010015 + 0.0418C + 0.074C^2$ . The viscosity

coefficients for solutions of sodium chloride and of potassium hydroxide are also calculated by means of the formula suggested by Euler.

The transport number of the anion in sodium hydroxide at a concentration of 84.2 grams per litre was found to be 0.85 at 20–25° and 0.858 at 15°; in potassium hydroxide at a concentration of 152 grams per litre, 0.75°.

H. M. D.

**Electrolytic Oxidation in presence of Fluorine Ions.**  
MARIO G. LEVI and F. AGENO (*Atti R. Accad. Lincei*, 1906, 15, ii, 549–555, 615–620. Compare Skirrow, Abstr., 1903, ii, 69, and Müller, Abstr., 1904, ii, 811 and 812).—Using solutions of chromium sulphate, normal as regards the salt and sulphuric acid, the authors find that the yield of chromic acid obtained on electrolysis is increased by the presence of hydrofluoric acid and by the use of platinised platinum electrodes. The highest yield obtained was 78% of chromic acid, a value comparable with that obtained industrially by means of peroxidised lead electrodes (compare Ahrens, *Elektrochemie*, 1903, 539, and Müller and Soller, Abstr., 1906, ii, 66); the amount of hydrofluoric acid present, 0.498*N*, was only about one-fifth of that used by Skirrow (*loc. cit.*). The diminution of the current density, due to the platinising of the electrodes, probably exerts a favourable influence on the yield of chromic acid.

The addition of sodium fluoride favours the electrolytic oxidation of sodium sulphite to dithionate, with which corresponds a higher anodic potential than with the sulphate, the other oxidation product of the sulphite. With smooth platinum electrodes, the yield of dithionate is raised from 18.6 to 21.3% by the presence in the solution of 1.25% of sodium fluoride and from 21 to 26.1% by 3% of the fluoride. When platinised platinum electrodes are used, the presence of fluorine ions is insufficient to raise the anodic potential to the value necessary for dithionate to be formed, so that the sulphite undergoes complete oxidation to sulphate.

The authors have also electrolysed either solutions of ammonium sulphate rendered alkaline by sodium or potassium hydroxide, or solutions of free ammonia, in presence of sodium or potassium fluoride, the electrodes being of smooth platinum and the cathode being separated by a diaphragm containing 20% sodium or potassium hydroxide solution, according to the fluoride used. The oxygen and nitrogen (by difference) in the anodic gases were determined, and also the nitrite and nitrate formed in the solution. In this oxidation also the fluorine ions produce a slight but appreciable increase in the yield of the compound with which corresponds the higher potential, that is, the nitrate.

Electrolysis of manganese salts in presence of hydrofluoric acid gave results agreeing with those of Skirrow (Abstr., 1903, ii, 69). For the estimation of the permanganate the authors used a method similar to Ballmann's spectroscopic method for estimating lithium in mineral waters (compare Ranzoli, Abstr., 1901, ii, 423), the appearance or disappearance of the characteristic striæ in the absorption spectrum of the permanganate being observed. Using an Auer light and a layer of solution 10 cm. in thickness, the minimum concentration of



permanganate for which these striæ are visible is 0.000002 gram per c.c.

The use of fluorine ions was also applied in the electrolysis of a number of organic compounds, but no useful results were obtained.

T. H. P.

**Specific Heat and Specific Gravity of Allotropic Modifications of Solid Elements.** ALBERT WIGAND (*Ann. Physik*, 1907, [iv], 22, 64—98).—From Richarz's theory (Abstr., 1893, ii, 404; *Ann. Physik*, 1899, 67, 704) it is possible to deduce the conclusion that the greater the specific gravity of any modification of an element the smaller is its specific heat. It is now shown, partly with data obtained by the author, that the rule is valid for the various modifications of carbon, boron, silicon, phosphorus, sulphur, arsenic, selenium, tellurium, and tin.

J. C. P.

**Variation with Temperature of the Specific Heat of Solid Elements.** ALBERT WIGAND (*Ann. Physik*, 1907, [iv], 22, 99—106).—Available data bearing on the relation of the specific heats of the elements to temperature are brought together and represented on a large diagram. The extent to which elements of low atomic weight and small atomic volume deviate from Dulong and Petit's law is discussed, and it is shown that the validity of the law is much more extensive at high temperatures than at low temperatures.

J. C. P.

**Phenomena accompanying Fusion and Crystallisation.** DANIEL VORLÄNDER (*Zeit. physikal. Chem.*, 1906, 57, 357—366).—Under normal conditions *p*-anisylideneanisidine, *p*-anisylidenephenetidine, and anisylidene-*p*-aminoacetophenone melt to isotropic liquids, but if drops of the liquid substances are supercooled a fluid anisotropic phase appears, exhibiting double refraction. The supercooling of the isotropic liquid is in fact of great importance in the search for fluid crystalline substances.

The following substances are capable of existence in two fluid crystalline phases (compare Lehmann, Abstr., 1906, ii, 836): anisylidene-aminoacetophenone, ethyl *p*-azoxybromocinnamate, ethyl anisylidene-*p*-aminocinnamate, and ethyl *p*-acetoxyazobenzeneacrylate. There are therefore for each of these substances three temperatures which correspond with a freezing point or a transition temperature: thus, solid crystalline  $\rightleftharpoons$  bright fluid crystalline  $\rightleftharpoons$  dark fluid crystalline  $\rightleftharpoons$  isotropic liquid. Another interesting substance is anisylidene-*p*-aminobenzoic acid, which exists in two solid modifications and also melts to a crystalline fluid.

The author has succeeded in observing fluid crystals with straight edges and regular angles, and the photographic reproductions accompanying the paper show that there is but little difference in the mode of growth of fluid and solid crystals. It is noteworthy that the form of fluid crystals is affected to a relatively slight extent by alterations in chemical composition.

J. C. P.

**Apparatus for Sublimation in a Vacuum.** R. KEMPF (*Chem. Zeit.*, 1906, 30, 1250. Compare Krafft and Weilandt, Abstr., 1896, ii, 635; Riiber, Abstr., 1900, ii, 468).—The apparatus described and figured consists of three glass parts: a long bulb which is inclined downwards, and in which the substance is heated, is ground into the end of a wide, horizontal tube which receives the sublimate; the other end of the tube is ground into a cap fitted with a tap. The nozzle of the cap is attached to a pump, and the bulb and a portion of the tube are inserted into an air-oven which is heated after the apparatus has been evacuated. The advantages claimed for the apparatus are that the sublimate cannot drop back on to the heated surface, that the sublimation may be carried out under any desired pressure or in the cathode-light vacuum, and that the sublimate can be removed quantitatively and the apparatus readily cleaned. G. Y.

**Distillation and Desiccation in Vacuum by Means of Low Temperatures.** ARSÈNE D'ARSONVAL and FRED. BORDAS (*Ann. Chim. anal.*, 1907, 12, 4—7).—The distilling flask or desiccator is connected with a water air-pump, the vapours are condensed on a surface cooled by liquid air or solid carbon dioxide and acetone, and the last traces are absorbed by especially prepared charcoal. A Crookes's vacuum bulb serves as manometer. For details the original article and illustration should be consulted. L. DE K.

**Ebullioscopic Behaviour of Aliphatic Acids with Abnormal Vapour Densities.** ERNST BECKMANN [with E. BERNHARD, EREMIE-POPA, and WERNER GABEL] (*Zeit. physikal. Chem.*, 1906, 57, 129—146).—The boiling point elevation constant  $K$  can be calculated by the formula  $K = 0.027^2/w$ , even for those solvents (formic, acetic, propionic, and butyric acids, &c.) the vapour densities of which are abnormally large at their boiling points. The following table gives the mean values of  $K$  for the four fatty acids mentioned, obtained experimentally by using such solutes as benzil, benzanilide, and diphenylamine, and also the values of  $K$  calculated from the latent heat of vaporisation:

Solvent.	$K$ . From b. p. experiments.	$K$ . From heat of vaporisation.
Formic acid ... ..	24.0	23.2
Acetic acid ... ..	29.9	30.7
Propionic acid ... ..	35.1	37.5
Butyric acid.....	39.4	33.4

The available data for the heat of vaporisation in many cases exhibit marked discrepancies, and in these cases at least the experimentally deduced values of  $K$  are to be preferred.

Sodium and potassium formates and potassium sulphate appear to be dissociated to a large extent in formic acid solution. Acetates, propionates, butyrates, and stearates have in general the normal molecular weight when dissolved in the corresponding acid, but it is noteworthy that strontium and calcium acetates exhibit a tendency to association in acetic acid solution. J. C. P.

**Thermostat for Low Temperatures.** W. KUNTZE (*Centr. Bakt. Par.*, 1906, ii, 17, 684—688).—A thermostat for low temperatures (about 20°) is described with sketches. It consists of a double-walled wooden box containing a lower zinc water chamber which may be heated when necessary and an upper one for cooling. When desired, the water in the lower chamber can be quickly cooled by means of a cooling tube connected with the upper cold water chamber.  
N. H. J. M.

**Behaviour of Certain Substances at Low Temperatures.** A. HEIDUSCHKA (*Arch. Pharm.*, 1906, 244, 569—571).—The following miscellaneous observations at the temperature of liquid air, -186°, are selected from those enumerated.

Alcoholic solutions of indigotinsulphonic acid and of certain sulphur dyes fluoresce.

The fluorescence of an alcoholic solution of methyl-violet BB was not diminished by admixture with an equal amount of aniline, although a solution of the dye in this solvent exhibited no fluorescence.

An alcoholic solution of methylene-violet RRA, from which the fluorescence had been removed at the ordinary temperature by the addition of alcoholic chrysoidine, recovered its fluorescence to some extent.

Solutions of ferric and aluminium hydroxides, of protargol, and of egg-albumin were not coagulated; on thawing, clear solutions were obtained.  
C. F. B.

**Course of Chemical Reactions at High Temperatures.** FRANZ FISCHER (*Chem. Zeit.*, 1906, 30, 1291—1295).—The influence of temperature on chemical equilibrium and on reaction velocity is discussed. As an instance of the formation of a substance more stable at high temperatures than at low, the fact that nitric oxide is obtained by the rapid cooling of a strongly heated mixture of nitrogen and oxygen is quoted. The application of similar reasoning to the reaction between oxygen and hydrogen explains why hydrogen peroxide is formed on allowing a hydrogen flame to impinge on a block of ice. Several experiments which have already been published elsewhere are described in illustration of the preparation and properties of ozone and hydrogen peroxide.  
P. H.

**Heat Developed on the Addition of Bromine to Certain Unsaturated Substances.** WALDIMIR F. LUGININ and IWAN A. KABLUKOFF (*J. Chim. Phys.*, 1906, 4, 489—506).—The heat developed by the addition of bromine by unsaturated acids of the oleic series and by certain terpenes has been measured, the reacting substances being dissolved in carbon tetrachloride. For the addition of 1 molecule of bromine to 1 molecule of the unsaturated compound, the following amounts of heat were found to be developed: undecenoic acid, 28,609 cal.; oleic acid, 28,757 cal.; elaidic acid, 27,131 cal.; euricic acid, 29,166 cal.; limonene, 28,548 cal.; carvone, 27,545 cal.; *d*-pinene (from Russian terebenthene), 35,784 cal.; *l*-pinene (from French terebenthene), 35,509 cal.; pinene, 36,237 cal. The differences

between the last three numbers are attributed to differences in the purity of the products. By the addition of 2 molecules of bromine to one molecule of limonene, 50,420 cal. are developed, but this result is somewhat indefinite because about 5% of the bromine used is liberated as hydrogen bromide. In the case of carvene the proportion of hydrogen bromide liberated is smaller (2.9%), and 48,936 cal. were obtained for the heat of addition of 2 molecules of bromine to 1 molecule of the hydrocarbon. The results indicate that the addition of the second molecule of bromine is accompanied by a much smaller development of heat than that of the first. H. M. D.

**Relation between Viscosity and Absorption Coefficient for Liquids.** MAX TRAUTZ and H. HENNING (*Zeit. physikal. Chem.*, 1206, 57, 251—254).—A summary of the authors' experimental data bearing on Winkler's formula (Abstr., 1892, 556) and a discussion of that worker's recent paper (Abstr., 1906, ii, 342). Some objection is taken to Winkler's method of calculation, and the experimental results do not conform so closely to the formula as has been represented. At the same time it is noteworthy that for variations in the absorption coefficient from 0.01 to 1300, and variations in the molecular weight of the absorbed gas from 2 to 160 the value of  $k$  remains of the same order of magnitude. J. C. P.

**Direct Measurements of the Osmotic Pressure of Solutions of certain Colloids.** BENJAMIN MOORE and HERBERT E. ROAF (*Biochem. J.*, 1906, 2, 34—73).—The osmometer employed consisted of a metal chamber, between the two halves of which a membrane of parchment paper could be fixed and supported by a platinum grid. The one half of the metal chamber was filled with the colloid solution and connected with a mercury manometer, the other half contained water, occasionally a salt solution.

A 10% gelatin solution was found to give a steady osmotic pressure of about 70 mm. of mercury at 30°. This pressure persists for a long period, and is therefore not an effect due to the initial presence of crystalloids, for these would gradually diffuse out and the osmotic pressure would fall to zero. The observed osmotic pressure increases with rise of temperature; the increase, however, is greater than if the osmotic pressure were proportional to the absolute temperature, and is probably connected with the partial dissociation of the solution aggregates in the gelatin solution. When the gelatin solution is kept for a short time at 70° or 80°, and is then brought back to 30°, the value of the osmotic pressure is considerably higher than that obtained before the heating; there is, however, a gradual recurrence to the previous value. If heating at 80° or 90° is continued for some time a permanent change is effected, and the solution has a higher osmotic pressure. At the same time, the physical properties of the gelatin solution are altered, and proteid derivatives are formed which pass through the membrane.

Other colloids, besides gelatin, which give a distinct osmotic pressure, are the serum proteids and gum acacia. Potato starch and gum tragacanth, on the other hand, appear to have such a high state of aggregation that they give no indication of osmotic pressure.

At the stage of hydrolysis of starch at which the blue colour with iodine has just disappeared the dextrins present give a permanent osmotic pressure. Sugars and uric acid behave as true crystalloids and pass through the membrane.

Addition of a considerable quantity of magnesium sulphate to serum causes, after an initial rise, a fall of osmotic pressure to a value which is less than that given by the original serum.

A lecithin or lanolin membrane is permeable to crystalloids, and hence the supposed presence of such a membrane will not explain the peculiar content of the cell in crystalloids. It is more probable that the cell protoplasm has selective absorptive powers for different ions, and that such ions exist in the cell in combination or adsorption with the cell substance. J. C. P.

**Velocities of Diffusion of Electrolytes.** GIUSEPPE BRUNI and B. L. VANZETTI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 705—715).—The authors have repeated some of the experiments made by Buscaglioni and Purgotti (*Atti R. Ist. Bot. Pavia*, 1905, New Series, 11), on the diffusion of electrolytes and have verified their results. When the two ends of a column of 5% gelatin are placed in contact with solutions of two salts, such as silver sulphate and barium chloride, capable of forming two different precipitates, two distinct septa form in the gelatin, one of each precipitate. That this result is to be explained by the independent migration of the ions, as stated by Buscaglioni and Purgotti (*loc. cit.*), is improbable, and the authors regard it as highly probable that the formation of the two septa depends on supersaturation phenomena (compare Morse and Pierce, *Abstr.*, 1904, ii, 14).

The hydrolysis of coloured salts, such as copper sulphate, may be readily demonstrated by diffusion into gelatin.

The velocity of migration of a substance into gelatin is nearly independent of the concentration of the solution.

Several cases have been met with which are in disaccord with Buscaglioni and Purgotti's hypothesis (*loc. cit.*) that the separate ions diffuse with velocities inversely proportional to the square roots of their weights. T. H. P.

**Modified van der Waals' Equation.** ALEXIUS BATSCINSKI (*Ann. Physik*, 1906, [iv], 21, 1001—1012).—The author's form of the equation is  $pv = RT' - A(1/k - 1/v)/(v - \lambda)$ , in which  $A$ ,  $k$ , and  $\lambda$  are constants. The applicability of this equation is tested in the case of ethyl ether with satisfactory results, and the conclusion is drawn that for ethyl ether and all other substances which obey the foregoing formula the molecular mass is the same in the liquid as in the gaseous state. J. C. P.

**Kinetics of Successive Reactions of the First Order.** ADAM RAKOWSKI (*Zeit. physikal. Chem.*, 1906, 57, 321—340).—A general mathematical study of successive reactions of the first order. The reactions for which detailed formulæ are deduced are those of the following types: (1)  $M_1 \rightarrow M_2 \rightarrow M_3$ ; (2)  $M_1 \rightarrow M_2 \rightleftharpoons M_3$ ; (3)

$M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow M_4$ . Even for these comparatively simple cases, and especially in the last case, very complicated formulæ are obtained, and the testing of the equations by experimental data becomes exceedingly difficult, if not impossible. J. C. P.

**Ionic Velocity and Ionic Hydration. I.** CHARLES G. CARROLL (*Amer. Chem. J.*, 1906, 36, 594—599. Compare Jones and Carroll, *Abstr.*, 1905, ii, 73).—The author shows that the following general law holds for solutions in water or methyl alcohol. The velocity of a given ion, under a constant fall of potential, is directly proportional to the valency of the ion, the cube root of the ionic (atomic) volume and the specific inductive capacity or dielectric constant of the solvent, and is inversely proportional to the viscosity coefficient of the solvent. The validity of the law is tested by means both of relative ionic velocities and of conductivity data, and it is shown that the law admits of a simple physical interpretation. T. H. P.

**Ionic Reactions in Acetone.** PAUL DUTOIT and HENRI DEMIERRE (*J. Chim. Phys.*, 1906, 4, 565—575).—The velocity of the reaction  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + \text{MI} = \text{CH}_2\text{I}\cdot\text{CO}_2\text{H} + \text{MCl}$ , where M represents sodium, potassium, or ammonium, has been investigated in acetone solution. The progress of the reaction was followed by measurement of the electrical conductivity which is almost entirely due to the alkali iodide, for the chloride is almost insoluble in acetone, and the two acids are only very slightly dissociated. The experimental data obtained at temperatures between 36° and 41° indicate that the reaction is bimolecular. The value of the constant calculated from the equation  $k = 1/t \cdot x/a(a-x)$  decreases as the reaction progresses, and this is found to be due to the fact that the change is reversible, equilibrium being reached when about 94% of the iodide has been converted into chloride.

In order to eliminate the influence of the reverse change in deducing the dependence of the velocity on the concentration, the initial velocities only have been compared. The value of  $k$  thus obtained in a series of experiments increases as the concentration diminishes, but  $k/\mu$ , where  $\mu$  is the molecular conductivity of the solution, remains constant. From this the authors conclude that the iodion is the active agent in the substitution process. H. M. D.

**Relationship of the Dissociation of Dissolved Substances to their Reactivity.** J. TIMMERMANS (*Bull. Soc. chim. Belg.*, 1906, 20, 305—313).—A critical review is given of recent results, experimental and speculative, bearing on Ostwald's generalisation regarding the intimate relation between chemical activity and state of ionisation, in the course of which the work recorded in the following abstracts is referred to: Rohland, 1899, ii, 144; 1900, ii, 468. Naumann, 1899, ii, 423; 1904, ii, 819; 1905, ii, 29, 30. Brühl, 1899, ii, 10. Kahlenberg, 1899, ii, 397; 1902, ii, 301. Walden, 1901, ii, 11; 1904, ii, 227; 1906, ii, 149. Moissan and Dewar, 1903, ii, 419. Plotnikoff, 1904, ii, 156. Beckmann, 1904, ii, 235. Franklin and

Kraus, 1905, ii, 298. Shroeder, 1905, ii, 306. Patten, 1905, ii, 36. Wallace Walker, Trans., 1904, 85, 1082.

Mercuric, aluminium, and ferric chlorides furnish solutions in methyl chloride, which exhibit marked electrical conductivities, and the solution of the last-named may even be electrolysed, yielding iron and chlorine. Solutions of ferric chloride, mercuric chloride, and cadmium nitrate in methylal do not conduct electricity, and similarly mercuric and ferric chlorides, dissolved in dimethylamine, scarcely conduct, whereas aluminium iodide in dimethylamine shows marked conductivity. Solutions of potassium iodide in melted iodine and of potassium chloride in liquid chlorine do not conduct.

Molecular weight determinations by the cryoscopic method of solutions of potassium iodide or mercuric iodide in melted iodine gave high results, probably due to the formation of additive compounds in these two cases. These results, the author concludes, lend no support to the views put forward by Brühl and by Wallace Walker (*loc. cit.*).

T. A. H.

**Reactions between Acids and Methyl-Orange.** VICTOR H. VELEY (*Zeit. physikal. Chem.*, 1906, 57, 147—167).—The action of acids (almost all organic) on a dilute solution of methyl-orange has been studied by a colorimetric method. Each tube of the colorimeter was charged with 20 c.c. of the methyl-orange solution. To the one tube were then added successive portions of 0.1 c.c. of acid (generally  $N/200$ ), and fresh methyl-orange solution was added to the other until the colours in the two tubes were equally intense. If  $x$  is the number of added portions of acid and  $y$  is the increase of depth in cm. in the second tube, then for all added acids which obey Ostwald's dilution law the relation between  $x$  and  $y$  is a linear one, and the order of value of the coefficients in the equations  $y = k_1x$ ,  $y = k_2x$ , &c., is the same as the order of the affinity constants of the acids. If the added acid does not obey Ostwald's dilution law, then the  $x$ - $y$  curve represents a parabola, or a straight line not passing through the origin. The coefficients in the linear equations for some dibasic acids exhibit a slight variation with concentration, analogous to the variation with concentration in the case of the affinity constants of these acids.

J. C. P.

**Velocity of Formation of Hydrogen Bromide from its Component Elements.** MAX BODENSTEIN and S. C. LIND (*Zeit. physikal. Chem.*, 1906, 57, 168—192).—At the temperatures at which the authors' experiments were carried out, namely, 224.7°, 251.4°, 277.5°, and 301.3°, the reaction  $H_2 + Br_2 = 2HBr$  proceeds completely from left to right. The results for the velocity are readily reproduced, and are independent of the glass surface of the containing vessel and of traces of foreign gases. The rate of change is very satisfactorily expressed by the empirical formula  $dx/dt = k(a-x)(b-x)^{1/2} / [m + x/(b-x)]$ , in which  $a$  and  $b$  are the initial concentrations of hydrogen and bromine respectively,  $x$  is the hydrogen bromide concentration at time  $t$ , and  $m$  is a constant for which the value 5.0 is chosen. The introduction of a denominator on the right hand side of the foregoing formula is due

to the fact that the combination of hydrogen and bromine is retarded by hydrogen bromide, so that the reaction is an example of negative autocatalysis in a homogeneous system. This retardation is a specific property of hydrogen bromide, and it is shown not to be due to any chemical combination of that compound with the bromine. The presence of other gaseous substances such as carbon tetrachloride, air, or water vapour does not cause any retardation of the reaction, although iodine has a very marked effect in that way. It will be noticed from the foregoing formula that the velocity of the change is proportional to the square root of the bromine concentration, and hence it is suggested that the bromine reacts in the atomic condition.

The temperature coefficient of the reaction has a value which is, if anything, slightly greater than usual. J. C. P.

**Rates of the Reactions in Solutions containing Potassium Bromate, Potassium Iodide, and Hydrochloric Acid.** ROBERT H. CLARK (*J. Physical Chem.*, 1906, 10, 679—700).—The influence of the concentration of each of the reagents on the velocity of the change has been determined by the measurement of the initial velocities. The fractional alteration in the concentration of the reagents was so small in the experiments that the velocity could be treated as practically constant during the interval of change and only in certain cases was it necessary to apply a small correction factor. The reaction was stopped at a particular point by the addition of an excess of an ammonium hydrogen carbonate solution. The data obtained indicate that the rate of liberation of iodine is proportional to the concentrations of the bromate and the iodide, and to the square of the concentration of the acid. The addition of chlorine in the form of sodium chloride does not alter the velocity, which remains the same whether the reaction takes place in air or in an atmosphere of carbon dioxide.

If iodide and bromide are both present in solution, these are oxidised independently, the bromide much more slowly than the iodide. In the presence of iodine which forms the ion  $I_3'$ , the velocity of the change is slightly increased in consequence of the oxidation of the triiodide by the bromic acid. This influence is, however, too small to cause any disturbance in the general character of the change.

The value of the temperature coefficient of the velocity between  $0^\circ$  and  $30^\circ$  is 1.85 per rise of  $10^\circ$ . H. M. D.

**Influence Exerted by a Salt in Various Concentrations on the Velocity of Decolorisation of Aqueous Solutions of Organic Dyes under the Influence of Light.** GUIDO BARGELLINI and ALDO MIELI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 773—778).—From the preliminary experiments here described, it appears that the addition of gradually increasing amounts of a salt to a solution of a dye, such as methylene-blue, causes firstly a diminution, and afterwards an increase, in the rate at which the solution is decolorised by the action of light. There is hence a minimum rate of decolorisation corresponding with a definite concentration of salt. With safranin and potassium chloride, decoloration is slowest in a solution containing about 5% of the salt, and with methyl-violet and magnesium sulphate



the minimum is attained when about 2.5% of the sulphate is present. With solutions of magenta the phenomenon is complicated by the formation of a considerable amount of precipitate. T. H. P.

**A Substance which Possesses Numerous Liquid Phases, of which Three at least are Stable in Regard to the Isotropic Liquid.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 359—362. Compare Abstr., 1906, i, 742).—Cholesteryl cinnamate, the substance in question, softens at 151°, and thereafter exhibits a brilliant display of colour until at 157° it is a thick, orange-red, doubly refracting fluid. If this is stirred, the fluid crystals are seen to form links of lustrous, bright green and violet laminae. As the temperature is raised the liquid becomes thinner, and at 199.5° it is nearly colourless. At that temperature the mass suddenly assumes a white enamel-like appearance, thickens, and separates into two anisotropic liquid layers. The interference colours have now entirely disappeared. On further heating, the substance changes at 201.3° into a clear, colourless, isotropic liquid.

The author thinks that this is a case where the transitions involved in the change solid  $\rightarrow$  liquid occur continuously instead of suddenly. This makes it possible to realise a whole series of labile intermediate conditions. J. C. P.

**Formation of Hydrosols by the Interaction of Ions.** ALFRED LOTTERMOSER (*Chem. Centr.*, 1906, ii, 1597; from *Verh. Ges. deut. Naturf. Aerzte*, 1905, ii, 87—89. Compare Abstr., 1906, ii, 429).—All amorphous silver salts may be obtained in the form of hydrosols by the interaction of ions, provided that an upper limit of concentration is not exceeded. For this purpose it is necessary, however, that an excess of one of the reacting ions should be present. If the latter have combined completely with the salts which practically are undissociated, precipitation of the hydrogel takes place. The existence of the hydrosol in the case of a given ion reaction depends therefore on the presence of a definite quantity of anions or silver ions, whilst, on the other hand, no excess of either ion can be detected in the hydrogel. The hydrosols, which owe their formation to silver ions and are therefore positively charged, are readily gelatinised by OH ions; bi- and multivalent ions have also a strong action. The hydrosols prepared by means of anions are practically insensitive, however, to the action of H ions. E. W. W.

**Hydrate Theory.** HARRY C. JONES (*Zeit. physikal. Chem.*, 1906, 57, 244—250).—In replying to Biltz's criticism (Abstr., 1906, ii, 737) the author defends his claim to be the originator of the hydrate theory as applied to abnormal freezing point depression phenomena. J. C. P.

**Theory of Colloidal Envelopes ("Umhüllung"). Ultramicroscopic Observations.** LEONOR MICHAELIS and LUDWIG PINCUSOHN (*Biochem. Zeit.*, 1906, 2, 251—263. Compare Quincke, Abstr., 1902, ii, 200; Bechhold, 1904, ii, 650; Biltz, 1904, ii, 392).—In continuation

of Raehlmann's work (*Phys. Zeit.*, 1904, 4, 884; *Pflüger's Archiv*, 1906, 112, 128), experiments have been conducted with suspensions of mastic and indophenol, obtained by dissolving the two substances in alcohol, pouring into water, and mixing the suspensions, using the same volume of indophenol, but varying amounts of mastic suspension. The indophenol suspension itself exhibits a red pseudofluorescence (Siedentopf, *Physik. Zeit.*, 1905, 6, 855), but after twenty-four hours the solution has become colourless, and a crystalline precipitate of indophenol is obtained. When a small amount of mastic suspension is present, a diminution of the pseudofluorescence is observed, and in the ultramicroscope numerous white mastic particles are observed with only a few coloured indophenol particles. When the amount of mastic has reached a certain value, the solution has a pure blue colour when observed in transmitted light, the red pseudo-fluorescence has completely disappeared, and also the coloured indophenol particles, and the suspension may be kept for seventy-two hours without undergoing alteration. Such a mixture contains the minimum amount of mastic required to "protect" the indophenol present. Experiments made on counting the number of particles present in a given volume and also in their electrolytic properties lead to the view that the two types of particles unite together to form larger particles, and that probably the union occurs between a particle of each component. The union produces a change in the physical properties of the particles, and this is closely related to the "protective action." The disappearance of the pseudofluorescence indicates that the union produces an alteration in the inner structure of the indophenol particles.

J. J. S.

**A Natural System of arranging the Chemical Elements, in which they fall into the Periodic Groups, based solely on the Atomic Volumes and the Combining Weights.** JAMES MONCKMAN (*Chem. News*, 1907, 95, 5—9).—As an extension of Lothar-Meyer's observations on the relation existing between the combining weights and the atomic volumes of the elements, the author has constructed a series of new curves by plotting combining weights against the tangents of the angles that Meyer's curves form with the horizontal. The ten curves so obtained arrange themselves naturally into three sets, which are termed exionic, endionic, and central; they comprise respectively the lightest, the heavier, and the heaviest elements. The central set consists of three lines and contains the triplets iron, cobalt, and nickel, ruthenium, rhodium, and palladium, osmium, iridium, and platinum. It is claimed for this system of classification that it satisfies a number of qualities that must be found in any perfect system of classification. For details of the system, as well as a tabular representation, the original should be consulted.

P. H.

**New Absorption Apparatus for Gases.** C. JOSEPH GÜLICH (*Chem. Zeit.*, 1906, 30, 1302).—The liquid absorbent is introduced into the top of a narrow vertical tube resting on a pivot, and escapes from it by side-tubes attached at right angles. By the flow of the liquid the tube is set into rapid rotation and a fine spray of liquid is

projected into the surrounding gas, thus ensuring efficient absorption. For details of the apparatus, the diagram in the original paper should be consulted.

P. H.

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## Inorganic Chemistry.

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**Behaviour of the Halogens towards each other.** H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 363—364).—In reviewing the studies that have been made from the point of view of the phase rule of the binary systems I + Cl, I + Br, Br + Cl, the author points out that ICl is a very stable compound, ICl<sub>3</sub> and IBr are feeble compounds, whilst no compound of bromine and chlorine exists. The combining power is therefore greatest in the most distant elements, and greater for the pair Br + I than for the pair Br + Cl. J. C. P.

**Density of Gaseous Hydrogen Chloride, Atomic Weight of Chlorine.** PHILIPPE A. GUYE and G. TER-GAZARIAN (*Compt. rend.*, 1906, 143, 1233—1235).—The recent values obtained for the atomic weight of chlorine are (for Ag = 107·93) 35·473 from the ratio Ag : Cl (Richard and Wells, *Abstr.*, 1905, ii, 450); 35·476 from the density of hydrogen chloride (Leduc corrected by Guye, *Abstr.*, 1905, ii, 442); 35·460 (Ag = 107·89) from the ratio Ag : Cl (Guye and Ter-Gazarian, *Abstr.*, 1906, ii, 750); and 35·463 from the synthesis of hydrogen chloride (Dixon and Edgar, *Abstr.*, 1905, ii, 696). In view of these discrepancies, the authors have redetermined the density of hydrogen chloride, using the method employed in the determination of the density of nitric oxide (*Abstr.*, 1906, ii, 20), the gas being prepared by the action of sulphuric acid on sodium chloride, dried over sulphuric acid and phosphoric oxide, liquefied at the temperature of liquid air, and submitted to a series of fractional distillations. The mean of four determinations of the weight of a litre of hydrogen chloride at *N.P.T.* is 1·6398 grams (Leduc obtained 1·6407), and the corresponding atomic weight of chlorine is 35·461, which is in close agreement with the last two values quoted above, but the authors regard it as provisional only. M. A. W.

**New Hydrogen Sulphide Apparatus.** FERNAND RANWEZ (*Ann. Chim. anal.*, 1907, 12, 7—9).—The apparatus consists essentially of a broad U-shaped tube constricted at the bend and also at a little above the bend as regards the limb which contains the iron sulphide. The top of this limb is closed with a perforated cork through which passes a rectangularly bent tube connected with the delivery tube by means of a small rubber tube which can be closed with a pinchcock. Acid is poured into the other limb, and when the rubber tube is not closed the acid comes in contact with the iron sulphide, and hydrogen sulphide is

evolved. On closing the rubber tube the acid is at once driven back into the other limb.  
L. DE K.

**Decomposition of Persulphates.** MARIO G. LEVI and E. MIGLIORINI (*Gazzetta*, 1906, 36, ii, 599—619. Compare Abstr., 1903, ii, 474).—The reaction of decomposition of persulphates obeys the law of unimolecular reactions in the cases of the sodium and potassium salts, but not in the case of the ammonium salt. Up to a temperature of 30—35°, solutions of persulphates can be kept unchanged for some days, the solution of the ammonium salt being most liable to change. Acids and, to a less degree, alkalis exert a marked accelerating action on the decomposition of persulphates. Platinum black causes slow catalysis of persulphates in solution, the greatest action taking place with ammonium persulphate; the amount of catalysis is a maximum in alkaline, and a minimum in acid solution. Lead and certain other metals also decompose persulphates in solution.

T. H. P.

**Selenates.** ENRICO RIMINI and GIOVANNI MALAGNINI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 561—563).—The acid selenate of hydrazine,  $N_2H_4 \cdot H_2SeO_4$ , is only slightly stable, as are also its solutions in water, in which it dissolves moderately readily. The double hydrazine copper selenate,  $[(N_2H_4)_2 \cdot H_2SeO_4 \cdot CuSeO_4]_2 + H_2O$ , is isomorphous with the corresponding double sulphate, and decomposes gradually when kept.

T. H. P.

**Experiments with the Hot-cold Tube in the Electric Furnace.** RAFFAELLO NASINI and FRANCESCO ANDERLINI (*Gazzetta*, 1906, 36, ii, 570—575).—No combination takes place between nitrogen and oxygen when heated in the hot-cold tube in the electric furnace at 2000°, nor does magnesium absorb argon appreciably at this temperature.

T. H. P.

**Copper Cathodes in Nitric Acid.** J. W. TURRENTINE (*J. Physical Chem.*, 1906, 10, 715—720).—The object of the author's experiments was to ascertain why nitric acid is reduced to ammonia when dilute solutions of the acid are electrolysed, whereas nitric oxide is the chief product in the ordinary contact action of copper on nitric acid.

On electrolysing a 5% nitric acid solution between copper electrodes at a current density of 8 amperes per square decimetre, it was observed that evolution of gas (nitric oxide) did not commence until the more dense copper nitrate solution, which collected in the lower part of the apparatus, came into contact with the cathode. This result appears to show that the copper ions are the cause of the incomplete reduction of the nitric acid, and in a further experiment in which copper was allowed to act on 10% nitric acid solution, means were devised for the removal of the copper ions as fast as these were formed. This removal of copper ions was effected electrolytically, and under such conditions it was found that the reduction product of the chemical action between copper and nitric acid is ammonia. The more rapid rate of solution when nitric oxide is the reduction product is attributable to the accelerating action of nitrous acid.

H. M. D.

**Preparation of Boron Sulphide from Manganese Boride.** JOSEF HOFFMANN (*Zeit. angew. Chem.*, 1906, 19, 2133—2134. Compare Abstr., 1906, ii, 745).—Manganese boride is recommended instead of ferroboration for the preparation of boron sulphide. The substance is heated in a current of hydrogen sulphide at the melting point of antimony, when the boron sulphide deposits in the cold part of the tube as a crystalline mass. It is rapidly decomposed by exposure to moist air. L. DE K.

**Production of Carbon from Carbides.** C. HAHN and ANTON STRUTZ (*Metallurgie*, 1906, 3, 727—732).—In connexion with the question as to the possible formation of petroleum by the action of water vapour on mineral carbides, the authors have investigated the action of various dry gases on carbides.

Heated calcium carbide is decomposed by dry steam, hydrogen chloride, or hydrogen sulphide, yielding amorphous carbon and the corresponding metallic compound. Acetylene is not formed unless moist steam is present. The same result is obtained with aluminium carbide. Manganese carbide, on the other hand, yields a glistening form of carbon, resembling graphite when heated in dry hydrogen chloride. Carborundum reacts with steam at 1300—1400°, yielding silica and carbon in such an intimate state of mixture that it is not possible to determine whether the carbon is amorphous or crystalline. C. H. D.

**Purification of Crystalline Silicon and some Results of the Presence of Impurities in the Preparation of Copper Silicide.** ÉMILE VIGOUROUX (*Bull. Soc. chim.*, 1907, [iv], 1, 16—19. Compare this vol., ii, 89).—Crystalline silicon, prepared by heating potassium silicofluoride with aluminium in a clay crucible and purifying in the usual way by treatment, first with dilute hydrochloric acid and then with dilute hydrofluoric acid, contains iron, which reveals itself by the formation of iron silicide,  $\text{FeSi}_2$ , when such silicon is used in making copper silicide (Abstr., 1906, ii, 168, and this vol., ii, 89).

The author suggests that crystalline silicon, prepared as above, should be purified by digesting it in a finely-powdered state for some hours with hydrofluoric acid diluted with its own volume of water, the operation being conducted in a platinum retort provided with a reflux condenser: the residue resulting from this treatment is then washed and heated during one or two hours in a platinum crucible with sulphuric acid. This treatment should be repeated until a sample of the material is entirely dissipated by treatment with a mixture of nitric and hydrofluoric acids, the acids leaving no residue on evaporation. When crude crystalline silicon is heated in a leaden dish with hydrofluoric acid, the products evolved include a gas burning with a blue flame, which deposits on a cold surface a yellow substance. The same gas, when passed through a heated glass tube, furnishes at the heated portion a similar yellow deposit. T. A. H.

**Action of Hydrogen on Silicon and Silica.** A. DUFOUR (*Ann. Chim. Phys.*, 1906, [viii], 9, 433—474).—A detailed account of work already published (*Abstr.*, 1904, ii, 398, 482). M. A. W.

**The Anhydrous Oxides of the Alkali Metals.** ÉTIENNE RENGADE (*Compt. rend.*, 1906, 143, 1152—1153).—The oxides of rubidium, potassium, and sodium can be obtained in a state of purity by means of the method employed in the preparation of caesium oxide, namely, partially oxidising the metal, and separating the unchanged metal by prolonged distillation in a vacuum (*Abstr.*, 1906, ii, 850); rubidium oxide,  $\text{Rb}_2\text{O}$ , forms small crystals which are golden yellow when hot and become pale yellow on cooling; potassium oxide,  $\text{K}_2\text{O}$ , is a greyish-white, confusedly crystalline mass, whilst sodium oxide,  $\text{Na}_2\text{O}$ , is white and amorphous. It is probable that in this method of preparation a lower oxide of the metal is first formed, which on heating decomposes into the oxide and metal (compare Forcrand, *Abstr.*, 1899, ii, 95). M. A. W.

**Optical Characters of Isomorphous Crystals.** GEORG WULFF (*Zeit. Kryst. Min.*, 1907, 42, 558—586).—Determinations of the optical constants of mixed crystals of potassium and caesium sulphates, of potassium and ammonium sulphates, and of rubidium and ammonium sulphates prove that there is no linear relation between the refractive indices of the mixed crystals and those of the end members of the series. L. J. S.

**Conductivities of Mixtures of Sulphuric Acid with Sulphates. Formation of Complex Salts of Hydrogen.** AUGUSTE HOLLARD (*Bull. Soc. chim.*, 1906, [iii], 35, 1240—1255).—When a 2% solution of sodium sulphate is added to a 6% solution of sulphuric acid in water, there is a diminution in electrical conductivity. When the addition is made to a 2% solution of sulphuric acid in water the conductivity no longer diminishes, but increases slightly, although it is still inferior to the sum of the conductivities of the components of the solution. On the other hand, if the addition is made to a 3% solution of sulphuric acid, the conductivity remains constant, whatever may be the quantity of sodium sulphate added. The conductivity also remains constant when a solution of magnesium, zinc, or cupric sulphate is added to a 3% solution of sulphuric acid, but with ammonium sulphate constancy is only exhibited by an 8% solution of sulphuric acid. These phenomena are due to the disappearance from the sulphuric acid solution, on the addition of solutions of the salts named, of hydrogen ions which combine to form the complex ions  $\text{HSO}_4$ .

The measurements on which these results are based and curves illustrating them are given in detail in the original. T. A. H.

**Action of Alkali Silicates on Soluble Metallic Salts.** ROBERT DOLLFUS (*Compt. rend.*, 1906, 143, 1148—1149).—When small crystals of metallic salts such as ferrous, copper or nickel sulphate, manganese chloride, uranium, or cobalt nitrate are thrown into a solution of sodium or potassium silicate, a semipermeable membrane of the

metallic silicate is formed round the crystal, and owing to the internal osmotic pressure, the low density of the metallic salt solution, and the air bubbles mechanically adhering to the crystal, the "artificial cell" increases in size, and presents the appearance of a vegetable growth.

M. A. W.

**Allotropic Silver and its Colours.** F. E. GALLAGHER (*J. Physical Chem.*, 1906, 10, 701—714).—The different colours of solutions of colloidal silver cannot be explained as an effect due to the difference in the refractive index of the colloidal particles and that of the surrounding medium. The author's experiments, on the other hand, indicate that the phenomenon is probably due to selective light absorption depending on the thickness of the layer of solution, the degree of coagulation, and the concentration of the particles in the solution.

Light is essential to the changes of colour, the rate of change depending on the intensity of the light. It is supposed to act by coagulating the colloidal suspension or by altering the concentration of the particles by increasing the reduction of the silver in solution. With increasing thickness of the absorbing layer or with increasing size of the particles, the amount of blue light transmitted decreases relatively much more rapidly than the amount of transmitted red light.

Ethyl alcohol, acetone, benzene, and other organic liquids prevent the colour changes from taking place in the light. The action appears to consist in the prevention of coagulation.

H. M. D.

**Distillation of the Alloys of Silver with Copper, with Tin, and with Lead.** HENRI MOISSAN and TOSIO WATANABE (*Compt. rend.*, 1907, 144, 16—19. Compare Abstr., 1904, ii, 617).—About 40 grams of each alloy of silver with copper, tin, and lead was distilled in the tube form of electric furnace and the residual alloy examined at short intervals. After a fifteen minutes' distillation of an alloy of equal weights of silver and copper, the residue contained 95.22% of copper and 3.62% of silver. Distillation of an alloy of the composition 36.98% of silver and 64.04% of tin left an alloy containing 2.83% of silver and 93.65% of tin after ten minutes. Similarly, with an alloy of 46.24% of silver and 52.95% of lead, an alloy containing 96.81% of silver remained after two and a half minutes. The conclusion is drawn that lead is more volatile than silver, and silver more volatile than copper or tin. The results agree with those obtained by Krafft (Abstr., 1896, ii, 464, 635), who used very small quantities of alloy and distilled in the cathodic vacuum.

E. H.

**Reversible Action of Oxygen on Magnesium Chloride.** FRITZ HABER and F. FLEISCHMANN (*Zeit. anorg. Chem.*, 1906, 51, 336—347).—The equilibrium constant of the reaction in question has been determined at different temperatures, and a formula representing the displacement of the equilibrium with temperature is suggested.

In carrying out the experiments, dry chlorine and oxygen in varying proportions, mixed with nitrogen, were led slowly over a mixture of magnesium oxide and chloride, contained in a porcelain tube heated in



an electric furnace, the gaseous mixture being analysed on entering and on leaving the tube. The temperatures were such that oxychloride was not formed, the reaction investigated being represented by the equation  $\text{MgCl}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{MgO} + \text{Cl}_2$ . The equilibrium constant corresponding with this equation is  $k_p = p_{\text{Cl}_2}/p_{\text{O}_2}^{\frac{1}{2}}$ ; it is the ratio of the partial pressures of the two gases.

The most satisfactory results were obtained at  $675^\circ$  and  $586^\circ$ , the mean value of  $k_p$  at the former temperature being 0.25, and at the latter temperature 0.18. From these results, by means of van't Hoff's equation connecting the displacement of equilibrium with temperature with  $Q$ , the heat developed in the reaction, the value of  $Q$  at the mean temperature of the experiments,  $630^\circ$ , is calculated as  $-5736$  cal., whilst Berthelot gives  $Q = -7800$  cal. at the ordinary temperature. It is known that  $Q$  in this case decreases with rise of temperature, and on approximate assumptions as to the variation of the specific heats of the gases with temperature it is calculated that at  $630^\circ$  the value of  $Q$  would be  $-5540$  cal., in satisfactory agreement with the value given above.

In conclusion, a formula is given which represents approximately the displacement of the equilibrium with temperature, but this problem cannot be solved satisfactorily until the variation of the specific heats of the reacting substances with temperature is known more accurately.

G. S.

**Action of Oxygen and Water Vapour on Magnesium Chloride.** WILHELM MOLDENHAUER (*Zeit. anorg. Chem.*, 1906, **57**, 369—390).—The experiments described in the first part of this paper were made quite independently of those of Haber (compare preceding abstract), and have led to practically the same conclusions.

The experiments on the equilibrium  $\text{MgCl}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{MgO} + \text{Cl}_2$  were carried out in a large porcelain tube, into which the magnesium chloride was introduced in concentrated solution and then rendered anhydrous by heating in a current of hydrogen chloride. The magnesium oxide for the reverse reaction was introduced in a similar way. The tube was then filled with oxygen or chlorine, as the case might be, kept for some hours at a high temperature, and the resulting mixture of gases analysed. The equilibrium was reached from both sides at  $550^\circ$ ,  $650^\circ$ , and  $700^\circ$ , the values of  $k = C_{\text{Cl}_2}/\sqrt{C_{\text{O}_2}}$ , where  $C_{\text{Cl}_2}$  and  $C_{\text{O}_2}$  represent the respective concentrations of chlorine and oxygen, being 17.4, 25.3, and 29.5 respectively. From these results,  $Q$ , the heat evolved in the reaction at  $600^\circ$ , is calculated as  $-5600$  cals., in good agreement with the calorimetric value when the variation of  $Q$  with temperature is taken into account.

The action of water vapour on magnesium chloride was investigated by a somewhat similar method. In the first place, by heating the chloride with aqueous vapour and hydrogen chloride until equilibrium was established and subsequently analysing the residue, it was shown that from  $350$ — $505^\circ$  there is an equilibrium represented by the equation  $\text{MgCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{MgCl}\cdot\text{OH} + \text{HCl}$ . At  $505$ — $510^\circ$  the oxychloride is decomposed, and above this point equilibrium is established according to the equation  $\text{MgCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{MgO} + 2\text{HCl}$ .

When equilibrium is attained at 350°, 400°, 500°, 600°, and 700°, the gaseous phase contains 69.4, 62.1, 50.2, 75.1, and 90.2 volumes of hydrogen chloride respectively. As the proportion of hydrogen chloride thus decreases with the temperature up to the point at which the oxychloride decomposes and beyond that point increases, it follows that in the first reaction heat is developed—in other words, half the hydrochloric acid is split off from magnesium chloride exothermically, whereas the reaction  $\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}$  is endothermic. The heat developed in the latter reaction, calculated from the displacement of the equilibrium with temperature, is in moderate agreement with the value obtained directly.

In addition to the hydrates of magnesium chloride described by van 't Hoff and Meyerhoffer, a seventh hydrate,  $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ , has been obtained by dehydrating the tetrahydrate in a current of hydrogen chloride above 111°.

The technical bearing of these results is also considered. G. S.

**Conditions of Precipitation of Metallic Sulphides.** MAURICE PADOA and L. CAMBI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 787—796. Compare Bruni and Padoa, *Abstr.*, 1906, ii, 157; MacLauchlan, *Abstr.*, 1903, ii, 716).—The authors have determined, for solutions of different salts of various concentrations and containing varying proportions of acid, the minimum and maximum pressures of hydrogen sulphide between which precipitation of the sulphide of the metal of the salt takes place. The salts examined were: (1) cadmium chloride in presence of hydrochloric acid; (2) zinc sulphate with sulphuric acid; (3) zinc chloride with hydrochloric acid; and (4) ferrous sulphate with sulphuric acid. In the first three cases, the pressures employed varied from 15 to 760 mm., and in the last from 200 mm. to 9.2 atmospheres. The pressures increase with the acidity of the solution. The two forms of apparatus used, one for pressures up to that of the atmosphere and the other for higher pressure, are described.

T. H. P.

**Colloidal Plumbic Acid.** ITALO BELLUCCI and NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 542—549).—When potassium plumbate, as free as possible from adherent alkali, is treated at the ordinary temperature with water, it undergoes complete hydrolysis into  $\text{PbO}_2 \cdot \text{Aq} + 2\text{KHO}$ . The plumbic acid remains in solution in the colloidal state, since cryoscopic measurements of the liquid indicate for the dissolved substances a molecular weight corresponding with  $\text{KHO}/2$ . The plumbic acid does not pass through a parchment membrane, and the solution, which appears turbid in reflected light, can be filtered, diluted with water, heated to boiling, and allowed to solidify without in any way changing the plumbic acid. The solution can be evaporated on the water-bath to a syrupy consistency without coagulating, and the residual gelatinous mass, provided it is not dried, is soluble in water, giving the hydrosol.

In this case the impurity which is essential for the maintenance of the plumbic acid in the condition of hydrosol, the so-called "Solbildner," is potassium hydroxide, the proportion of which is gradually diminished

by continued dialysis until, after 104 hours, the percentage of  $K_2O$  is 1.87, and that of  $PbO_2$ , 98.13. This proportion of  $K_2O$  is of the same order as the amounts of hydrochloric acid essential for the existence of hydrosols of aluminium, chromium, and ferric hydroxides.

T. H. P.

**Properties of the Plumbic Hydrosol.** ITALO BELLUCCI and NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 631—635. Compare preceding abstract).—Two neutral colloidal solutions of plumbic acid containing (1) 0.3174 gram  $PbO_2$  and 0.0081 gram  $K_2O$ , and (2) 0.1288 gram  $PbO_2$  and 0.0330 gram  $K_2O$  per 100 c.c. were found to cause no depression of the freezing point of water, although other solutions containing varying proportions of alkali gave small depressions.

The coagulating actions of the anions (potassium salts) decrease according to the series: (1) iodide, ferrocyanide, tartrate, fluoride; (2) acetate, chromate, iodate, nitrate, sulphate, thiocyanate, chloride, bromide, dichromate, permanganate, chlorate, perchlorate, ferricyanide; (3) periodate, oxalate, carbonate, arsenate, and those of the cations (chlorides) according to the series: (1) aluminium, ferric, calcium, strontium, barium, magnesium, cadmium, mercury, manganese, nickel, cobalt, copper; (2) ammonium, caesium, lithium, potassium, rubidium, sodium. The anions and cations of series (1) produce total coagulation, and those of series (2) partial coagulation, whilst the anions of class (3) are without coagulating action.

On increasing the volume of the coagulating solution used, it was found that the coagulating action was always increased, but not to the same extent for all electrolytes.

T. H. P.

**Solubility and Oxidation Potential of Lead Disulphate and Dioxide.** FRIEDRICH DOLEZALEK and KARL FINCKH (*Zeit. anorg. Chem.*, 1906, 51, 320—327. Compare Abstr., 1906, ii, 597).—The solubility of plumbic sulphate in solutions of sulphuric acid of different strengths has been determined directly at 22°. The concentration of the acid is conveniently expressed as the number of mols. of acid present per mol. of water. The curve representing the solubility rises rapidly from zero at 0.3 mol. to a maximum at 0.6 mol. of acid, slowly falls to a minimum value at 1 mol. of acid, and beyond that point gradually rises. These results are in complete accord with the observations in a previous paper that below a concentration of 0.3 mol. of acid a higher sulphate cannot exist, being hydrolysed to the dioxide, that between 0.3 and 0.6 mol. of acid the solution is in equilibrium with the basic sulphate,  $PbOSO_4 \cdot H_2O$ , and beyond the latter point with the normal sulphate,  $Pb(SO_4)_2$ . The solubility of the former is increased, that of the latter at first diminished, by increasing acid concentration, so that the maximum solubility coincides with the transition point. The gradual increase of solubility beyond a concentration of 1 mol. of acid is due in all probability to formation of complexes.

Lead dioxide, prepared by hydrolysis of the salts of quadrivalent lead, has approximately the same solubility in concentrated sulphuric

acid as the disulphate, and has therefore been changed to the latter. The dioxide, prepared by electrolysis or by chemical oxidation of lead salts, is much less soluble. Contrary to the observations of Elbs and Rixon (*Abstr.*, 1903, ii, 427), and in agreement with these results, lead dioxide is very slightly soluble in an acid solution containing less than 0.3 mol. of the latter per mol. of water. By means of a formula connecting the change of solubility with the acid concentration, the solubility of the peroxide at lower acid concentrations has been calculated; it falls off very rapidly with dilution of the acid.

The oxidation potential of the disulphate with different concentrations of sulphuric acid has been measured at 11.5° against a hydrogen electrode; the *E.M.F.* attains a maximum value of 1.9 volts at a concentration of acid corresponding with the maximum solubility of the disulphate. A formula has also been deduced showing the strength of acid which produces the most powerful oxidising effect at different temperatures.

G. S.

**Bismuth-thallium Alloys.** MASUMI CHIKASHIGÉ (*Zeit. anorg. Chem.*, 1906, 51, 328—335. Compare Heycock and Neville, *Trans.*, 1892, 61, 888; 1894, 65, 31).—As a result of his investigation of this system by Tamman's method of thermal analysis, the author draws the conclusion that the two metals form a compound  $\text{Bi}_5\text{Tl}_3$ , whilst there are indications of the formation of a second compound,  $\text{BiTl}_3$ , under certain conditions.

The freezing point curve of the system shows three maxima at 212° and 37%, 303.5° and 88.7%, and 302° and 99.2% by weight of thallium respectively, the former of which corresponds with a compound  $\text{Bi}_5\text{Tl}_3$ ; and there are three eutectic points at 197° and 20%, 186° and 53%, and 297° and 93% by weight of thallium respectively. The first maximum and the second eutectic point were not observed by Heycock and Neville. The compound  $\text{Bi}_5\text{Tl}_3$  forms a series of mixed crystals from 35.5—38.5% of thallium; another series extends from 66.3—88.75% of thallium. The cooling curve of alloys from 60—76% of thallium shows a transition point at 90°, which may indicate that at that temperature the mixed crystals last mentioned react to form a compound  $\text{BiTl}_3$ .

As regards the maxima at 88.7° and 99.2% of thallium, the alloys in this region behave as mixed crystals and not as chemical compounds; and it is therefore considered that no chemical combination has taken place. Heycock and Neville, who obtained similar results, regarded them as being due to the presence of impurities in their thallium, but it is pointed out that this cannot be the case, as the thallium used in the present experiments was quite pure.

The compound  $\text{Bi}_5\text{Tl}_3$  is soft and difficult to polish, the fresh surface is light grey in colour, but rapidly becomes yellow, and the compound is oxidised by long contact with air.

G. S.

**Preparation of Pure Copper.** ÉMILE VIGOUROUX (*Bull. Soc. chim.*, 1907, [iv], 1, 7—10).—Copper turnings, freed from any visible solid impurity, are heated with hydrochloric acid, a few drops of nitric acid being added to the mixture from time to time to facilitate

solution. The black liquid so produced is filtered in the absence of air into a large excess of recently-boiled, cold distilled water. The mother liquor is decanted from the precipitated cuprous chloride and a fresh supply of distilled water added to the latter. Excess of aluminium, in large fragments, is added to this mixture, which is then set aside until the cuprous chloride is completely reduced. The excess of aluminium is then picked out with wooden tongs and the precipitated copper washed by decantation with water, digested with hydrochloric acid, again washed with distilled water, and finally reduced by heating in a current of hydrogen.

Copper may also be prepared by reducing cuprous chloride with soft iron, but the latter, unlike aluminium, does not attack cupric chloride. Cupric sulphate is reduced by aluminium, but the action proceeds slowly, especially in concentrated solutions of the sulphate even when these are warmed. T. A. H.

**Commercial Copper Silicides.** ÉMILE VIGOUROUX (*Bull. Soc. chim.*, 1906, [iii], 35, 1233—1237. Compare Abstr., 1906, ii, 168, and Lebeau, *ibid.*, ii, 29).—It is pointed out that Lebeau's statement (*loc. cit.*), that chemists who have worked on copper silicides have assumed that a silicide represented by the formula  $\text{Cu}_2\text{Si}$  exists, is inaccurate, since the author had shown (*Proces-verb. Soc. Sci. phys. nat. Bordeaux*, July 18th, 1901) that the maximum quantity of silicon which could be combined with copper was about 10%, corresponding with the formation of a compound  $\text{Cu}_4\text{Si}$ .

Three specimens of commercial copper silicides, reputed to contain 20%, 15%, and 10% of silicon respectively, have been analysed and found to contain as impurities free silicon, iron silicide,  $\text{FeSi}_2$ , manganese silicide,  $\text{MnSi}_2$ , in addition to iron, calcium, and aluminium present in the form of silicides or aluminosilicides. The method of analysis adopted depends essentially on treating the raw material with nitric acid, and is described in detail in the original. T. A. H.

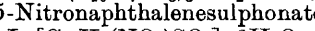
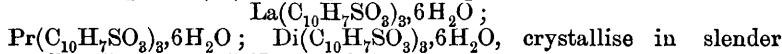
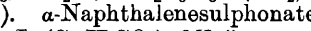
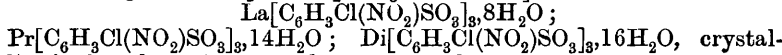
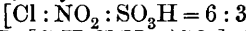
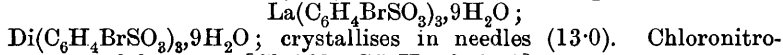
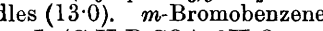
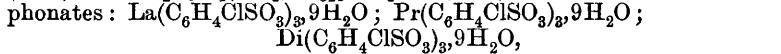
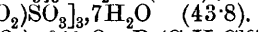
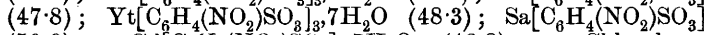
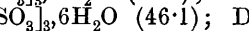
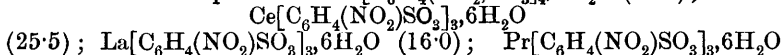
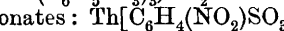
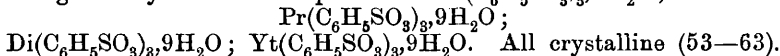
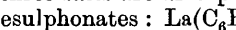
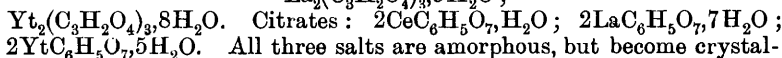
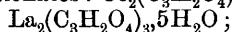
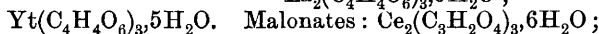
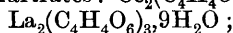
**Cuprous Sulphate.** FRITZ FOERSTER and F. BLANKENBERG (*Ber.*, 1906, 39, 4428—4436).—Acid cupric sulphate solutions dissolve copper forming a cuprous salt, until an equilibrium is established as expressed by the equation  $2\text{Cu}^{++} \rightleftharpoons \text{Cu}^+ + \text{Cu}$ . At the ordinary temperature the concentration of cuprous sulphate is small, but increases on heating. A similar equilibrium is established in ammoniacal cupric sulphate solution which, in presence of copper, is decolorised if the copper concentration is below  $N/10$ , or when heated in stronger solution; this becomes coloured again on cooling. From a solution containing 0.5 mol. cupric sulphate and 8.7 mol. ammonia, a colourless crystalline compound,  $\text{Cu}_2\text{SO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , is obtained, which in presence of moisture decomposes into copper and a cupric compound. Cuprous chloride forms a similar crystalline compound with ammonia. E. F. A.

**Some Reactions of Mercuric Iodide.** N. A. ORLOFF (*Chem. Zeit.*, 1906, 30, 1301).—A methyl alcohol solution of palladous chloride converts mercuric iodide into the chloride with formation of palladous iodide. Freshly precipitated silver chloride turns yellow with a methyl

alcohol solution of mercuric iodide, but in this case a double compound of the two salts is formed. An aqueous solution of thallium chloride gives, with a methyl alcohol solution of mercuric iodide, a red precipitate of the latter, but an aqueous solution of bismuth chloride remains quite clear and colourless on adding an alcoholic solution of mercuric iodide. L DE K.

**Adsorption Compound formed by Iodine with Basic Praseodymium Acetate.** N. A. ORLOFF (*Chem. Zeit.*, 1907, 31, 45).—The precipitate obtained by the addition of ammonia to a solution of praseodymium acetate gives with iodine a violet-blue adsorption compound similar in properties to the corresponding lanthanum compound (Biltz, *Abstr.*, 1904, ii, 339). W. H. G.

**Preparation of Pure Neodymium Oxide and Two New Methods of Separation of Rare Earths.** OTTO HOLMBERG (*Chem. Centr.*, 1906, ii, 1595—1597; from *Chem. Lab. Univ. Upsala*. Pamphlet, 114 pages).—The following organic salts of rare metals have been prepared. The figures in brackets give the solubility of the anhydrous salt in 100 parts of water at 15°. Tartrates:  $\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_6)_3, 6\text{H}_2\text{O}$ ;



$\text{Pr}[\text{C}_{10}\text{H}_6(\text{NO}_2)\text{SO}_3]_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{Di}[\text{C}_{10}\text{H}_6(\text{NO}_2)\text{SO}_3]_3 \cdot 9\text{H}_2\text{O}$ , crystallise in needles (0·2). 1:7-Nitronaphthalenesulphonates:

$\text{La}[\text{C}_{10}\text{H}_6(\text{NO}_2)\text{SO}_3]_3 \cdot 9\text{H}_2\text{O}$ ;  
 $\text{Pr}[\text{C}_{10}\text{H}_6(\text{NO}_2)\text{SO}_3]_3 \cdot 11\text{H}_2\text{O}$ ;  $\text{Di}[\text{C}_{10}\text{H}_6(\text{NO}_2)\text{SO}_3]_3 \cdot 9\text{H}_2\text{O}$ , crystallise in slender needles (about 1·2).

The salts of *m*-nitrobenzenesulphonate show the greatest differences of solubility and are also best adapted for separation on account of their slight isomorphism. Whilst the ratio of the solubilities of didymium and lanthanum ammonium nitrates is 1·6:1, that of the *m*-nitrobenzenesulphonates is 3:1. When 200 grams of didymium oxide which contained some praseodymium and samarium (at. wt. 142·4) were dissolved in *m*-nitrobenzenesulphonic acid and fractionated into twelve portions, samarium, gadolinium, and yttrium accumulated in the mother liquors; on further separation the twelve original fractions yielded fifty-two. The differences in the atomic weights determined by the oxide-sulphate method gave an indication of successful separation. The fractions containing the most neodymium were again treated and the middle portions still further fractionated; fractions 7—13 then gave a constant atomic weight = 144·0—144·1. The absorption bands of a solution of neodymium chloride were measured for eight different concentrations varying from  $2N$  to  $N/64$  (Forsling), and the maxima between 689·5 and 342  $\mu\mu$  are tabulated in the original paper. The spectra showed no trace of absorption bands of samarium, lanthanum, yttrium, or praseodymium, but the first and last fractions of the last series contained a small quantity of samarium or praseodymium. Four series of atomic weight determinations gave values varying from 144·01 to 144·13, or a mean value = 144·08.

A mixture of samarium and gadolinium has also been submitted to the *m*-nitrobenzenesulphonic acid and to the picric acid methods of separation. Gadolinium separated first and then samarium and yttrium, whilst cerium accumulated in the mother liquors. After continued fractionation the potassium sulphate method eventually yielded almost pure samarium oxide which gave an atomic weight = 150. Pure gadolinium compounds were prepared from other fractions. Gadolinium could not be readily separated from terbium by the *m*-nitrobenzenesulphonic acid method, but by means of picric acid and partial precipitation with ammonia, gadolinium of atomic weight = 156 was finally obtained. Samarium may be separated from gadolinium by Urbain-Lacombe's bismuth magnesium nitrate method.

Experiments have also been made on a terbium material which contained yttrium, gadolinium, samarium, and neodymium by means of *m*-nitrobenzenesulphonic acid and picric acid. Paucity of material, however, prevented the complete isolation of terbium. E. W. W.

**Absolute Atomic Weight of Dysprosium.** GUSTAVE D. HINRICHS (*Compt. rend.*, 1906, 143, 1143—1145).—The author has applied his method of calculating atomic weights (Abstr., 1893, ii, 163, 277, 316, 317; 1894, ii, 39, 87, 276; 1900, ii, 534, 539; 1905, ii, 517; 1906, ii, 450) to Urbain's analytical data for the atomic weight of dysprosium (Abstr., 1906, ii, 855), and finds the value  $\text{Dy} = 162·5$  ( $S = 32$ ,  $H = 1$ ). M. A. W.

**Solubility of Carbon in Manganese Sulphide.** M. HOUDARD (*Compt. rend.*, 1906, 143, 1230—1233).—When manganous sulphate is reduced by means of excess of sugar carbon at the temperature of the electric furnace the product has a black metallic appearance, and consists of manganese sulphide containing dissolved graphite (compare Mourlot, *Abstr.*, 1896, ii, 25), the quantity varying from 0·002% to 3·20% according as the heating was prolonged during 2 or 25 minutes respectively, and similar results are obtained when pure manganese sulphide is fused in the electric furnace with 10% of sugar carbon. The graphite obtained from the fusions is non-intumescent; yields with Brodie's mixture the pale yellow, crystalline oxide (*Abstr.*, 1873, 348), which on burning gives black pyrographitic acid; its ignition temperature is 640° (Moissan, *Abstr.*, 1896, ii, 165; 1903, ii, 141), and it contains 98·01—98·92% of carbon, and 0·209—0·218% of ash.

Manganese sulphide at the temperature of the electric arc converts a particle of diamond almost completely into that form of graphite which is insoluble in fuming nitric acid. M. A. W.

**A New Manganese Silicide.** GUSTAV GIN (*Compt. rend.*, 1906, 143, 1229—1230).—When rhodonite is reduced in the electric furnace, a crystalline silicomanganese is obtained having the percentage composition: Mn=68·64—69·26; Fe=4·40—3·18; Al=0·74—0·60; Si=25·02—25·51; C=0·16—0·18; S=0·01; P=0·01; and containing 95% of a crystalline *manganese silicide*,  $\text{Mn}_3\text{Si}_2$  (compare Lebeau, *Abstr.*, 1904, ii, 343; and Vigouroux, *Abstr.*, 1905, ii, 822), which forms brilliant, prismatic crystals, sometimes 5 cm. long,  $D^{15}$  6·05, m. p. 1250°—1300°; is attacked by chlorine with incandescence at a red heat, is not changed by oxygen at the ordinary temperature, but superficially oxidised at 500°; is readily attacked by the gaseous halogen acids, by nitric or hydrochloric acid or aqua regia, or by fused alkali carbonates or mixtures of carbonates and nitrates, whilst sulphuric acid has no action on the compound. M. A. W.

**Influence of Chromium on the Solubility of Carbon in Iron and on the Formation of Graphite.** PAUL GOERENS and A. STADELER (*Metallurgie*, 1907, 4, 18—24).—It is known that a part of the chromium in iron-chromium-carbon alloys is present as the carbide  $\text{Cr}_2\text{C}_3$ ; it is not known, however, whether definite double carbides of iron and chromium are formed, or whether the two carbides,  $\text{Cr}_2\text{C}_3$  and  $\text{Fe}_3\text{C}$ , merely form solid solutions with one another. The authors have melted iron with ferro-chromium in presence of an excess of carbon, and have determined the freezing point and composition of the resulting alloys. It is necessary to heat to about 1600° to insure saturation with carbon.

The presence of chromium increases the solubility of carbon in iron, so that when 62% of chromium is reached 9·2% of carbon is dissolved. The freezing point of these alloys increases with increasing chromium content; the results are recorded in a diagram with triangular co-ordinates. The position of the martensite-cementite eutectic point is displaced in the direction of higher carbon by addition of chromium, so



that an alloy containing 5% of chromium and 4.7% of carbon is entirely composed of eutectic.

Microscopic examination confirms the above results. When the eutectic point is passed, crystals appear which at first have the appearance of cementite, but with increase of chromium resemble more and more closely the crystals of chromium carbide. The formation of graphite is hindered by the addition of chromium, even when silicon is present. C. H. D.

**Copper and Iron [Alloys].** HERMANN WEDDING and WILHELM MÜLLER (*Stahl. u. Eisen*, 1906, 26, 1444—1447).—Copper alloys with iron in all proportions. The alloys are conveniently prepared by Goldschmidt's aluminothermic method. The malleability of iron is reduced by addition of copper, but the hardness and strength are increased.

An alloy containing 7.77% of copper and 0.14% of carbon does not show any separate micrographic constituent, but the crystal grains are more curved and interlocked than in pure iron. In alloys containing more carbon, the presence of copper hinders the formation of pearlite, causing segregated cementite to appear. The transformation temperature is lowered to 620—640° by the addition of copper.

C. H. D.

**Soluble Iron Sulphide.** A. KONSCHIEGG and HANS MALFATTI (*Zeit. anal. Chem.*, 1906, 45, 747—751).—A preliminary paper on the behaviour of iron sulphides towards alkali sulphides. Ferrous sulphide does not dissolve in aqueous potassium or sodium hydroxide, but the mixture of ferrous sulphide and sulphur formed on adding ammonium sulphide to ferric chloride yields a dark green solution. The authors assume the presence of a polysulphide of iron with acidic properties, which in presence of alkali hydroxides forms a true solution, and not one containing colloidal iron. In the absence of ammonium chloride, ferric hydroxide or basic phosphate dissolves in ammonium sulphide to a dark green liquid, which is precipitated by ammonium chloride and also by a large excess of ammonium polysulphide (compare also de Koninck, *Abstr.*, 1906, ii, 397).

L. DE K.

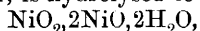
**Ferrous Compounds of Nitric Oxide.** WILHELM MANCHOT and K. ZECHENTMAYER (*Annalen*, 1906, 350, 368—389. Compare Gay, *Abstr.*, 1885, 1109; Thomas, *Abstr.*, 1899, ii, 368, 426).—The authors have investigated quantitatively the absorption of nitric oxide by aqueous and alcoholic solutions of ferrous salts under varying conditions. The results are tabulated and expressed in curves, and the following conclusions are drawn. The absorption of nitric oxide by a ferrous salt results from the formation of a chemical compound containing Fe and NO in the proportion 1 : 1. Under all conditions, therefore, the limit of absorption is reached when 1 mol. of nitric oxide has been absorbed for each ferrous atom present, and corresponds with the conversion of Fe<sup>II</sup> into Fe<sup>III</sup>. The formation of the compound is a reversible reaction; the degree of dissociation varies with the ferrous salt, but is dependent also on the pressure, temperature, concentration of the ferrous

salt, presence of indifferent solutes, and nature of the solvent, to an extent which is in agreement with the laws of chemical dissociation.  
G. Y.

**Cryoscopy of Colloidal Solutions of Ferric Hydroxy-chloride.** G. MALFITANO and LEOPOLD MICHEL (*Compt. rend.*, 1906, 143, 1141—1143. Compare Abstr., 1906, ii, 450, 526, 647).—Attempts to determine the molecular mass of the granules of colloidal ferric hydroxychloride from the difference between the freezing point of a colloidal solution and the filtrate obtained by filtering the solution through a collodion membrane (Abstr., 1906, ii, 526) were unsuccessful, as the differences were sometimes negative and sometimes positive.  
M. A. W.

**Acid Functions of Nickel Dioxide.** ITALO BELLUCCI and S. RUBEGNI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 778—787. Compare Bellucci and Clavari, Abstr., 1905, ii, 823).—The authors have confirmed the existence of the compound  $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$  prepared by Dudley (Abstr., 1897, ii, 171). The alkali, which is only removed by very thorough washing with water, exists in combination with the nickel oxides in the form of the *nickelite*,  $\text{Na}_2\text{Ni}_3\text{O}_6$ , or  
 $2\text{NiO}_2 \cdot \text{NiO} \cdot \text{Na}_2\text{O}$ ,

which the authors have prepared and analysed. This compound, when washed with boiling water, is hydrolysed to the compound



whilst the potassium compound,  $\text{NiO}_2 \cdot \text{NiO} \cdot \text{K}_2\text{O}$  (compare Hoffmann and Hiendlmaier, Abstr., 1906, ii, 747), on hydrolysis with iced water yields the compound  $\text{NiO}_2 \cdot \text{NiO} \cdot 2\text{H}_2\text{O}$ . In both cases, the product of hydrolysis retains unchanged the crystalline appearance of the original alkali nickelite.  
T. H. P.

**Nickel Chromates.** MAX GRÖGER (*Zeit. anorg. Chem.*, 1906, 51, 348—355. Compare Abstr., 1906, ii, 451).—Normal aqueous solutions of nickelous chloride were mixed with normal solutions of sodium, potassium, and ammonium chromates, left for some days, and the resulting precipitates washed and dried. All the products were reddish-brown in colour and proved to be basic chromates of nickel containing varying proportions of alkali chromates. They are hydrolysed by water, alkali chromate and acid chromates of nickel going into solution and highly basic chromates of nickel remaining behind. Unlike the behaviour of the corresponding manganese and cobalt compounds, no higher oxide of nickel was found in the residue.

By interaction of stronger solutions, three crystalline double chromates were obtained. The compound,  $\text{NiCrO}_4 \cdot \text{K}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$ , occurs in yellow needles which are stable in the air but undergo hydrolysis with water. The compound,  $\text{NiCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$ , was obtained in green crystals (compare Briggs, Trans., 1903, 83, 391). By a slightly different method, a second nickel ammonium chromate, of the probable formula  $(\text{NH}_4)_2\text{CrO}_4 \cdot \text{NiCrO}_4 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$ , was isolated in well-formed, orange-brown prisms. This compound is

stable in the air but is hydrolysed by water with formation of basic nickel chromates. G. S.

**The Reduction of Oxides by Aluminium. Preparation of Chromium.** EMILE VIGOUROUX (*Bull. Soc. chim.*, 1907, [iv], 1, 10—13. Compare Abstr., 1905, ii, 822).—Commercial chromium, prepared by the “thermit” process, has the advantage of being free from carbon, but frequently contains silicon, aluminium, iron, and portions of slag. A much purer material can be prepared on a small scale by a modification of this process, which consists in mixing from 10% to 20% of dried chromium trioxide with the dried chromium sesquioxide and then incorporating the necessary quantity of aluminium powder. The mixture is heated in a crucible lined with magnesia. Under these conditions a vigorous reaction ensues, which, when 20% of chromium trioxide has been added, lasts about a minute, the contents of the crucible becoming thoroughly melted and the slag separating readily from the metal. The chromium produced contains as impurities 0·36—0·4% of silicon and 0·74—0·85% of aluminium and iron. T. A. H.

**Definite Compounds formed by Chromium and Boron.** ARMAND BINET DU JASSONEIX (*Compt. rend.*, 1906, 143, 1149—1151).—Chromium-boron alloys (this vol., ii, 30) contain the two definite compounds  $\text{Cr}_3\text{B}_2$  and  $\text{CrB}$  dissolved respectively in a medium less rich in boron, which can only be isolated in a state of purity from the nearly homogeneous alloys the composition of which is close to that of their own. The *boride*,  $\text{Cr}_3\text{B}_2$ , isolated from an alloy containing 11·6% of boron by the action of hydrogen chloride below a red heat, has  $D^{15} 6\cdot7$ , burns in fluorine when gently heated, and is attacked with incandescence by chlorine below a red heat; the action of bromine is less vigorous, whilst iodine vapour has only a superficial action at a red heat. When heated in air or oxygen, it becomes covered with a vitreous layer of the borate; it is converted into a mixture of boron and chromium sulphides together with unchanged boron by the action of boiling sulphur; it is completely soluble in concentrated or dilute hydrofluoric, hydrochloric, or sulphuric acid, and is oxidised with incandescence by fused alkali hydroxides or carbonates; it is not acted on by nitric acid or alkali solution, or by nitrogen at a white heat.

The *boride*,  $\text{CrB}$ , isolated by the action of hydrogen chloride or chlorine below a red heat on the alloy containing 16% of boron, has  $D^{15} 6\cdot1$ , and whilst its chemical properties closely resemble those of the lower boride,  $\text{Cr}_3\text{B}_2$ , it is in general more readily attacked; it takes fire in cold in contact with fluorine, and when heated in nitrogen at a white heat forms a greyish-black substance which liberates ammonia on treatment with fused potassium hydroxide.

M. A. W.

**The Violet and Green Varieties of Chromium Chloride.** F. JOST (*Ber.*, 1906, 39, 4327—4330. Compare Recoura, Abstr., 1886, 508; Piccini, Abstr., 1895, ii, 229; Werner and Gubser, Abstr., 1901, ii, 453).—The author shows by determinations of the molecular

weight by the ebullioscopic method of the violet and green varieties of chromium chloride respectively in methyl alcoholic solution that the water plays a different rôle in the green chloride and violet chlorides. The violet salt gives values for its molecular weight varying from 54.7 to 60.3, whereas the green salt gives values varying from 33.1 to 33.4.

The molecular conductivity of a solution of the violet salt in methyl alcohol varies from 67.7 to 97.7, whereas the green modification gives values varying from 43.6 to 64.2.

The experiments quoted are in accordance with Werner's theory in so far that in the green hydrate the water is more loosely bound than in the violet.

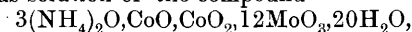
A. McK.

**Cobaltimolybdates.** CARL FRIEDHEIM and F. KELLER (*Ber.*, 1906, 39, 4301—4310).—The cobaltimolybdates described by the authors are distinguished from cobaltomolybdates in that chlorine is evolved when they are boiled with hydrochloric acid. They are characterised by possessing a colour varying from brilliant green to dark green.

The compound  $3(\text{NH}_4)_2\text{O}, \text{CoO}, \text{CoO}_2, 12\text{MoO}_3, 20\text{H}_2\text{O}$  is obtained by adding a 30% aqueous solution of ammonium persulphate to a mixture of cobaltous acetate and ammonium paramolybdate, acidifying with dilute acetic acid, and then slowly heating. It may also be prepared by the action of cobaltous acetate on the ammonium permolybdate,  $3(\text{NH}_4)_2\text{O}, 5\text{MoO}_3, 2\text{MoO}_4, 6\text{H}_2\text{O}$ . It forms green, rhombic plates and dissolves in water to a green solution. With concentrated sulphuric acid, oxygen is evolved; ammonia is evolved by the action of potassium or sodium hydroxide. It is reduced by sulphurous acid. Hydrogen peroxide causes the evolution of oxygen whilst permolybdates are formed.

The compound  $2(\text{NH}_4)_2\text{O}, \text{CoO}, \text{CoO}_2, 10\text{MoO}_3, 12\text{H}_2\text{O}$ , best obtained from cobaltous acetate, ammonium paramolybdate, and hydrogen peroxide, forms dark green rhombic crystals.

The compound  $3\text{K}_2\text{O}, \text{CoO}, \text{CoO}_2, 10\text{MoO}_3, 11\text{H}_2\text{O}$ , obtained either from cobaltous acetate, potassium persulphate, and potassium paramolybdate or from cobaltous acetate and ammonium permolybdate and potassium chloride, or by the addition of potassium chloride to a cold saturated aqueous solution of the compound

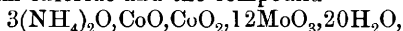


forms greenish-white, rhombic crystals.

The compound  $3\text{K}_2\text{O}, \text{CoO}, \text{CoO}_2, 12\text{MoO}_3, 15\text{H}_2\text{O}$ , prepared by the addition of potassium chloride to an aqueous solution of the compound  $2(\text{NH}_4)_2\text{O}, \text{CoO}, \text{CoO}_2, 10\text{MoO}_3, 12\text{H}_2\text{O}$ , forms olive-green crystals.

The compound  $3\text{BaO}, \text{CoO}, \text{CoO}_2, 9\text{MoO}_3, 25\text{H}_2\text{O}$ , prepared by the addition of barium chloride to an aqueous solution of the compound  $2(\text{NH}_4)_2\text{O}, \text{CoO}, \text{CoO}_2, 10\text{MoO}_3, 22\text{H}_2\text{O}$ , is bright green.

The compound  $\frac{1}{2}(\text{NH}_4)_2\text{O}, 1\frac{1}{2}\text{BaO}, \text{CoO}, \text{CoO}_2, 10\text{MoO}_3, 18\frac{1}{2}\text{H}_2\text{O}$ , prepared from barium chloride and the compound



is bright green.

A. McK.

**Preparation of Titanium Tetrachloride.** ÉMILE VIGOUROUX and G. ARRIVAUT (*Bull. Soc. chim.*, 1907, [iv], 1, 19—21).—Commercial ferrotitanium, containing about 55% of titanium, is employed as a raw material. This, in a coarsely powdered condition, is placed in a wide porcelain tube heated in a Mermet furnace. A current of dry chlorine is passed over the heated alloy, and the reaction commences when the latter is at a dull red heat. This method has the disadvantage that considerable quantities of ferric chloride are formed, which are liable to block the tube unless they are periodically removed. This difficulty may be overcome by digesting the finely powdered ferrotitanium with dilute hydrochloric acid, which leaves a product containing 80—90% of titanium with small quantities of titanium dioxide. The latter may be removed by levigation, and the residue is treated as before, when it furnishes crude titanium tetrachloride and leaves in the porcelain tube a small residue of titanium dioxide. The titanium dioxide obtained as a by-product may also be converted into the tetrachloride by mixing it with carbon and heating in a current of chlorine. The crude titanium tetrachloride is filtered to remove suspended ferric chloride, and the filtrate on fractional distillation yields the pure tetrachloride, b. p. 136°.

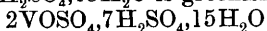
T. A. H.

**Colloidal Compound of Thorium with Uranium.** BÉLA SZILARD (*Compt. rend.*, 1906, 143, 1145—1147).—Thorium hydroxide, precipitated by means of ammonia and well washed, partially dissolves in a hot solution of uranium nitrate forming a deep red colloidal mixture, which on separation in a centrifugal apparatus and drying in a vacuum over sulphuric acid, forms small, brilliant, carmine red, transparent plates which are amorphous and have the following percentage composition: Th = 72—74, U = 4—5.5, H<sub>2</sub>O = 12—13, O = 10—11. The dry compound is stable towards heat and light, dissolves without decomposition in hot water, and yields the corresponding salts when dissolved in dilute acids; it has  $D_{18.2}^{20} 4.82$ — $5.45$ , and when thrown into water produces a sharp hissing with evolution of a gas the nature of which is at present not determined. The compound is more readily prepared by heating the mixture of thorium hydroxide and uranium nitrate in an autoclave at 200° under 15 atmos. pressure. When uranyl chloride replaces uranium nitrate in the above reaction, the colour of the colloidal compound is reddish-yellow; the reaction proceeds very slowly when uranium acetate or sulphate is employed in place of the nitrate, whilst thorium nitrate has no action on thorium hydroxide.

M. A. W.

**Some Sulphates of Quadrivalent Vanadium.** GUSTAVE GAIN (*Compt. rend.*, 1906, 143, 1154—1156. Compare this vol., ii, 32).—By the action of different quantities of sulphuric acid on the deep blue liquid obtained when a mixture of the oxides V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>4</sub> is treated with a saturated solution of sulphur dioxide, the author has prepared three *acid vanadyl sulphates* belonging to the same group as those prepared by Koppel and Behrendt (*Abstr.*, 1903, ii, 551), whilst two other members of the same series have been prepared by the action

of sulphuric acid on red hydrated hypovanadic acid,  $V_2O_4 \cdot 2H_2O$ . These new acid vanadyl sulphates are crystalline and possess blue colours:  $2VOSO_4 \cdot 3H_2SO_4 \cdot 15H_2O$  is azure blue,  $2VOSO_4 \cdot 4H_2SO_4 \cdot 16H_2O$  is turquoise blue,  $2VOSO_4 \cdot 5H_2SO_4 \cdot 15H_2O$  is greenish-blue,



is bright blue, and  $2VOSO_4 \cdot 8H_2SO_4 \cdot 16H_2O$  is very bright blue.

M. A. W.

**Preparation and Chemical Properties of Antimony Pentafluoride.** OTTO RUFF [and, in part, with GRAF, HELLER, and KNOCH] (*Ber.*, 1906, 39, 4310—4327. Compare Ruff and Plato, *Abstr.*, 1904, ii, 265).—Additional details for the preparation of antimony pentafluoride by the action of hydrogen fluoride on antimony pentachloride are given. In the course of the preparation it is probable that a compound,  $SbF_5 \cdot 5HF$ , is formed from which the hydrogen fluoride must be completely eliminated before the antimony pentachloride is distilled.

Antimony pentafluoride has b. p.  $149-150^\circ$  instead of  $155^\circ$  as formerly stated by Ruff and Plato (*loc. cit.*).

Chlorine apparently has no action on antimony pentafluoride; bromine forms a viscid, dark-brown mass, possibly containing the compound  $SbF_5 \cdot Br$ .

Iodine reacts with antimony pentafluoride with development of heat and the formation either of a bluish-green liquid or of a dark brown or bluish-green solid, according to the amount of pentafluoride used. When an excess of pentafluoride is used and the mixture is heated at  $160-220^\circ$ , the compound  $(SbF_5)_2I$  is formed as a dark bluish-green, crystalline mass, m.p.  $110-115^\circ$ , which does not lose iodine at  $240^\circ$ ; by prolonged heating in a current of carbon dioxide, practically no iodide is given off, but the excess of antimony pentafluoride distils over. Water decomposes it with hissing and separation of iodine.

If an excess of iodine is used, and the temperature is raised above the b. p. of iodine, the compound  $SbF_5I$  is formed by the action of iodine on antimony pentafluoride after the excess of iodine is evaporated off. When heated above  $260^\circ$ , iodine is evolved. The compound  $SbF_5I$ , m. p. slightly below  $80^\circ$ , is dark brown and differs from the compound  $(SbF_5)_2I$  in undergoing slow decomposition with water.

The solution of sulphur in antimony pentafluoride is dark blue and yields the compound  $SbF_5S$ , m. p. about  $230^\circ$ . It is very hygroscopic and when acted on by moist air yields sulphur; antimony trichloride and thionyl fluoride are also formed. The action of water probably proceeds according to the equations  $2SbF_5S + H_2O = 2SbF_3 + S + SOF_2 + 2HF$  and  $SOF_2 + H_2O = SO_2 + 2HF$ .

Antimony pentafluoride is acted on by phosphorus with production of flame and the formation of yellow vapour, which sublimes.

The majority of metals, when dry, do not act on antimony pentafluoride. When heated with sodium, rapid combustion occurs with the formation of white vapour. Antimony dust reduces it to the trifluoride. With little water, it forms the solid hydrate,  $SbF_5 \cdot 2H_2O$  (*loc. cit.*). Its aqueous solution is not decomposed in the cold by

hydrogen sulphide or by potassium iodide; action does not occur until the temperature is raised.

On the addition of sodium hydroxide or of sodium carbonate, it forms sodium hydrogen pyroantimonate in quantitative yield.

When its aqueous solution is evaporated, the syrupy residue contains a hydrate of antimony pentafluoride, which, when heated, is decomposed with formation of water, hydrofluoric acid, and antimonie acid; the syrup, however, does not form anhydrous antimony pentafluoride when heated with sulphuric acid or phosphoric oxide.

When a current of hydrogen sulphide is passed over it, sulphur, hydrogen fluoride, and an antimony thiofluoride are formed.

When a current of dry ammonia is passed over it, a vigorous action occurs and the pentafluoride becomes coated with a yellowish-red crust which prevents further action. When heated, however, with liquid ammonia at  $100^{\circ}$  in a platinum tube, it forms *diamino-diantimony-trifluoroimide dihydrofluoride*,  $\text{NH}(\text{SbF}_3 \cdot \text{NH}_2 \cdot \text{HF})_2$ , a white powder which is very readily decomposed by atmospheric moisture; it is slowly acted on by water with formation of antimonie acid; its aqueous solution is acid towards litmus.

Antimony pentafluoride is acted on by nitrogen sulphide, sulphur dichloride, and chromyl chloride respectively. When heated to above  $100^{\circ}$  with molybdenum pentachloride, it forms a molybdenum fluoride and antimony pentachloride, the latter parting with some of its chlorine to form double compounds with the excess of antimony pentafluoride. With tungsten hexachloride, it forms tungsten hexafluoride. It reacts vigorously with phosphorus trichloride with the formation of phosphorus trifluoride. With phosphoric oxide, it forms phosphorus oxyfluoride. It forms a series of crystalline compounds with arsenic trifluoride. With antimony trifluoride, it forms compounds varying in composition from  $\text{SbF}_5 \cdot 2\text{SbF}_3$  to  $\text{SbF}_5 \cdot 5\text{SbF}_3$ . Hydrogen chloride is evolved when it is mixed with tin tetrachloride, titanium tetrachloride, or silicon tetrachloride. Colloidal silicic acid, when warmed with antimony pentafluoride, forms antimonie acid and silicon tetrafluoride.

The behaviour of antimony pentafluoride towards various carbon compounds was also investigated. Filter paper, cork, wood, and india-rubber are attacked at once. The action with benzene is vigorous, hydrogen fluoride being evolved. Ether, alcohol, acetone, glacial acetic acid, ethyl acetate, carbon disulphide, light petroleum, toluene, and chloroform all react with antimony pentafluoride. With carbon tetrachloride at about  $45^{\circ}$ , a gas is evolved which readily liquefied and is probably  $\text{CCl}_3\text{F}$ .

The compound  $\text{SbF}_5 \cdot 2\text{NH}_3$  is obtained by the action of liquid ammonia on antimony trifluoride as a yellow powder which loses ammonia in contact with moist air. It is less stable than the compound obtained from antimony pentafluoride. A. McK.

**Alloys of Palladium and Silver.** RUDOLF RUER (*Zeit. anorg. Chem.*, 1906, 51, 315—319. Compare this vol., ii, 32).—The freezing-point curve falls regularly from the melting point of palladium,  $1541^{\circ}$ , to that of silver,  $961.5^{\circ}$ ; unlike the system palladium-copper, the curve is slightly concave to the axis of concentration. It follows that the

metals form a complete series of mixed crystals with no indication of chemical combination, and this conclusion is confirmed by microscopic observations.

The hardness of the alloys lies between that of the components and increases with the proportion of palladium.

The micro-structure of the alloys is described and illustrated by six microphotographs. G. S.

**Alloys of Palladium and Gold.** RUDOLF RUER (*Zeit. anorg. Chem.*, 1906, **51**, 391—396. Compare preceding abstract)—The freezing-point curve of the system falls continuously from the melting point of palladium to that of gold; like the corresponding curve for palladium-silver alloys, it is concave to the axis of concentration. The metals form a continuous series of mixed crystals, and there is no indication of chemical combination.

Alloys containing more than 10% of palladium are white. The hardness increases with increase in the amount of palladium until 70% of the latter element is present, but beyond this point decreases.

The fact that none of the three elements, copper, silver, gold, enter into chemical combination with palladium is in accordance with Tammann's rule (*Abstr.*, 1906, ii, 346), according to which either all or none of the elements of a natural group in the narrower sense enter into chemical combination with another element. G. S.

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## Mineralogical Chemistry.

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**Gases Enclosed in Coal and Certain Coal Dusts.** F. G. TROBRIDGE (*J. Soc. Chem. Ind.*, 1906, 25, 1129—1130).—Analyses are given of the gases extracted at the ordinary temperature and at 100° from the coal of the Busty Seam at Birtley, Co. Durham. Separate data have been obtained for (1) bright coal; (2) “dant”; (3) surface dust; (4) dust from timbers. The bright coal not only yields the largest volume, but also the largest proportion of combustible gas. The combustible gas from the bright coal and from the “dant” consists almost entirely of methane, whereas that from the dust appears to contain higher hydrocarbons. The analytical data confirm the observation made by Bedson that oxygen and nitrogen, the former preferentially, are absorbed by coal on exposure to the air. Analyses of the gas occluded in coal and dust from the Fernie Mine (B.C.) are also communicated.  
H. M. D.

**Chalcopyrite Crystals from Japan.** WILLIAM E. FORD (*Amer. J. Sci.*, 1907, [iv], 23, 59—60).—A crystallographic description is

given of peculiar wedge-shaped and lath-shaped crystals of chalcopyrite from Arakawa, Japan; they owe their unusual development to the symmetrical suppression of certain faces.

JACOB BECKENKAMP (*Sitz.-Ber. phys.-med. Ges. Würzburg*, 1906) has examined similar crystals from the same locality and concludes that they belong to the pyramidal (hemimorphic) class of the orthorhombic system, and that the higher symmetry more usually exhibited by chalcopyrite is the result of twinning.

L. J. S.

### Formation of Quartz and Tridymite in Silicate Fusions.

P. D. QUENSEL (*Centr. Min.*, 1906, 728—737).—A continuation of previous work (this vol., ii, 34). A mixture of oligoclase and quartz heated with an equal amount of tungstic oxide for six hours at 900° resulted in the formation of quartz; the same mixture at 1200° gave only glass. Amorphous silica with five parts of sodium tungstate heated for six hours at 1200° gave tridymite; at lower temperatures only a glass was formed. The melting point of tridymite was determined to be about 1560°, that is, about 100° lower than that of quartz.

Diagrams illustrate the temperature limits of the formation and stability of quartz, tridymite, and silicic acid (compare Day and Shepherd, *Abstr.*, 1906, ii, 770).

L. J. S.

**Crystal Measurements.** CARL HLAUATSCH (*Zeit. Kryst. Min.*, 1907, 42, 587—595).—The results of goniometric measurements are given of the following: raspite from Broken Hill, New South Wales; a triclinic rhodonite-like slag of unknown origin and composition; and dibromohydroxydeoxybenzoin,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH}, \text{H}_2\text{O}$ . The slag crystals have  $D = 3.44$  and were found to contain much manganese; they are therefore assumed to belong to the triclinic group of slag materials with the composition  $(\text{Mg}, \text{Fe}, \text{Mn})\text{SiO}_3$  studied by J. H. L. Vogt, and the name "vogtite" is proposed for them.

L. J. S.

### Nepouite, a new Hydrated Silicate of Nickel and Magnesium.

E. GLASSER (*Compt. rend.*, 1906, 143, 1173—1175).—The new mineral is from Népoui in New Caledonia, and is met with as a fine crystalline powder or as an incrustation in nickelferous peridotite. The colour varies with the percentage of nickel from bright green to pale yellowish-green. The hardness is 2—3. The minute crystals have the form of hexagonal plates or are vermiform with a six-sided cross-section; they have a distinct basal cleavage and prismatic cleavage, as in the chlorites. The crystals are optically negative with a small axial angle; the acute bisectrix is nearly perpendicular to the basal cleavage; birefringence, 0.036—0.038. The following analyses (Ia, IVa, and Va by F. Pisani) give the formula  $3(\text{Ni}, \text{Mg})\text{O}, 2\text{SiO}_2, 2\text{H}_2\text{O}$ ; nickel and magnesium replace each other in all proportions. The mineral is near to, but distinct from, garnierite, noumeite, and connarite.

	SiO <sub>2</sub> .	NiO.	MgO.	FeO.	CaO.	Al <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
I.	32·84	49·05	3·64	1·90	0·50	0·97	9·64	98·54	} 3·24
Ia.	32·30	49·75	3·75	1·65	n. d.	0·89	10·48	98·82	
II.	33·03	46·11	6·47	2·20	trace	1·39	10·61	99·81	3·18
III.	35·05	39·99	11·80	1·22	0·58	1·13	10·05	99·82	2·89
IV.	40·07	18·21	29·84	0·25	0·53	0·72	11·98	101·60	} 2·47
IVa.	41·1	18·1	30·0	n. d.	n. d.	n. d.	—	—	
V.	32·36	50·70	3·00	0·62	trace	0·69	12·31	99·68	} 3·20
Va.	32·50	50·20	3·47	0·83	n. d.	0·82	10·20	98·02	

L. J. S.

**Chemical Composition of Amphibole.** SAMUEL L. PENFIELD and F. C. STANLEY (*Amer. J. Sci.*, 1907, [iv], 23, 23—51).—The following analyses (the results quoted are in each case the means of the duplicate analyses) were made on carefully-selected and pure material, with the object of deducing a general formula to express the wide variations in composition which are exhibited by the several varieties of amphibole. I, Tremolite, large, white crystals from Richville, near Gouverneur, New York; II, tremolite, white, bladed crystals from Lee, Massachusetts; III, actinolite, dark green crystals in talc from Greiner, Tyrol; IV, actinolite, dark green crystals from Russell, St. Lawrence Co., New York; V, actinolite, dark olive-green crystal from Kragerö, Norway; VI, actinolite, dark greenish-black crystals of unusual habit, from Pierrepont, St. Lawrence Co., New York; VII, hornblende, black crystal, from Renfrew, Ontario, Canada; VIII, hornblende, black crystals, from Edenville, Orange Co., New York; IX, hornblende ("hudsonite"), black and massive, from Cornwall, Orange Co., New York (fluorine determination added to the analysis given by S. Weidman, *Abstr.*, 1903, ii, 436); X, hornblende, small, greenish-black crystals, from Monte Somma, Vesuvius; XI, basaltic hornblende, black crystals, from Bilin, Bohemia; XII, hornblende, light brown cleavage masses, from Grenville, Quebec, Canada (compare B. J. Harrington, *Abstr.*, 1904, ii, 52).

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	F <sub>2</sub> .	Total (less Loss O for at 110°.	F <sub>2</sub> .	Sp. gr.
I.	57·45	—	1·30	0·18	0·22	0·07	24·85	12·89	0·54	0·67	1·16	0·77	0·09	99·87	2·997
II.	57·69	0·14	1·80	0·00	0·55	trace	24·12	13·19	0·22	0·48	1·56	0·37	0·10	100·07	2·980
III.	56·25	0·00	1·24	0·78	5·50	0·48	21·19	12·08	0·28	0·19	1·81	0·04	—	99·84	3·047
IV.	54·80	0·10	2·58	2·50	4·75	trace	20·30	12·08	0·24	0·82	1·00	0·77	0·11	100·33	3·092
V.	51·85	1·26	4·36	2·58	5·46	0·35	19·48	10·60	0·35	2·15	1·21	0·46	0·13	100·02	3·137
VI.	52·31	0·28	2·69	3·00	6·68	0·70	10·27	11·88	0·50	0·78	1·42	0·93	0·08	100·20	3·111
VII.	43·76	0·78	8·33	6·90	10·47	0·50	12·63	9·84	1·28	3·43	0·65	1·82	0·10	99·73	3·200
VIII.	41·99	1·46	11·62	2·67	14·32	0·25	11·17	11·52	0·98	2·49	0·61	0·80	0·08	99·63	3·285
IX.	36·86	1·04	12·10	7·41	23·35	0·77	1·90	10·59	3·20	1·20	1·80	0·27	—	99·88	—
X.	39·48	0·30	12·99	7·25	10·73	1·00	11·47	12·01	2·39	1·70	0·76	0·50	0·12	100·23	3·288
XI.	39·95	1·68	17·58	7·25	2·18	trace	14·15	11·96	1·98	3·16	0·41	0·30	0·13	100·45	3·226
XII.	45·79	1·20	11·37	0·42	0·42	0·39	21·11	12·71	1·69	2·51	0·67	2·76	—	99·90	3·110

These analyses show that fluorine and water must be regarded as essential constituents of amphibole. The identity in crystalline form of the several varieties of the group suggests that a complex metasilicic acid, H<sub>8</sub>Si<sub>4</sub>O<sub>12</sub>, or perhaps H<sub>16</sub>Si<sub>8</sub>O<sub>24</sub>, must have a controlling influence (mass effect) on the isomorphous replacement of the bases and basic radicles; for this amphibole acid a ring formula is suggested, which is referred to as an amphibole ring. The hydrogen atoms of the acid are considered to be largely replaced by the bases R<sup>1</sup>O and by K<sub>2</sub>O, Na<sub>2</sub>O,

H<sub>2</sub>O and F<sub>2</sub>, whilst the sesquioxides are introduced in the form of the basic radicles  $[R^{III}_2O(OH,F)_2]^{II}$  and  $[R^{III}_2O_4R^{II}Na_2]^{II}$ . The analyses (I—III) of the simpler varieties, tremolite and actinolite, give very closely the metasilicate ratios without the assumption of any complex radicles. In all the analyses calcium oxide replaces one-fourth of the hydrogen atoms of the acid. L. J. S.

**Crystallographic Observations on Certain Minerals of Brosso and Traversella.** LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 636—644).—The author gives the results of measurements of crystals of: villarsite, which is crystallographically identical with olivine; siderite [ $c=0.8184$ ]; chalcopyrite [ $c=0.98645$ ]; blende; galena; arsenical pyrites; tetrahedrite; cerussite [ $a:b:c=0.60960:1:0.72255$ ]. T. H. P.

**Yttrocrasite, a new Yttrium-thorium-uranium Titanate.** WILLIAM E. HIDDEN and CHARLES H. WARREN (*Amer. J. Sci.*, 1906, [iv], 22, 515—519).—The crystal examined was found in Burnet Co., Texas, not far from the well-known gadolinite locality in Llano Co. It weighed 60 grams, and had a thin, dull brown coating; on a fresh surface the material is black, with a bright, pitchy lustre and an uneven to small conchoidal fracture, resembling polycrase or euxenite in appearance. The crystal is orthorhombic: its hardness is  $5\frac{1}{2}$ —6, and D 4.8043. Under the microscope, thin splinters are pale yellow to colourless, and transparent; in polarised light it is seen to consist of a mixture of isotropic and feebly birefringent material, with sometimes a minute spherulitic structure. The mineral thus appears to have resulted by the alteration of an originally anhydrous species. The material is infusible before the blowpipe; it is easily decomposed by hydrofluoric acid and by strong boiling sulphuric acid. Details of the method of analysis are given. The results obtained by Warren are:

TiO <sub>2</sub> .	(Y,Er) <sub>2</sub> O <sub>3</sub> *.	Ce <sub>2</sub> O <sub>3</sub> , &c.	Fe <sub>2</sub> O <sub>3</sub> .	WO <sub>3</sub> .	UO <sub>3</sub> .	UO <sub>2</sub> .	ThO <sub>2</sub> .	PbO.
49.72	25.67	2.92	1.44	1.87	0.64	1.98	8.75	0.48
	MnO.	CaO.	CO <sub>2</sub> .	H <sub>2</sub> O.	H <sub>2</sub> O (hygrosc.).	Total.		
	0.13	1.83	0.68	4.36	0.10	100.57 †		

\* Mol. wt. 268.4.

† Also a little Pb<sub>2</sub>O<sub>5</sub> and traces of Ta<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, MgO.

Helium and nitrogen could not be detected. The analysis gives the ratios,

H<sub>2</sub>O : R<sup>II</sup>O(CaO, &c.) : R<sup>III</sup>O<sub>3</sub>(Y<sub>2</sub>O<sub>3</sub>, &c.) : R<sup>IV</sup>O<sub>2</sub>(ThO<sub>2</sub>, &c.) : TiO<sub>2</sub>, &c. = 6 : 1 : 3 : 1 : 16.

The mineral is therefore essentially a hydrous titanate of yttrium earths and thorium, and for it the new name, *yttrocrasite*, is proposed.

The total radioactivity of the mineral was found by B. B. Boltwood to correspond to 10% of thorium and 2.08% of uranium. L. J. S.

**Volcanic Materials from the Gulf of Naples.** RAMÓN LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1906, 4, 193—202).—The analysis of certain almost colourless and transparent round crystals, gathered on

the shore of Torre del Greco in the Bay of Naples, gave the following result :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss.	
55.40	22.85	11.10	9.20	1.45	100.00

The formula deduced from these numbers is  $\text{KNaAl}_2(\text{SiO}_3)_4$ , showing that the mineral is one of the leucite group so often found in modern volcanic rocks. The volcanic origin of these crystals was demonstrated by the fact that on some were still to be found adherent black nodules of lava.

A specimen of Vesuvian lava ejected from the principal crater on October 31st, 1905, and collected on the following day, gave the following analysis :

SiO <sub>2</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.
48.050	10.900	19.500	7.600	3.024	6.360

Smaller quantities of K<sub>2</sub>O, Li<sub>2</sub>O, Cl, P<sub>2</sub>O<sub>5</sub> and loss amounted together to 4.566%.  
G. T. M.

**Composition of Volcanic Ash collected at Ottajano, Vesuvius, on April 14th, 1906.** G. COSYNS (*Bull. Soc. chim. Belg.*, 1906, 20, 159—162).—The ash lost, when completely dried at 110°, 0.28% of water and 0.03% of hydrogen chloride. 1.68% was soluble in water at 15°, and this consisted of sodium chloride (0.761%), calcium sulphate (0.854%), magnesia, alumina, silica, ferric chloride, &c. From 3—4% of the dust was magnetic, and this portion consisted of magnetic oxide of iron (94.5%), titanium dioxide (2.11%), lime, silica, &c., 3.4%. The washed powder had the following composition :

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Al <sub>2</sub> O <sub>3</sub> .	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	MnO.	Cr <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .
48.65	16.25	11.21	14.76	3.94	3.19	2.83	0.02	0.009	0.115	0.6

Also traces of As, F, B, Zn, Li, Te, Cl, S.

The mineral composition, therefore, would appear to be augite (50%), leucite (40%), biotite, magnetite, &c. (10%). When extracted with chloroform or ether, the ash yielded 0.002% of Silvestri's "vaselin"; when heated to a high temperature it fused, swelled, and evolved reducing gases.  
T. A. H.

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### Physiological Chemistry.

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**Resistance of Mammalian Red Corpuscles towards Hæmolytic Agents.** D. RYWOSCH (*Pflüger's Archiv*, 1907, 116, 229—251). —The resistance of the fresh and washed red corpuscles towards numerous hæmolytic agents (water, saponin, chloroform, acetone, &c.) was investigated. The results obtained with the corpuscles from

various animals are arranged in columns in order of resistance. Every column shows a different order; even the fresh and the washed corpuscles give different results.

W. D. H.

**Sero-mucoid in Blood.** H. W. BYWATERS (*Proc. Physiol. Soc.*, 1906, iii—iv., *J. Physiol.*, 35).—Pavy has shown that the carbohydrate yielded by mucoids is greater after acid hydrolysis than after hydrolysis with 10% alkali. The non-coagulable proteid of blood behaves in this way, and this fact, as well as its non-diffusibility, lends support to Zanetti's view that it is a mucoid (sero-mucoid) and not a proteose. The amount of sero-mucoid carbohydrate expressed as dextrose in grams per litre of blood was found to vary from 0·07 to 0·08 in the fasting dog, from 0·097 to 0·11 when fed on bread or milk, and from 0·18 to 0·24 when fed on dog-biscuit; that is to say, an increase occurs after a diet consisting largely of carbohydrate. If the sero-mucoid is concerned in the transport of carbohydrate, this is what would be expected.

W. D. H.

**Fate of Cholesterol and its Esters in the Animal Organism.** HUGO PRIBRAM (*Biochem. Zeit.*, 1906, 1, 413—424).—The resistance of the red corpuscles towards the hæmolytic action of such substances as saponin is believed to be due to the materials of which their membranes are composed. Cholesterol is one of these, and fluids containing cholesterol protect the corpuscles from hæmolysis. So far as the present experiments go these views are supported. The main conclusion drawn, however, is that feeding an animal on cholesterol or its esters increases the amount in the blood-serum, and this is believed to be mainly in the form of free cholesterol.

W. D. H.

**Photo-biological Sensitisers and their Proteid Compounds.** GUNNI BUSCK (*Biochem. Zeit.*, 1906, 1, 425—540).—A complete review of previous work is given, and a number of experiments are described from which the following conclusions are drawn. An intense light, rich in rays of short wave-length, is capable of destroying red blood-corpuscles. The negative results previously obtained are attributed to the source of light being too feeble. The substance contained in blood serum, *alexin*, which acts as a poison to *Paramœcium*, may be destroyed by exposure to ultra-violet light, but may be sensitised by means of light of greater wave-length.

The addition of various photobiological sensitisers, such as derivatives of fluorescein and sodium dichloroanthracenedisulphonate, to mammalian blood produces various alterations in the properties of the blood and of the sensitiser. Thus the property of coagulating may be diminished or completely destroyed, as may also the action of the alexin of the serum on *Paramœcium*. The presence of the serum is also capable of diminishing or completely destroying the characteristic behaviour of the sensitisers to micro-organisms, animal tissues, toxins, and enzymes, the effect being most pronounced in the case of organised structures. Many of the chemical and physical characteristics of the sensitisers are also affected by the serum. Different sera produce somewhat different results, the effect being most marked with a serum of feeble "alkalesence." Glue, gum arabic, starch, peptone,

theobromine, and glycine do not produce the same effects as serum, but egg-albumin does.

The action of the sensitisers is ascribed to the formation of compounds with the albumins of the serum, these compounds having properties very different from those of their components. The eosin-serum compound is insoluble in water, but dissolves in serum in acid, alkaline, or neutral solution; it also dissolves in alkali or in dilute acid, and may be precipitated by means of ammonium sulphate.

J. J. S.

**Blood-pigment of *Thalassochelys Corticata*.** FRANZ BARDACHZI (*Zeit. physiol. Chem.*, 1906, 49, 465—471).—The blood-pigment of this turtle appears to give the same physical constants as the hæmoglobin of mammals.

W. D. H.

**Action of Alkalies, Lithium Salts, and Lithium Water on the Gastric Secretion.** M. MAYEDA (*Biochem. Zeit.*, 1907, 2, 332—338).—The investigation was undertaken in view of the action certain mineral waters possess of increasing digestion. By experiments on dogs with a Pawloff fistula, it was shown that alkalis stimulate the secretion, and that lithium salts and mineral water containing lithium are specially efficacious in this direction.

W. D. H.

**Influence of Physostigmine, Euphthalmine, and Dionine on the Gastric Secretion.** M. PEWSNER (*Biochem. Zeit.*, 1907, 2, 339—343).—Pawloff's discovery of secretory nerves of the stomach has rendered the action of alkaloids on the secretion of special interest. Physostigmine acts like pilocarpine in increasing the secretion; euphthalmine falls into the atropine group in diminishing it. Dionine, a derivative of morphine, stimulates the secretion; it, however, acts more rapidly than morphine; its narcotic action is less.

W. D. H.

**The Inhibition of Peptic Digestion by Combining the Free Hydrochloric Acid with Amphoteric Amino-compounds.** HERMANN JASTROWITZ (*Biochem. Zeit.*, 1906, 2, 157—172).—The addition of amphoteric amino-compounds to pepsin-hydrochloric acid inhibits its fermenting properties. The substances used were glycine, alanine, glutamic acid, and Witte's peptone, and of these glycine, alanine, and peptone produce the greatest effect. The inhibition is due to the removal of part of the hydrochloric acid in combination with the amino-compounds.

J. J. S.

**The Relationship of Pepsin and Rennin in the Child's Stomach.** JULIUS WOHLGEMUTH and H. ROEDER (*Biochem. Zeit.*, 1907, 2, 421—427).—There is no truth in the statement that the child's stomach membrane yields an excess of rennin in proportion to pepsin. The rennetic and peptic activity are parallel. Pawloff's view that the two actions are due to one complex substance is thus confirmed.

W. D. H.



**Digestion of Proteids.** W. GRIMMER (*Biochem. Zeit.*, 1906, 2, 118—143).—A number of details regarding acidity of stomach contents, alkalinity of intestinal contents, and amounts of digestive products in different parts of the alimentary canal at different periods are given. The observations were carried out on herbivora, mainly horses. Absorption occurs in the stomach as peptone, and in the small intestine as peptone and crystalline cleavage products.

W. D. H.

**Digestion and Absorption in the Stomach.** G. LANG (*Biochem. Zeit.*, 1906, 2, 225—242).—The experiments were made on dogs, and the proteid given was fibrin: appropriate fistulæ rendered possible the examination of the material in the stomach or leaving it. The main result was that on the average 30% of the fibrin was undissolved; of the remaining 70%, 60% was in solution mainly as proteose, and the remaining 10% was not recovered, and had presumably been absorbed.

W. D. H.

**Physiology of the Digestive Tract.** I. ALOIS KREIDL (*Pflüger's Archiv*, 1907, 116, 159—162). II, III. ALBERT MÜLLER (*ibid.*, 163—170, 171—185).—The papers mainly relate to the muscular tissue, removal of which produces in dogs remarkably little effect; there is hypersecretion and hyperacidity in the stomach. During digestion in the normal dog, no free hydrochloric acid was found; the acid which reaches its highest value on a flesh diet is all combined.

W. D. H.

**Chemistry of Digestion.** VII. **Gastro-lipase.** E. S. LONDON (*Zeit. physiol. Chem.*, 1906, 50, 125—128).—In a dog with an ordinary gastric fistula, fat is split to the extent of 17—23%. If the operation is a pyloric fistula and is performed so as to prevent any return of the intestinal contents and secretions into the stomach, this is reduced to 2—5%.

W. D. H.

**Activation of Trypsin in Man.** JULIUS WOHLGEMUTH (*Biochem. Zeit.*, 1906, 2, 264—270).—Several observers have stated already that the human pancreatic juice contains trypsinogen, not trypsin; this is confirmed in the present case, in which the juice was obtained from a fistula. Experiments with the juice *in vitro* show that tryptic action is doubled in the presence of bile. Liver juice has a still greater effect, but whether this is due to bile is uncertain. Activation was also produced by glycine, alanine, and leucine, feebly by tyrosine, and not at all by glutamic and aspartic acids.

W. D. H.

**Milk Curdling Ferment in Human Pancreatic Juice.** JULIUS WOHLGEMUTH (*Biochem. Zeit.*, 1907, 2, 350—356).—Human pancreatic juice contains a rennetic ferment mainly in the form of pro-ferment. Its activation by intestinal juice or by hydrochloric acid runs parallel to the activation of trypsin.

W. D. H.

**Ferments and Antiferments.** MARTIN JACOBY (*Biochem. Zeit.*, 1906, 2, 144—147).—Fibrin filaments soaked in trypsin and then well washed retain some of the enzyme so that they rapidly dissolve in an alkaline fluid. If placed in dilute hydrochloric acid, they do not, and the acid dissolves out the trypsin from them. Inhibition of the action of enzymes which have been absorbed by fibrin can be brought about by the antiferments of blood-serum. Pepsin and trypsin rapidly render transparent blood-serum which has been rendered cloudy by dilution and boiling. W. D. H.

**Ferments and Antiferments. III.** MARTIN JACOBY (*Biochem. Zeit.*, 1906, 2, 247—250. Compare this vol., ii, 38, and preceding abstract).—The behaviour of sodium carbonate to pepsin precipitates is similar to that of dilute hydrochloric acid to trypsin precipitates; thus pepsin is readily removed from fibrin masses by treatment with very dilute sodium carbonate solution.

The presence of an antipepsin in blood serum has been demonstrated by the flock method, and the antipepsin is present even after the serum had been subjected to dialysis. J. J. S.

**Digestion in Animals. V. An Absorption Dog.** E. S. LONDON. VI. **Proteid and Carbohydrate Digestion in the Alimentary Tract.** E. S. LONDON and W. W. POLOWZOWA (*Zeit. physiol. Chem.*, 1906, 49, 324—325; 326—396. Compare Abstr., 1906, ii, 778).—The first paper is mainly concerned with experimental methods in the preparation of intestinal fistulæ in dogs for the purpose of studying absorption. The second is an elaborate study of the different stages in digestion and absorption in various parts of the alimentary canal, using dogs prepared in such ways. The various degrees of digestion and absorptive activity for proteids and carbohydrates are stated numerically and in curves. Digestion is greatest for carbohydrates in the lower ileum, for proteids in the upper ileum. Absorption, stated in milligrams per square centimetre, diminishes as the food passes from the small into the large intestine. In the stomach, no absorption of proteids or carbohydrates occurs. Absorption of carbohydrates is at a maximum in the duodenum, of proteids in the jejunum. Particulars are also given as to the amount of juices secreted. The proteid of bread is better absorbed than egg-white because of the greater porosity of the bread, not because of the carbohydrate admixture. W. D. H.

**Lactase and the Adaptation of the Intestine to Lactose.** R. H. ADERS PLIMMER (*J. Physiol.*, 1906, 35, 20—31).—No evidence of the adaptation of the intestinal secretion to the administration of lactase was discoverable. Different animals vary a good deal in the amount of lactase formed at different periods of life. W. D. H.

**Action of Non-proteid Nitrogen Compounds on Animal Metabolism.** OSKAR KELLNER (*Pflüger's Archiv*, 1907, 116, 203—206. Compare Abstr., 1906, ii, 690).—Polemical.

W. D. H.

**Trimethylamine as a Normal Product of Metabolism and its Estimation in Urine and Fæces.** FILIPPO DE FILIPPI (*Zeit. physiol. Chem.*, 1906, 49, 433—456).—Trimethylamine derived from the choline group of substances is a normal product of metabolism in animals and men. Directions for estimating it in the distillate of urine and fæces are given.

W. D. H.

**Importance of Individual Amino-acids in Metabolism: Addition of Tryptophan to Zein.** EDITH G. WILLCOCK and F. GOWLAND HOPKINS (*J. Physiol.*, 1906, 35, 88—102).—When zein is the only nitrogenous food given to young mice they soon die. If tryptophan, which is absent from zein, is given in addition, the survival of the animals is greatly prolonged, and it adds to their well-being, although they also ultimately die, and growth is not maintained. The addition of tyrosine (already present in zein) in equivalent amounts has no such effect. It is suggested that the tryptophan is directly utilised as the normal precursor of some specific hormone or of some substance essential to life.

W. D. H.

**Action of Asparagine in Animal Metabolism.** CURT LEHMANN (*Pflüger's Archiv*, 1906, 115, 448—451). **Action of certain Amino-substances in the Metabolism of Carnivora.** W. VÖLTZ (*ibid.*, 452—455. Compare Abstr., 1906, ii, 560).—Polemical against Kellner.

W. D. H.

**Nuclein-metabolism.** ALFRED SCHITTENHELM and JULIUS SCHMID (*Zeit. physiol. Chem.*, 1906, 50, 30—35. Compare this vol., ii, 41).—Previous researches have shown that the complicated process of uric acid formation occurs in different organs with different intensities in various animals. Thus it occurs in the spleen of the ox and not that of the pig; guanase and adenase are both present in the ox liver, but only guanase in the rabbit's liver, &c. (Jones and Austrian). On such a hypothesis the formation of uric acid is difficult to explain, and the absence of purine bases in the urine in appreciable quantities shows that they do not circulate freely in the blood, but must be changed somewhere. In the present research, guanase was found in the pig's spleen, adenase in the rabbit's liver, and similar ferments in other organs of rabbit, cat, human beings, &c. A number of negative results were, however, also obtained, and the suggestion is made that the preparation of the extracts may be at fault, or non-activation of the ferments may explain the results.

W. D. H.

**Human Chyle.** J. MOLYNEUX HAMILL (*J. Physiol.*, 1906, 35, 151—162).—Human chyle collected from a surgical case is bluish-white, and becomes yellower as the fat increases; it is alkaline, and clots rapidly, but the clotting is prevented by oxalates. As much as 4 litres were sometimes obtained in twelve hours. Its average composition was: solids, 3·87%; ash, 0·83%; fat, 1·3% (very variable); total nitrogen, 0·36%; extractive nitrogen, 0·01%. 4·2 grams of lecithin and 5·2 grams of cholesterol were found in every 100 grams of ether extract. Lipase and amylase were present. The largest amount of

fat occurs six hours after a meal. The ratio of the higher to the lower fats is greater in the chyle than in the food. Lecithin given by the mouth raises the ether-soluble phosphorus of the chyle. Petroleum given by the mouth is not found in the chyle. W. D. H.

**Human Chyle.** TORALD SOLLMANN (*Amer. J. Physiol.*, 1907, 17, 487—491).—The chyle was collected from a surgical wound in the neck; at first the flow was continuous; eight days later the amount obtained was about 300 c.c. in the twenty-four hours, after which the flow gradually ceased as the wound healed. At the time the present observations were made the amount collected varied from 0.1 to 14 c.c. every five minutes. Its appearance was creamy except after a fast, when it was almost clear. It coagulated readily. Its composition was: water, 92.75 to 92.89%; solids, 7.11 to 7.25%; ash, 0.6%; sodium chloride, 0.68%; proteids, 1.85% (but variable); chloroform extract, 0.07%, and ether extract, 1.93%. The fat is unusually low in amount. A single dose of potassium iodide had no effect on the rate of flow; it appeared in the urine eight to twenty minutes later, but was not found in the chyle until three hours later; there is, however, some doubt concerning the correctness of the analysis made before that time. None was found in either fluid twenty-seven hours later; it disappears at the same time in both. Sodium salicylate and santonin after administration were not discovered in the chyle. W. D. H.

**Cerebro-spinal Fluid.** FRENKEL-HEIDEN (*Biochem. Zeit.*, 1906, 2, 188—189).—The total proteid in human cerebro-spinal fluid, removed by lumbar puncture in various diseases, varied from 0.35 to 3 per 1000. It was highest in a case of progressive paralysis, and in another of tubercular meningitis, but these are cases where the amount is small in both diseases. The amount of non-proteid nitrogen is relatively high, and may even be greater than that of proteid nitrogen. Ammonia is absent, but the most abundant non-proteid nitrogenous substance is stated to be urea. W. D. H.

**The Cause of the Electrotonic Excitability of Nerve.** JACQUES LOEB (*Pflüger's Archiv*, 1907, 116, 193—202).—A theory based on the physical work of the author and his colleagues. W. D. H.

**Action of Inorganic Salts on the Nerves of the Isolated Mammalian Heart.** WILLIAM H. HOWELL and W. W. DUKE (*J. Physiol.*, 1906, 35, 131—150).—An isolated cat's heart perfused with Locke's solution is sensitive to the stimulation of the accelerator nerves for some hours. An increase of calcium chloride to certain concentrations (described in full) produces similar effects, and of sodium or potassium chlorides the opposite. The action of the accelerator nerves is within certain limits favoured by the calcium increase, but the opposite effect of potassium chloride was not marked. Increase of calcium in the circulating fluid had no distinct effect on the inhibitory influence of the vagus nerve. W. D. H.

**The Normal Heart Rhythm, and the Artificial Rhythm Produced by Sodium Chloride.** A. J. CARLSON (*Amer. J. Physiol.*, 1907, 17, 478—486).—Further experiments on the heart of *Limulus* in special reference to the mode of conduction of the cardiac rhythm.

W. D. H.

**Occurrence of Bromine in Normal Human Organs.** EGON PRIBRAM (*Zeit. physiol. Chem.*, 1906, 49, 456—464).—The brain, liver, spleen, and thyroid of men contain normally no appreciable amounts of bromine.

W. D. H.

**Composition of Flesh on Different Nutriment.** MAX MÜLLER (*Pflüger's Archiv*, 1907, 116, 207—228).—Experiments on dogs on different diets are recorded with special reference to what happens to proteid food, and how in the body it is split into a nitrogenous, and a carbon rich residue; and how far the latter serves for fat formation.

W. D. H.

**Method of Combination of Creatine in Muscle.** FUMICHIKO URANO (*Beitr. chem. Physiol. Path.*, 1907, 9, 104—115).—Muscle contains about 0.4% of creatine; a man weighing 60 kilos. will therefore have from 90 to 100 grams of creatine in his muscles. Creatine, like creatinine, is easily dialysable, but it does not pass readily into the surrounding lymph and blood. The present experiments on freshly killed muscle show that it does not readily diffuse out; the same is true for the dialysable phosphoric acid compounds in the muscles. Both must be combined in the muscular protoplasm. This view is confirmed by Folin's observation that creatine given with the food is partly retained in the body, presumably because the muscles have the power of fixing it.

W. D. H.

**Effect of Adrenaline on the Hepatic and Muscular Glycogen.** K. AGADSHANIANZ (*Biochem. Zeit.*, 1906, 2, 148—153).—The muscles of animals treated with adrenaline are free from glycogen. The results on the liver were conflicting. Gatin-Gruzewska's methods for obtaining glycogen were employed.

W. D. H.

**Tissue Respiration.** HORACE M. VERNON (*J. Physiol.*, 1906, 35, 53—87).—The experiments described on the excised kidney of rabbits and cats prepared with oxygenated saline solution show that the initial gaseous metabolism which at first is as great as in the living animal rapidly dwindles. The influence of various other factors, including certain chemical reagents, is also described. The tissue proteids in the course of the experiments were dissolved out by the perfusing liquid without affecting the tissue respiration: the latter, therefore, apparently depends on non-nitrogenous side chains of the "biogen" (Verworn) molecules.

W. D. H.

**The Ferments of the Placenta.** M. SAVARÈ (*Beitr. chem. Physiol. Path.*, 1907, 9, 141—148).—The placenta causes the disappearance of glyoxylic acid as Schloss showed that the liver also does, but its activity is less than that of the liver, although greater than that of brain and

muscles. Its action in causing the coagulation of fibrinogen solutions may be due to the blood it contains. It also has proteolytic, deamidising, and ereptic action, which possibly are the result of post-mortem changes. Its oxydase and diastatic action appears to be related to its metabolism.

W. D. H.

**Action of Drugs on the Uterus.** ARTHUR R. CUSHNY (*J. Physiol.*, 1906, 35, 1—19).—Methods are described for obtaining graphic records of uterine movements; these are increased by stimulation of the hypogastric nerves; and a similar effect is produced by nicotine and by adrenaline; pilocarpine antagonises inhibition, and is antagonised by atropine. Quinine, aloin, and barium chloride also increase the movements; alcohol has little or no effect, and that of chloroform and ether is very slight. The results obtained with ergot were the same as those described by Dale.

W. D. H.

**Causes of the Coloration of Animal Fibres.** WILHELM SUIDA (*Zeit. physiol. Chem.*, 1906, 50, 174—203. Compare Abstr., 1905, i, 714; 1906, i, 445).—The behaviour of various dyes such as para-magenta, crystal-violet, magenta, methylene blue, crystal-ponceau, orange II, and fast-yellow, and of mordants towards various amphoteric substances, has been examined. The substances used include glycine, alanine, leucine, tyrosine, phenylalanine, sarcosine, phenylglycine, phenylglycine-phenylglycine, phenylaminodiacetic acid, phenylglycine-*o*-carboxylic acid,  $\alpha$ -naphthylglycine, creatine, arginine nitrate, histidine hydrochloride, cystine, aspartic acid, asparagine, glutamic acid hydrochloride, tryptophan, oxanilic acid, aminodiphenyloxamic acid, anthranilic acid, acetylanthranilic acid, methyl anthranilate, *m*- and *p*-aminobenzoic acids, and aminophenylpyrazolonecarboxylic acid. Only those compounds yield insoluble derivatives with both basic and acid dyes which contain a phenyl radicle attached to the nitrogen atom, and which exhibit about equal basic and acidic properties. Tryptophan yields no precipitates, and arginine nitrate and histidine hydrochloride behave in a characteristic manner.

The behaviour of carbamide, biuret, phenylcarbamide, alloxan, alloxanthin, uric acid, caffeine, guanidine carbonate, triphenylguanidine, aniline, *p*-aminophenol, and of aminoguanidine nitrate towards dyes has also been studied. Sparingly soluble coloured salts of guanidine are readily obtained, that from crystal-ponceau having the composition  $C_{41}H_{58}O_{17}N_{16}S_4$ .

The authors think it probable that the property possessed by certain animal fibres of combining with both acidic and basic dyes is due to the presence of different complexes in the molecule, since on hydrolysis it is found that certain of the hydrolytic products can fix acid dyes whilst other of the products fix basic dyes.

Further experiments with wool and silk indicate that these act selectively towards given dyes, and that silk is more decidedly acidic than wool.

J. J. S.

**Staining of Fat by Basic Aniline Dyes.** J. LORRAIN SMITH (*J. Path. Bact.*, 1907, 11, 415—420).—Fatty acids unite with the

colour base in aqueous solution, but neutral fats fail to do so. Shaking a neutral fat with carbon dioxide gradually decomposes it, and staining of the liberated fatty acid then occurs. That a ferment in the tissues may aid the action is suggested, but the question is left unsettled. The hydrolysing action of carbon dioxide occurs also with carbohydrates. The carbol-fuchsin method of staining tubercle bacilli is really a form of fat-staining.

W. D. H.

**Positive Heliotropism produced by Acids, especially Carbon Dioxide, and Negative Heliotropism produced by Ultra-violet Light.** JACQUES LOEB (*Pflüger's Archiv*, 1906, 115, 564—581).—The experiments recorded were performed on various copepods, volvox, and other low organisms, and the main results are contained in the title. The explanation adopted is on physico-chemical lines as opposed to the teleologico-anthropomorphic standpoint of some authors.

W. D. H.

**Formation of Lactose.** FRANCIS H. A. MARSHALL and J. M. KIRKNESS (*Biochem. J.*, 1906, 2, 1—6).—The experiments recorded on guinea pigs indicate that the removal of the mammary glands does not produce glycosuria after a subsequent parturition, and that at such a time there is normally no increase of dextrose in the blood such as one would anticipate were Bert's hypothesis that lactose is formed from dextrose correct. Glycosuria may sometimes occur in normal animals. The sugar in the urine is then dextrose; if lactose is present, its amount is insignificant. Such glycosuria is probably comparable to post-operation glycosuria, and neither it nor the glycosuria which occurred in Porcher's experiments after removal of the mammary glands during lactation can be regarded as supporting Bert's views. The hormone which excites the mammary glands must act solely on these organs, and not on the liver or other organs in addition; it is quite inactive in the absence of the mammary glands, and is ineffective in causing them to regenerate. Shattock's statement that these glands do not elaborate any internal secretion necessary for the growth of the fœtus is confirmed.

W. D. H.

**Opsonins in Milk.** GERMAN SIMS WOODHEAD and W. A. MITCHELL (*J. Path. Bact.*, 1907, 11, 408—414).—Opsonins occur in milk in greater relative quantity than in the blood. It is possible that this may play a part during milk feeding of infants in imparting to them passive immunity against tuberculosis.

W. D. H.

**Unusual Bilirubin-concretion in the Liver.** CARL KAISERLING (*Biochem. Zeit.*, 1907, 2, 312—318).—The concretion was found in the interior of an *Echinococcus* cyst in the liver of a man. It was found to consist of fat and bilirubin.

W. D. H.

**Effects of Ligature of One Ureter.** FRANCIS A. BAINBRIDGE (*J. Path. Bact.*, 1907, 11, 421—425).—Miss Amos's statement that this operation results in hydronephrosis is confirmed. There is temporary loss of weight, but no permanent ill effects. The secretory

power of the kidney for nitrogenous substances is not entirely lost even two months later. The initial pressure in the ureter is low, but bears no relation to blood pressure. No evidence of absorption was obtained, even when potassium iodide was introduced at a pressure of 50—80 mm. of mercury into the renal pelvis. W. D. H.

**Metabolic Balance of Nitrogen and Sodium Chloride.** M. LETULLE and MLE. M. POMPILIAN (*Compt. rend.*, 1906, 143, 1188—1191).—In general the quantity of nitrogen and sodium chloride excreted varied with the amounts ingested. The need for the two substances presents individual differences in different people. W. D. H.

**Methylguanidine in Urine.** W. ACHELIS (*Zeit. physiol. Chem.*, 1906, 50, 10—20; FRIEDRICH KUTSCHER, *ibid.*, 21).—Methylguanidine is a constant constituent in the urine of man, horse, and dog. In the last named animal dimethylguanidine is probably also formed. It probably arises from creatine; but abundant administration of creatinine into the intestine and subcutaneous injection of methylguanidine produces no appreciable rise of the latter substance in the urine. In a creatine-free diet, if creatinine is given, only a part reappears as such in the urine.

Kutscher awards Achelis priority in the discovery. W. D. H.

**Diurnal Variations in Uric Acid Excretion.** JOHN B. LEATHES (*J. Physiol.*, 1906, 35, 125—130).—Two experiments on man are described in which a uniform purine-free diet was taken, one with a high the other with a low nitrogen intake. The amount of creatinine is independent of the nitrogen intake, but special attention is directed to the fact that the excretion of this substance is greater during the day, especially in its early hours, than during the night. The same variations are even more marked in the case of uric acid. This is not a sign that the kidney is less active at night, for the excretion of total nitrogen is as high as, or even higher than, during the daytime. The discussion of the meaning of the variation is postponed until more experiments are performed. W. D. H.

**Colloidal Nitrogenous Substances, Insoluble in Alcohol, in Urine.** ERNST SALKOWSKI (*Chem. Centr.*, 1906, ii, 1622; from *Berl. Klin. Woch.*, 42, No. 51, 52).—The quantity of nitrogen contained in the precipitate obtained from urine by means of alcohol has been found to be equal to 3.5% of the total nitrogen of normal urine, whilst in pathological urines it amounted to 8—9%, and in a case of acute atrophy of the liver to 28.1%. In these determinations the precipitate was not dissolved and reprecipitated. The nitrogenous constituents of the precipitate which are soluble in water do not permeate a colloidal membrane, and the solutions do not give the biuret, the Millon, or the Adamkiewicz reaction. Further experiments showed that the precipitate formed by alcohol in a solution prepared by dialysing normal urine consisted of at least two substances which contained different quantities of nitrogen and could be separated to a certain extent by means of



animal charcoal. The substance which is present in the larger proportion and is not absorbed by the charcoal is readily hydrolysed by acid, but is not attacked by ptyalin; it is probably a carbohydrate which contains nitrogen, and is a constituent of that portion of the alcohol precipitate which is soluble in water but does not pass through a colloidal membrane. It appears probable that the excess of extractive material or "colloidal nitrogen" in pathological urines is connected with the presence of this substance, and it is possible that in many cases in which an increased quantity of phenols has been detected this substance also plays a part.

E. W. W.

**Influence of Nutrition on the Excretion of Bile Salts and Cholesterol.** EDWARD H. GOODMAN (*Beitr. Chem. Physiol. Path.*, 1907, 9, 91—103).—The experiments were made on a dog with a biliary fistula. The administration of blood corpuscles, meat, and egg-white increased the total amount of bile and usually that of cholic acid secreted. Administration of cholic acid greatly increased the amount in the bile. The excretion of the cholesterol ran parallel to that of the cholic acid. Brain in the food greatly increased the amount of cholesterol in the bile, but did not raise the amount of cholic acid more than white of egg did. Cholesterol does not appear to be a precursor of cholic acid.

W. D. H.

**A New Nitro-prusside Reaction in Urine.** V. ARNOLD (*Zeit. physiol. Chem.*, 1906, 49, 397—405).—The urine passed after taking meat, or meat extract, gives the following reaction. If a drop of 4% sodium nitroprusside solution is added to 10—20 c.c. of the urine, and then 5—10 c.c. of a 5% solution of sodium or potassium hydroxide, the result is a pure violet colour which rapidly becomes purple, and in the course of a minute passes through brownish-red into yellow.

The reaction occurs most markedly one or two hours after taking the meat, or beef-tea, and is entirely absent if such food is abstained from.

The reaction is different from that given by creatinine, or the acetone group of substances. It is not due to indole or methyl mercaptan. The substance to which it is due is not volatile.

If the urine is deeply coloured, the best result is obtained after previous decolorisation by animal charcoal.

W. D. H.

**Chemistry of Cancer. IV. Indole in the Stomach in Carcinoma.** ALBERT ALBU and CARL NEUBERG (*Biochem. Zeit.*, 1906, 1, 541—543. Compare Abstr., 1906, ii, 875).—Normally, indole is found only in the faeces and as indoxyl in the urine. It was found in the stomach contents in a case of carcinoma of that organ. This is believed to originate by autolytic action from the cancerous tissue.

W. D. H.

**Cystinuria. II.** ADOLF LOEWY and CARL NEUBERG (*Biochem. Zeit.*, 1907, 2, 438—454. Compare Abstr., 1906, ii, 103).—The observations were made on the same patient as before. At the time of the first research he had passed cystine crystals for eighteen years; since then a cystine calculus had formed. The administration of other amino-acids than those used before was undertaken. He was not capable of

burning glycine completely, but passed 20% of it in the urine. Glycyl-glycine was then given, a dipeptide which is unaffected by pancreatic juice; this behaved as in a normal person, about 10% being passed in the urine, and part of this as glycine. Polypeptides behaved in the same way. Glutokyrin was given, but neither it nor its cleavage products (arginine, lysine, glutamic acid, glycine) were found in the urine; there were traces of monoamino-acids in the urine, but it is questionable whether they originated from the glutokyrin given. The cleavage products (abiuretic) of 105 grams of fibrin were then given. In healthy men, these are completely burnt, but in the patient, the amount of cystin passed increased and a basic substance, probably histidine, was found in the urine. The urine contained no tyrosine, tryptophan, or glycine. The meaning of these results is discussed, several possible explanations being put forward. Similar results were obtained with other cystinuric patients, but the observations are not so complete. W. D. H.

**Glycæmia and Glycosuria.** E. LIEFMAN and R. STERN (*Biochem. Zeit.*, 1906, 1, 299—308).—Various observers give the normal percentage of sugar as varying from 0.05 to 0.33%. The question of method is important, and Knapp's is regarded as the best. The blood of twenty normal men was examined; the mean found was 0.086%, the highest being 0.105, the lowest 0.005. In comparison with this a number of bloods from diabetic cases were examined; in some cases the percentage rose to 0.5 or even more than 1, in most it was more than 0.2, and even a small excess over the normal (0.115) led to the appearance of sugar in the urine. This was not, however, always the case, and percentages of 0.16 or even 0.18 did not cause glycosuria, or the sugar in the urine was very small in amount. This is attributed to "tolerance," the most marked cause of which (external tolerance) depends on the permeability of the urinary filter to sugar. In certain febrile cases, especially pneumonia, this tolerance, even if dextrose is administered in large quantities, is very marked. W. D. H.

**Amino-acid Metabolism in Gout.** JULIUS WOHLGEMUTH (*Biochem. Zeit.*, 1906, 1, 332—338).—The majority of observers agree that the amount of amino-acids in normal urine is negligible, but there is a difference of opinion as to whether or not they are increased in amount in gout. Glycine is the acid to which most attention has been directed. Kionka believes that excess of glycine in the blood is the determining cause of an attack of gout. The present observations on a patient who had suffered for thirty-seven years from the disease lend no support to this theory. The best method of detecting glycine is stated to be the naphthylcarbimide method of Neuberg and Manasse. The urine gave no evidence of the presence of amino-acids. Forty-five grams of glycine were then given by the mouth; 0.5 gram was recovered in the urine, but no attack of gout ensued. Twenty-five grams of leucine were given, and none passed into the urine. Thirty-five grams of inactive alanine were then given; the *D*-alanine was completely burnt in the body, and of the *L*-alanine only 1.8 grams was recovered in the urine. Such observations show there is no diminution in a gouty person of the power to burn and utilise amino-acids. W. D. H.

**Experimental Leucocytosis.** W. HENWOOD HARVEY (*J. Physiol.*, 1906, 35, 115—118).—The leucocytosis which follows the injection of pilocarpine, muscarine, and barium chloride is a lymphocytosis of purely mechanical origin, and is due to the contraction of the spleen and lymphatic glands produced by the drugs mentioned. It is inhibited by atropine. A similar lymphocytosis follows excitation of the splenic nerve.

W. D. H.

**The Urine in Rabies.** CH. PORCHER (*Biochem. Zeit.*, 1906, 2, 291—306).—The observations were made on goats infected with rabies material. Glycosuria is a constant symptom, and the occurrence of sugar in the urine and of Negri's corpuscles in the nerve centres go together.

W. D. H.

**Action of Nickel Salts on the Animal Organism.** W. S. DZIERGOWSKY, SIMON K. DZIERGOWSKY, and N. O. SCHUMOFF-SIEBER (*Biochem. Zeit.*, 1906, 2, 190—218).—The amount of nickel dissolved from cooking vessels by various acids and various foods was estimated and the results given in tables. Such admixture is harmless, simply because the metal is not absorbed. The experiments were made on dogs.

W. D. H.

**Fate of the Cresols in the Organism and their Influence on the Metabolism and Intestinal Putrefaction of Carnivora.** D. JONESCU (*Biochem. Zeit.*, 1906, 1, 399—407).—50 to 53% of *m*-cresol, 65 to 70% of *o*-cresol, and 73 to 76.5% of *p*-cresol are burnt in the organism; their relative toxicity varies inversely with these numbers. They cause a decrease in the ammonium salts of the urine in dogs. The cresols are excreted mainly as ethereal sulphates, and to a small extent in combination with glycuronic acid. The amount in the latter combination increases with their toxicity, and increases also on feeding with carbohydrates.

W. D. H.

**The Influence of Inosite on the Frog's Heart.** FRITZ SACHS (*Pflüger's Archiv*, 1906, 115, 550—554).—Inosite, added to Ringer's solution used for perfusion experiments in the cold-blooded (frog's) heart, has a favourable influence on its beat, even more so than sugar has.

W. D. H.

**Physiological Behaviour of Inosite.** PAUL MAYER (*Biochem. Zeit.*, 1907, 2, 393—403).—Inosite is widely distributed in animal and vegetable tissues; it is not found in the urine, and in diabetes it is equally well destroyed in the body, and has no influence on the sugar output. The present research shows it has no effect on glycogen formation. After large doses in men and rabbits, a small amount passes unchanged into the urine, especially if it is given subcutaneously. It does not cause the formation of lactic acid. The urine, however, sometimes contains a dextrorotatory organic acid, which yields a barium salt soluble in water and insoluble in alcohol, but was not identified.

W. D. H.

**Behaviour of Starch in the Organism.** GIUSEPPE MOSCATI (*Zeit. physiol. Chem.*, 1906, 50, 73—96).—Starch solutions can be introduced without harmful results in animals either subcutaneously or intravenously. Starch does not leave the body by the various secretions or excretions, but is incorporated in various organs and converted into glycogen.

W. D. H.

**Physiological Action of Periplocin.** JOHANN FEIGL (*Biochem. Zeit.*, 1907, 2, 404—414).—Periplocin is a glucoside derived from plants of the genus *Periploca*, used in Africa as an arrow-poison. It produces paralytic symptoms, and is specially powerful as a heart poison.

W. D. H.

**Behaviour of Phytin in the Organism.** OSKAR HORNER (*Biochem. Zeit.*, 1907, 2, 428—434).—The experiments on dogs and rabbits were undertaken to ascertain the value of phytin (anhydro-oxy-methylenediphosphoric acid, Posternack, Abstr., 1903, ii, 607, 680) as a phosphorised food. After it is given, the phosphoric acid of the urine (in the dog) rises somewhat (from 0.87—1.0 to 1.31—1.43), and that of the faeces from 0.2 to 4.7. It is calculated that 35% is absorbed. Similar results were obtained in the rabbit, but the experiments are incomplete.

W. D. H.

**Behaviour of Acetylglucosamine in the Animal Body.** KURT MEYER (*Beitr. chem. Physiol. Path.*, 1907, 9, 134—140).—Acetylglucosamine given by the mouth to rabbits soon killed the animals; during the few days they lived nitrogenous katabolism was increased; the sugar in the urine was increased, glycosuria having been produced by phloridzin, but the conclusion that the material administered gave rise to sugar is put forward with reserve.

W. D. H.

**Physiological Action of Arecoline.** HUGO MEIER (*Biochem. Zeit.*, 1907, 2, 415—420).—This alkaloid from the Areca nut falls into the nicotine-pilocarpine group so far as its physiological action is concerned. All these produce paralytic, which may be preceded by convulsive, effects by acting both on the central and peripheral parts of the nervous system. In nicotine poisoning the central action, in pilocarpine poisoning the peripheral action, is the more prominent: the two are about equal in the case of arecoline.

W. D. H.

**Poisoning by Carbon Monoxide.** G. G. NASMITH and D. A. L. GRAHAM (*J. Physiol.*, 1906, 35, 32—52).—Guinea-pigs living in a dilute carbon monoxide atmosphere are able, by increasing the quantity of hæmoglobin and the number of their red corpuscles, to maintain an oxygen-carrying capacity equal to that which they originally possessed. There is also an increase in the eosinophil and pseudo-eosinophil leucocytes. Different doses cause, however, different histological changes in the colourless corpuscles, which are described in full.

W. D. H.

**Cause of the Poisonous Action of a Pure Sodium Chloride Solution and of the Removal of the Action by Potassium and Calcium.** JACQUES LOEB (*Biochem. Zeit.*, 1906, 2, 81—110).—A solution of pure sodium chloride isotonic with sea water is at least four times as poisonous for fertilised eggs of sea urchins as for non-fertilised eggs. The same holds good for solutions of other neutral salts, and the sudden increase in poisonous properties is probably due to the increased velocity of certain chemical reactions caused by the fertilisation. For the development of fertilised eggs of *Strongylocentrotus purpuratus* an initial concentration of  $>10^{-6}n$  hydroxyl ions is necessary. The hydroxyl ion concentration of sea water lies between  $10^{-6}$  and  $10^{-5}n$ . The poisonous nature of a solution of pure sodium chloride of slightly acid reaction increases with the concentration of the hydroxyl ions. When the initial concentration of the hydroxyl ion in a pure sodium chloride solution is that favourable for development, the eggs are rapidly destroyed, yielding two cytolytic forms (compare Abstr., 1906, ii, 694). The transformation of the eggs into one form is retarded by the addition of calcium and the other transformation by the addition of potassium. Hence both are necessary to destroy the poisonous action of pure sodium chloride solution.

If the concentration of the hydroxyl ions is below that necessary for the development of the eggs, the addition of potassium cyanide to, or removal of oxygen from, the sodium chloride solution does not affect the poisonous action. If the hydroxyl ion concentration  $>10^{-6}$  then the withdrawal of oxygen or the addition of potassium cyanide retards the "black" cytolysis hæmolysis.

J. J. S.

**Amylene Hydrate** [*tert.*-Amyl Alcohol] as a Poison. S. LOEWENSTEIN (*Biochem. Zeit.*, 1906, 2, 111—117).—As much as 30 grams of pure amylene hydrate was administered to a patient in a single day without serious effect; the main results were increased secretion of mucous liquid in the throat and formation of large blisters on the feet. None of the ordinary effects of poisoning with amyl compounds was observed. Its narcotic action is attributed to the presence of the ethyl group, as triethylcarbinol is a most pronounced hypnotic.

J. J. S.

**Modifications of Toxins.** J. MORGENROTH and O. ROSENTHAL (*Biochem. Zeit.*, 1907, 2, 383—392).—The changes which toxins undergo, for instance into toxoids, undoubtedly occur, but no correct idea of the chemical processes involved is forthcoming. Toxoids cannot be reconverted into toxins. In the present experiments the poison of the *Crotalus*, named hæmorrhagin, was investigated; it receives its name from the capillary hæmorrhages which are the constant sign of its action. The addition of dilute hydrochloric acid annuls its toxicity; 0.2 c.c. *N*/400 hydrochloric acid added to 5 c.c. of a solution of the poison was found to be sufficient for this purpose. Neutralisation of the acid does not restore the toxicity.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

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**Coagulation of Milk by *Bacillus coli communis*.** C. JOCELYN O'HEHIR (*J. Path. Bact.*, 1907, 11, 405—407).—The coagulation of milk by this bacillus is due to the production of acid, probably lactic acid. Attempts to isolate any coagulative enzyme failed.

W. D. H.

**Action of the Bulgarian Ferment on Milk.** GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Ann. Inst. Pasteur*, 1906, 20, 977—990).—The lactic organism isolated from “yoghourt” or curdled Bulgarian milk (compare Cohendy, *Compt. rend. Soc. Biol.*, 1906, 60) acts with varying intensity on the three chief constituents of milk. It dissolves about one-tenth of the casein, a small part of which is used to build up its cells, and it also hydrolyses the fat to a very slight extent. By the aid of a lactase which is doubtless an endo-lactase, it hydrolyses almost the whole of the lactose, afterwards transforming the resultant dextrose and galactose into a mixture of *l*- and *d*-lactic acid in which the latter predominates. Besides the lactic acid, which may amount to 25 grams per litre, small quantities of succinic, acetic, and probably formic acids are formed. The volatile products contain neither alcohol, acetone, nor acetyl-methylcarbinol.

T. H. P.

**Propionic Acid Fermentation in Emmentaler Cheese.** ED. VON FREUDENREICH and ORLA JENSEN (*Centr. Bakt. Par.*, 1906, ii, 17, 529—546).—Most of the propionic acid in Emmentaler cheese is produced from lactates by specific propionic acid bacteria; acetic acid and carbon dioxide are also produced, the latter being the chief cause of the formation of cavities in the cheese.

In addition to the pure propionic acid fermentation there is generally also a pure acetic acid fermentation of calcium lactate, induced both by propionic acid and lactic acid bacteria.

N. H. J. M.

**Coagulation Produced by Borates. Agglutination of Yeast.** II. HENRI VAN LAER (*Bull. Soc. chim. Belg.*, 1906, 20, 277—288).—The quantity of borax necessary to induce coagulation in certain yeasts is difficult to determine, owing to the rapidity with which de-coagulation occurs. The quantity of borax required is greater for dead than for living yeast, and the granules formed are larger and denser the greater the quantity of borax employed. Dead yeast, preserved for some time under aseptic conditions, is less readily coagulated than freshly killed yeast; this is due probably to the formation of anti-coagulating acids in the preserved yeast without bacterial intervention. Coagulation by borax is greatly favoured by the presence of free sodium hydroxide and to a just perceptibly less extent by ammonia solution.

T. A. H.

**Source of the Succinic Acid formed during Alcoholic Fermentation.** RUDOLF KUNZ (*Zeit. Nahr. Genussm.*, 1906, **12**, 641—645).—The experiments described prove that the succinic acid, formed during the fermentation of sugar by yeast, is derived from the substance of the yeast, and is probably a decomposition product of the latter. It is not formed from the sugar. W. P. S.

**Action of Alkaline Phosphates on Cells and Ferments.** THOMAS BOKORNY (*Chem. Zeit.*, 1906, **30**, 1249—1250. Compare Abstr., 1895, ii, 174).—Infusoria, rotifers, and similar micro-organisms are killed immediately by a 5% solution of disodium hydrogen phosphate, or more slowly by a 2.5% solution, whilst a 1% solution does not affect the mobility of the organisms in twenty-four hours. The action of the dipotassium salt is more marked.

Pressed yeast commences to putrefy in ten days in a 10% solution of disodium hydrogen phosphate, in five days in a 15% solution, or in eight days in a solution containing 10% each of the disodium and dipotassium hydrogen phosphates. Microscopic examination of these solutions shows that numerous living bacteria are present, but that the yeast cells are destroyed. Putrefaction does not commence in eight days in a 15% solution of the dipotassium salt.

Fermentation and culture experiments with these solutions after three days and before putrefaction show that the yeast cells and the zymase are destroyed, but that the invertase is more resistant. As zymase, invertase, and maltase are killed by a 1% but not by a 0.5% solution of sodium hydroxide, the dialkali hydrogen phosphates must be hydrolysed in 15% solution to the extent of at least 1%. G. Y.

**Genesis of Proteid by a Pathogenic Microbe.** J. GALIMARD and L. LACOMME (*Compt. rend.*, 1906, **143**, 1182—1184. Compare Abstr., 1906, ii, 695).—The microbe of "green diarrhoea" was grown in a medium the only nitrogenous constituent of which was glycine. Growth occurred as in ordinary broth, and at the end of 119 days some glycine was recovered, but the greater part had been utilised in the formation of the proteid of the microbe's protoplasm; the properties of the proteid resemble those of a mucoid. A fatty material was also formed, which is probably lecithin. W. D. H.

**Chemical Studies of the Cell and its Medium. I. Liquid Culture Media.** AMOS W. PETERS (*Amer. J. Physiol.*, 1907, **17**, 443—478).—The physical and chemical properties of culture media are considered. Special attention is directed to phenolphthalein acidity, methyl-orange alkalinity, total salts and estimation of individual salts, electrical conductivity, oxygen consumption, and organic nitrogen. The biological aspects of the question are postponed. W. D. H.

**Distribution of Hydrogen Cyanide in the Vegetable Kingdom.** MAURITS GRESHOFF (*Arch. Pharm.*, 1906, **244**, 397—400, 665—672).—A list of plants which yield hydrogen cyanide is given, with indications of whether they are known to yield benzaldehyde also, or a substance analogous with this or with acetone. C. F. B.

**Composition of Juices Extracted from Roots.** GUSTAVE ANDRÉ (*Compt. rend.*, 1906, 143, 972—974).—The amounts of extract, nitrogen and ash, were determined in the root-juices of different plants obtained under pressures of 3, 12.5, and 25 kilos. per square centimetre. It was found that the density of the juices diminished as the pressure under which they were obtained increased. The relation, however, between the amounts of ash and extract and of nitrogen and extract showed very slight variations. N. H. J. M.

**Distribution of Vicianin and its Diastase in Leguminous Seeds.** GABRIEL BERTRAND and M<sup>lle</sup>. L. RIVKIND (*Compt. rend.*, 1906, 143, 970—972; compare this vol., i, 68).—Nearly all the seeds examined (about sixty varieties) were found to contain the diastase which acts on vicianin. The following do not contain appreciable amounts: *Cassia fistula*, *Ceratonia siliqua*, *Galega officinalis*, *Lathyrus sylvestris*, *Gleditschia triacanthos*, *Lupinus albus*, *Sophora japonica*, *Vicia narbonensis*. Vicianin was only found in one species, *Vicia* (*V. angustifolia* and *V. macrocarpa*). The only seeds which were found to contain neither the glucoside nor the diastase were those of *Vicia narbonensis*. N. H. J. M.

**Function of Iodine in Marine Algæ.** FRANCESCO SCURTI (*Gazzetta*, 1906, 36, ii, 619—625).—The author's experiments on *Sargassum linifolium* and *Cystoseira discors* show that the proportion of iodine contained in them varies with the state of development of the algæ, reaching its maximum in spring, when maturation commences, and its minimum in autumn; the percentage of ash is greatest when maturation is at an end. The amount of iodine present decreases rapidly if the algæ are left in the sea. Brown algæ contain a greater proportion of iodine than green algæ.

From these results it is concluded that iodine holds in algæ the place held by chlorine in the phanerogams, and that it acts, therefore, as an excitant of the reproductive phase. T. H. P.

**Principles of Atractylis Gummifera (Sicilian Masticogna).** FRANCESCO ANGELICO (*Gazzetta*, 1906, 36, ii, 636—644. Compare Le Franc, *Compt. rend.*, 1868, 67, 936 and 1873, 76, 438).—From the latex of *Atractylis gummifera* the author has separated: (1) a pale yellow, highly elastic caoutchouc, yielding, when treated with nitrous anhydride, a *nitrosite*,  $C_{10}H_{15}O_7N_2$ , which is deposited from a mixture of ethyl acetate and ether as a yellow powder decomposing at about 165°; (2) a small quantity of a *substance* separating from methyl alcohol in white crystals which soften at about 165°, and have m. p. about 173°.

From the root, which is poisonous, he has isolated the potassium atractilate,  $C_{30}H_{52}O_{18}S_2K_2$ , of Le Franc (*loc. cit.*), which crystallises from aqueous alcohol in shining, white needles, loses valeric acid at 160° and chars at 190°. This compound, which is the poisonous principle of the root, gives a characteristic reaction with sulphuric acid. When it is heated with the acid an odour of valeric acid is at once observable, and the colour of the liquid passes through wine-red to



brownish-red; if left at rest for a few minutes the liquid gradually assumes a violet colour, and after some hours this colour disappears and a violet, crystalline powder is deposited. The potassium compound is a complex glucoside in which sulphuric acid exists in the form of a compound ester.

When hydrolysed by heating with dilute sulphuric or hydrochloric acid, potassium atractilite yields: (1) sulphuric acid; (2) valeric acid; (3) a pentose, and (4) a colloidal acid substance, which is readily soluble in methyl or ethyl alcohol, gives a pale reddish-violet coloration with concentrated sulphuric acid, and decomposes when it is melted. If the hydrolysis is effected by means of alkali, acidification of the liquid causes the deposition of a substance which separates from methyl alcohol in small, white crystals melting at  $168^{\circ}$ .

The fatal doses of potassium atractilite are given for several animals.  
T. H. P.

**Presence of Prulaurasin in *Cotoneaster Microphylla*.** HENRI HERISSEY (*J. Pharm. Chim.*, 1906, [vi], 24, 537—539. Compare Abstr., 1906, i, 31).—Prulaurasin was obtained from branches with leaves of *Cotoneaster microphylla*.  
N. H. J. M.

**Enzymes in the Spores of *Fuligo Varians*.** HEINRICH SCHROEDER (*Bietr. chem. Physiol. Path.*, 1907, 9, 153—167).—The enzymes present in the spores of this variety of tan fungus are a milk curdling ferment, a proteolytic ferment, a catalase, and a tyrosinase. The material gives the guaiacum reaction. W. D. H.

**Glucosides of the *Jasminaceæ*: Syringin and Jasmiflorin.** J. VINTILESCO (*J. Pharm. Chim.*, 1906, [vi], 24, 529—536).—*Jasminum nudiflorum* contains several glucosides, including syringin, and probably a glucoside having a rotatory power of about  $\alpha_D - 145^{\circ}$ , to which the name *jasmiflorin* is given. Syringin was also obtained in a pure state from *J. fruticans*.  
N. H. J. M.

**Chemical Composition of *Linaria Vulgaris*.** TIMOTHÉE KLOBB and A. FANDRE (*Bull. Soc. chim.*, 1906, [iii], 35, 1210—1220. Compare Walz, *Jahr. pharm.*, 1853, 43, and Schlagdenhauffen and Reeb, *J. Pharm., Alsace-Lorraine*, 1901 and 1902).—The flowers on extraction with light petroleum yield (1) a saturated hydrocarbon, which may have the formula  $C_{16}H_{34}$ ,  $C_{26}H_{54}$  or  $C_{57}H_{122}$ . It crystallises from ether in fine nacreous lamellæ, m. p.  $57^{\circ}$ , and when heated at  $100^{\circ}$  exhales the odour of melted paraffin. (2) A substance which crystallises from alcohol in nacreous, hexagonal plates, m. p.  $138^{\circ}$ , and gives the characteristic reactions of a phytosterol.

By extracting the flowers with alcohol, mannitol was obtained, and in addition *linarin*,  $C_{14}H_{16}O_7$  (linaric acid of Schlagdenhauffen and Reeb), which slowly crystallises from glacial acetic acid in colourless microscopic needles, m. p.  $265^{\circ}$ , is readily attacked by oxidising agents, and when boiled with Fehling's solution furnishes a distillate containing *linarodin*,  $C_9H_{10}O_2$ , which may be purified by redistillation, and then has m. p.  $36.5^{\circ}$ , and sublimes at a higher temperature.

When first prepared it has an aromatic odour simultaneously recalling those of anise and of Tonquin beans, but this disappears on purification, though the pure substance develops the odour on heating at  $100^{\circ}$ . When dissolved in warm nitric acid, a white precipitate separates after a time, which crystallises from ether in slender needles. Linarodin does not recolour Schiff's reagent, and separates unchanged on cooling its solution in warm sodium bisulphite solution.

The whole plant, deprived of roots, on extraction with light petroleum, yields a *hydrocarbon*, which was not obtained free from oxygenated substances. This crystallises from ether in hexagonal or rhombic lamellæ, m. p.  $57^{\circ}$ .  
T. A. H.

**Digestion and Secretory Activity in the Endosperm of Ricinus.** D. BRUSCHI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 563—567).—The endosperms of *Ricinus communis* removed from non-germinated seeds are incapable of initiating autodigestion. But even if germination has only just commenced prior to the separation of the endosperms, the latter undergo autodigestion, the fat and contents of the aleurone cells greatly diminishing, the starch disappearing, firstly from within the nucleus and then from the whole cell, and the sugar accumulating in the neighbourhood of the cellulosic walls. Since, in the germination of *Ricinus*, starch is not found in the endosperm, the first product of digestion of the isolated endosperms must be assumed to be, not starch, but sugar, which, not being absorbed by the embryo, is converted into starch so that the sugar in the cell may be prevented from increasing beyond the allowable limit. Subsequently, when the endosperm has consumed the reserve of albumin and oil, the starch disappears again. The products of autodigestion are allowed to exude into the surrounding liquid, in which appear dextrose, sucrose, phosphoric acid, calcium, and magnesium. The amounts of these substances emitted into the liquid are influenced to a marked extent by the presence in solution of various compounds.  
T. H. P.

**Presence of Allantoin in, and Absence of Solanine from, Tobacco Seeds.** FRANCESCO SCURTI and F. PERCIABOSCO (*Gazzetta*, 1906, 36, ii, 626—632. Compare Starke, *Abstr.*, 1902, ii, 166).—The authors show that tobacco seeds do not contain solanine, but that they contain: (1) allantoin, this being the first occasion on which this substance has been observed in seeds; (2) a higher *alcohol*,  $C_{26}H_{44}O$ , of the cholesterol group which separates from alcohol with  $\frac{1}{2}H_2O$  in colourless, nacreous crystals, m. p.  $134$ — $135^{\circ}$ ; when shaken with sulphuric acid, its chloroform solution turns first blood-red and then cherry-red; it absorbs more than 2 atoms of iodine per mol., and it forms an *acetyl* derivative which separates from alcohol as a crystalline powder, m. p.  $130^{\circ}$ .  
T. H. P.

**Influence of the Valency of Metals on Toxicity.** HENRI MICHEELS (*Compt. rend.*, 1906, 143, 1181—1182).—Wheat germinates better in solutions of sodium chloride if calcium chloride in small amounts or an equivalent amount of salts of other bivalent metal are added to it. The results confirm those of Loeb on animal organisms.  
W. D. H.

**Reduction of Nitrates in Musts and Wines.** F. ROSSI and FRANCESCO SCURTI (*Gazzetta*, 1906, 36, ii, 632—635).—Egger (Abstr., 1885, 842) has shown that unadulterated wines, when tested with a sulphuric acid solution of diphenylamine, give no indication of the presence of nitrates (compare Borgmann, Abstr., 1888, 753).

Formento (*Staz. sper. agrar. ital.*, 1889, 17, 158), Leone (*Gazzetta*, 1895, 25, 433), and others have asserted that this depends, not on the absence of nitrates from the must, but on a process of denitrification occurring either during the fermentation or as a consequence of the action of micro-organisms always present in wine. The authors find, however, that no such destruction of added nitrates occurs during either fermentation of grape must or storing of wine provided that proper conditions of fermentation or storage are maintained. Only when the must or wine undergoes secondary changes does any destruction of nitrates take place.

As all well water contains small quantities of nitrates, its addition to wine as an adulterant may be detected by means of a sulphuric acid solution of diphenylamine. T. H. P.

**Presence of Boric Acid in Genuine Sicilian Wines.** E. AZZARELLO (*Gazzetta*, 1906, 36, ii, 575—587).—The author has examined spectroscopically the ashes of 84 samples of Sicilian wines, all of which were found to contain boric acid. In six cases quantitative estimations of the amount of the acid gave from 0.0191 to 0.0410 gram per litre. T. H. P.

**Lecithans of Wine.** GIUSEPPE PLANCHER and A. MANARESI (*Gazzetta*, 1906, 36, ii, 481—492).—From the results of their own investigations, and those of other workers, on different wines, the authors conclude that all wines contain lecithans (compare Koch, Abstr., 1903, i, 301), the amount of which largely determines the nutrient value of wine. Contrary to the statement of Weirich and Ortlieb (Abstr., 1904, ii, 304), it is found that no relation exists either between the proportions of total phosphorus and lecithans present in wines, or between the contents of alcohol and lecithans. With the exception of the stones, the parts of the grape richest in lecithans are those adhering to the skin. Pasteurisation of the wine at 65—70° has no destructive action on the lecithans; at higher temperatures, the lecithans are decomposed to some extent without undergoing complete destruction, which is, indeed, not effected by concentrating the must over an open fire to about three-quarters of its volume (compare Weirich and Ortlieb, *loc. cit.*). T. H. P.

**Bitterness of Wines.** AUGUSTE TRILLAT (*Compt. rend.*, 1906, 143, 1244—1247).—The bitterness sometimes acquired by the red wines of Bourgogne has been attributed to secretions of microbes, and to decomposition of the colouring matter of the wine. It is probably due to the production of resins from aldehyde and ammonia. Diseased wines were found to contain both compounds in considerable amounts; and it was found that certain wines soon acquired the bitter taste after addition of very small quantities of acetaldehyde and ammonia.

N. H. J. M.

**Influence of Light on the Nitrogen of Wheat.** J. DUMONT (*Compt. rend.*, 1906, 143, 1179—1181).—The more refrangible rays are those which are most efficacious in producing migration of nitrogenous material, especially gluten, in wheat grains during maturation. They provoke or favour the formation of proteid, and so are of physiological importance. W. D. H.

**Distribution of Phosphorus in Foods.** BALLAND (*Compt. rend.*, 1906, 143, 969—970).—A *résumé* of the results of 600 determinations of phosphoric acid in cereals, vegetables, fruit, meat, eggs, &c., recently published in *Les Aliments*. N. H. J. M.

**Nitrogen Fixation in Soils.** THEODOR PFEIFFER, PAUL EHRENBURG and E. REICHENBACH (*Chem. Centr.*, 1906, ii, 1624—1625; from *Mitt. Landw. Inst. K. Univ. Breslau*, 3, 899—927).—For soil investigations the object of which is to obtain a nitrogen-balance, large numbers of nitrogen estimations are essential. The soil samples can be dried without loss of nitrogen after addition of dilute acid. Warmbold's statement that abundant fixation of free nitrogen takes place in sterilised soils was not confirmed. No results have as yet been published which indicate any notable activity of nitrogen-fixing bacteria in soils under practical conditions; existing evidence rather points the other way. N. H. J. M.

**Soils of the Northern Portion of the Great Plains Region: The Second Steppe.** FREDERICK J. ALWAY (*Amer. Chem. J.*, 1906, 36, 580—594).—The large yields of grain obtained in the Canadian Northwest have been erroneously attributed to the constant supply of water furnished by the melting ice stored in the soil (Crookes, *Pres. Address Brit. Assoc.*, 1898).

It is shown that the high yields are due to moisture stored during the previous summer and not to the frost of the preceding winter, as the soil of the southern portion does not at any depth remain permanently frozen. The surface soils are rich in nitrogen, and the subsoils very rich in carbonates; both surface and subsoils contain plenty of potassium and phosphoric acid.

The yields of cereals vary with the rainfall of the crop season, but show a still closer relation to the total available moisture. With favourable conditions of moisture, the surface soil is usually rich enough to produce very large yields. The relative fertility of different areas seems to depend on the nature of the subsoil. N. H. J. M.

**Removal of "Black Alkali" by Leaching.** FRANK K. CAMERON and H. E. PATTEN (*J. Amer. Chem. Soc.*, 1906, 28, 1638—1649).—Neutral salts, such as chlorides, in the presence of carbonates can be removed comparatively readily and completely from the soil. Continued leaching of "black alkali" soils results in increased rapidity of percolation and a reduction of the amount of normal carbonates in the soil water owing to a great extent to their conversion into hydrogen carbonates. The latter are at first rapidly removed; subsequently very small amounts are found in the soil water and the

decrease is then so slow that the amount remains practically constant for an indefinite period.

Both the time and the amount of water necessary for reclaiming "black alkali" soils are probably much greater than in the case of "white alkali."  
N. H. J. M.

**Amount and Composition of Drainage Waters, Rain, Dew, and Canal Water Collected During the Years 1903-4, 1904-5, 1905-6.** W. H. MORELAND (*Rep. Cawnpore Agric. Stat.* for the year ending June 30, 1906, 23-29).—Four drain gauges, similar to those at Rothamsted (*Abstr.*, 1882, 890) were constructed at Cawnpore in 1903. The area is in each case 1/1000 acre (6 ft.  $\times$  7.26 ft.) and the depth 36 inches and 72 inches, the intention being to have two permanently uncropped, and two cropped when sufficient comparative records have been obtained without vegetation.

The soil has for some years been regularly manured and cropped.

Nitrogen as nitrates and ammonia is determined in mixed samples of the drainage twice a month, and the present paper contains the full results from June, 1904, to Oct., 1905; also analyses of rain-water and dew, 1904-5 (compare *Abstr.*, 1906, ii, 487), and canal-water.

The results for the twelve months, June, 1904, to May, 1905, obtained with one of the 36-inch and one of the 72-inch gauges, both uncropped, are as follows:—

Depth of soil. inches.	Rain- fall. inches.	Drainage. inches.	N per million		N per acre	
			as $\text{NH}_3$	as $\text{N}_2\text{O}_5$	as $\text{NH}_3$ lb.	as $\text{N}_2\text{O}_5$ lb.
36	49.20	22.57	0.06	11.10	0.31	56.7
72	,,	21.78	0.07	21.61	0.32	106.5

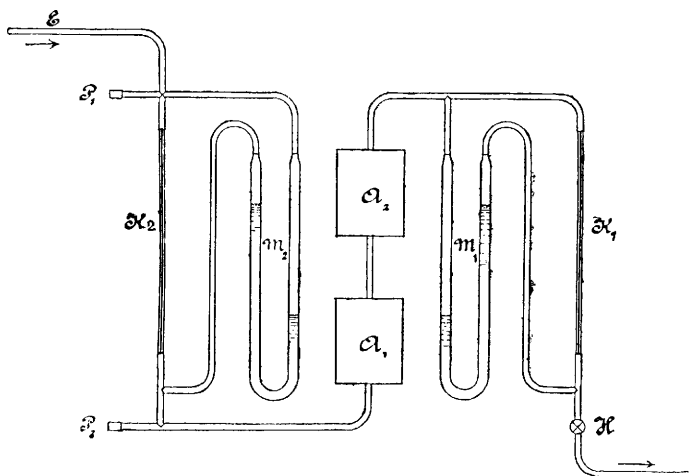
The small amounts of ammonia are attributed to dew deposited on the funnels below the soil.  
N. H. J. M.

## Analytical Chemistry.

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**The Autolysator. New Apparatus for Continuous Automatic Gas Analysis.** HUGO STRACHE, RUD JAHODA, and U. GENZKEN (*Chem. Zeit.*, 1906, **30**, 1128—1130).—In the diagram showing the principle of the apparatus,  $K_1$  is a capillary tube which communicates with the differential pressure gauge,  $M_1$ , the lower end of which is connected through the stopcock,  $H$ , to a filter-pump. By regulating the stopcock,  $H$ , a steady flow of gas through the tube,  $K_1$ , can be maintained, as shown by the reading of the pressure gauge,  $M_2$ . The gas enters the apparatus by a tube,  $E$ , which is connected to a similar capillary,  $K_2$ , and gauge,  $M_2$ . So long as none of the gas is absorbed by the reagents contained in the vessels,  $A_1$  or  $A_2$ , the

pressures indicated by the two gauges will be identical; when, however, absorption takes place a proportionately larger volume of gas will be drawn through  $K_2$ , and accordingly the gauge,  $M_2$ , will register a larger difference of pressure. If the constancy of the flow of gas through  $K_1$  is regulated automatically by the stopcock,  $H$ , the percentage of gas being absorbed may be directly read off the gauge,  $M_2$ ,



provided it has been graduated accordingly beforehand. Variations in the pressure indicated by the gauge,  $M_2$ , are automatically recorded in the form of a curve drawn on a revolving cylinder by a pen floating on water which moves up and down in obedience to the alteration of level in the gauge. The recording apparatus is inserted between the points,  $P_1$  and  $P_2$ . P. H.

**Burette Arrangement.** P. PANNERTZ (*Zeit. anal. Chem.*, 1906, 45, 751—754).—The apparatus is a modification of the one described by Flemming (*Chem. Zeit.*, 1904, 28, 818). The chief improvement consists in the fact that a Wouff bottle containing the standard liquid and holding the burette and the air-tube is substituted for the flask with a doubly-perforated cork. A three-way stopcock is employed which renders possible a connexion or disconnexion between the reservoir, outer air, and the elastic ball. For further particulars the illustrations in the original should be consulted. L. DE K.

**Apparatus for Dissolving and Evaporating to Dryness.** CONSTANTIN ZENGELIS (*Zeit. anal. Chem.*, 1906, 45, 758—760).—The apparatus, which admits of rapid evaporation without risk of loss by spirting, consists of a 300—400 c.c. Phillips's beaker with spout and furnished with two holes opposite each other about 3 cm. from the top. The rim is bent inwardly, and during the heating a watch-glass is placed over it concave side downwards. This watch-glass has a hole through

which passes a glass rod which is expanded at one place, so that the rod will be held up by the watch-glass with its drawn-out point about 1 cm. from the bottom of the beaker.

The beaker should be heated on a sand-bath or an asbestos plate.

L. DE K.

**Determination of the Calorific Power of Gases and Volatile Liquids.** E. GOUTAL (*Ann. Chim. anal.*, 1906, 12, 1—3).—The combustion of gaseous hydrocarbons becomes imperfect in presence of too large an excess of oxygen; in practice, therefore, several trials should be made with varying amounts of oxygen.

When determining the calorimetric power of liquid combustibles, these are weighed in sealed glass bulbs through the drawn-out points of which passes the usual iron conducting-wire. The bulb is placed in the porcelain capsule suspended in the bulb, and the usual course is that the points are broken before closing the apparatus in order to admit the oxygen. The author, however, recommends not breaking the points but using a source of electricity more powerful than that furnished by the bichromate battery which is generally sold with the apparatus, the glass bulb then being fractured within the closed apparatus. On account of the somewhat violent action, a platinised bomb should be employed or otherwise a non-enamelled one made of ferro-nickel. The combustion will now be always complete. L. DE K.

**Fluorine in Mineral Waters.** P. CARLES (*Compt. rend.*, 1907, 144, 37—39).—Fluorine has been detected in a large number of mineral waters of Bourbon by evaporating several litres, adding calcium acetate, collecting and washing the calcium fluoride, and decomposing by sulphuric acid in a platinum capsule covered with a glass plate. Minute directions are given in the original paper. The amounts of fluorine were estimated by comparison of the etched glass with a series of glasses etched by varying amounts of sodium fluoride under the same conditions. E. H.

**Estimation of Uncombined Sulphur.** E. BERGER (*Compt. rend.*, 1906, 143, 1160—1161).—Uncombined sulphur is readily and rapidly oxidised to sulphuric acid by the action in the cold of fuming nitric acid containing a little potassium bromide. For the estimation of uncombined sulphur, the author recommends adding 10 c.c. of fuming nitric acid and 0.5 to 1 gram of pure potassium bromide to a weighed quantity of the substance containing 0.1—0.2 gram of sulphur; after some minutes, evaporating to dryness on a water-bath, and precipitating the sulphuric acid with barium chloride, all traces of nitric acid having previously been removed by the usual process. M. A. W.

**Micro-chemical Detection of Phosphorus.** F. H. SCOTT (*J. physiol.*, 1906, 35, 119—124).—Acids readily remove most of the phosphorus from nuclein compounds in some soluble form, but not as inorganic phosphates. The whole principle of the methods of Lilienfeld, Monti, and Macallum is therefore wrong, and all deductions as to the distribution of phosphorus compounds (other than inorganic



orthophosphates) by the use of these methods are regarded as valueless.  
W. D. H.

**Separation of Arsenic from Copper as Ammonium Magnesium Arsenate.** FRANK A. GOOCH and M. A. PHELPS (*Amer. J. Sci.*, 1906, [iv], 22, 488—492).—A series of experiments showing that even very small quantities of arsenic, if present in the higher state of oxidation, may be estimated accurately in the presence of much copper as ammonium magnesium arsenate, which may then be collected in a Gooch crucible, and converted into pyroarsenate.

In order to obtain correct results, the hydrochloric solution should be poured with constant stirring into an excess of magnesium mixture, which may, if necessary, be placed in a freezing mixture. The precipitate always retains copper, from which it may be freed by a reprecipitation; if more than 0.005 gram of arsenic is present, it is necessary to reprecipitate two or even three times.  
L. DE K.

**Different Behaviour of Organic and Inorganic Compounds of Arsenic towards Reagents, and Estimation of Arsenic in the Urine.** C. E. CARLSON (*Zeit. physiol. Chem.*, 1906, 49, 410—432).—In cases of arsenical poisoning the urine should be examined, the best results being obtained by electrolysis. Arsenic occurs in the urine as arsenious or arsenic acid. In animals it is obtained after breathing hydrogen arsenide. Organic arsenic compounds used as medicaments appear to pass through the organism without producing the toxic effects of inorganic compounds; this, at any rate, is true for cacodylic acid and its salts. The greater part appears unaltered in the urine; another part is reduced in the stomach, liver, and intestine to a volatile cacodyl oxide, which leaves the body mainly by the expired air.

W. D. H.

**Copper Spirals for Use in Combustions of Nitrogenous Substances.** KARL HEYDENREICH (*Zeit. anal. Chem.*, 1906, 45, 741—745).—Copper spirals reduced in a current of hydrogen may be freed from traces of this gas by heating in a current of carbon dioxide for about half an hour, and then placing them in a vacuum over calcium oxide and sulphuric acid. Reduction with methyl alcohol vapour instead of hydrogen cannot be recommended, as a deposit of carbon is likely to form on the surface; in one experiment not less than 0.0972 gram of carbon dioxide was formed on heating ten copper spirals so prepared in a current of oxygen. Attention is called to the hygroscopic properties of the spirals.  
L. DE K.

**Phosphomolybdic Acid as a Reagent for Potassium.** A. SCHLICHT (*Chem. Zeit.*, 1906, 30, 1299—1300).—When ammonium phosphomolybdate is fused with sodium carbonate and nitrate, and the resulting mass dissolved in water and acidified with nitric acid, a solution is obtained which gives a distinct yellow precipitate with even very dilute solutions of potassium salts.  
L. DE K.

**Assay of Barium Peroxide.** A. LÖB (*Chem. Zeit.*, 1906, 30, 1275).—One gram of the sample is dissolved in 50 c.c. of  $N/2$  hydrochloric acid preferably with addition of 20 c.c. of 10% manganous sulphate and then titrated with  $N/4$  permanganate (1 c.c. = 0.0221 gram peroxide). This process agrees very well with the iodometric method, which is carried out as follows: 0.5 gram of the sample is dissolved in a stoppered flask in 50 c.c. of water and 5 c.c. of hydrochloric acid ( $D\ 1.124$ ), 20 c.c. of 10% potassium iodide are added, and the liberated iodine titrated with standard thiosulphate.

The peroxide cannot be titrated with permanganate in sulphuric acid solution, as the barium sulphate formed occludes large quantities of the peroxide which escape the reaction.

L. DE K.

**Volumetric Estimation of Zinc.** JOSEPH A. MULLER (*Bull. Soc. chim.*, 1907, [iv], 1, 13—16).—This process is based on that of Pouget (Abstr., 1899, ii, 695). The zinc solution is neutralised with ammonia, sodium acetate is added, and the mixture, slightly acidified with acetic acid, is saturated with hydrogen sulphide. The excess of the latter is eliminated by heating the mixture to  $50^\circ$  and passing a rapid current of carbon dioxide. Hydrochloric acid is added to dissolve the zinc sulphide and then a known volume of standard iodine solution. The mixture is shaken vigorously for several minutes, and the excess of iodine titrated with sodium thiosulphate solution.

Details are given of the preliminary treatment necessary in applying this method of estimation to zinc in ores.

T. A. H.

**Rapid Estimation of Mercuric Chloride in Very Dilute Solutions.** JOSÉ R. CARRÁCIDO (*Anal. Fis. Quim.*, 1906, 4, 314—316).—When ammonia is added drop by drop to a mercuric chloride solution containing one part of the salt in 10,000 of water, a white ring is formed which increases in thickness as the ammonia penetrates the dilute solution. This alteration in the size of the ring is due to the solubility of mercuriammonium chloride in excess of ammonia. Similar appearances are observed with solutions of the following concentrations: 1 in 20,000 and 1 in 30,000; but the limit is reached when the strength is reduced to 1 in 40,000, as only a very faint ring is obtained. By the use of standard solutions of mercuric chloride this process furnishes a means for estimating colorimetrically the amount of mercuric chloride in dilute solutions. Sodium chloride does not interfere, but hydrochloric acid or ammonium chloride must be absent, because in the presence of either of these reagents the mercuric ammonium chloride and the ammonium chloride combine to form the double salt  $NH_2HgCl, NH_4Cl$  which is deposited as a sandy, crystalline precipitate without giving rise either to a ring or a turbidity.

G. T. M.

**Iodometric Estimation of Basic Alumina and of Free Acid in Aluminium Sulphate and Alums.** SETH E. MOODY (*Amer. J. Sci.*, 1906, [iv], 22, 483—487).—Fifteen grams of the material are dissolved in water, the insoluble matter is collected, and the filtrate diluted to one litre. Twenty-five c.c. are then boiled in a suitable

apparatus with potassium iodide-iodate mixture and the resulting free iodine is collected into a receiver containing potassium iodide. After slightly acidifying with dilute sulphuric acid, the solution is titrated as usual with thiosulphate. The residual liquid in the distilling flask is filtered, and the precipitate, which contains besides alumina, ferric oxide and zinc oxide, is collected and examined further by the usual gravimetric process. In other aliquot portions of the solution are estimated the ferrous and ferric oxides by titration and also any zinc by electrolysis.

From the amount of iodine liberated and the alumina found, the quantity of free sulphuric acid and free alumina respectively may be readily calculated, due allowance being made, of course, for the presence of ferrous and ferric iron, also for ammonia and zinc. In calculating it should be remembered that 1 mol. of alumina = 6I, 1 mol. of ferric oxide = 6I, 1 mol. of ferrous oxide = 2I, 5 mols. of zinc oxide = 8I, 1 mol. of ammonia = 1I, and 1 mol. of sulphuric acid = 2I.

L. DE K.

**Titration of Ferrous Salts with Alkali Hypoiodite.** ERWIN RUPP and M. HORN (*Arch. Pharm.*, 1906, 244, 571—575).—By the use of potassium hydroxide instead of sodium potassium tartrate (*Abstr.*, 1903, ii, 244) the experiments can be shortened.

A measured quantity of the ferrous solution is mixed with a liberal excess of  $N/10$  iodine solution, and approximately  $N$ , or 5%, aqueous potassium sodium hydroxide is added with shaking until the mixture has a distinctly alkaline reaction (the volume required will be about one-third that of the iodine solution). After a few minutes half as many grams of oxalic acid (or less well as many c.c. of glacial acetic acid) are added as there were c.c. of  $N$  alkali used. After five to ten minutes more, the mixture is diluted to about 100 c.c. and titrated with  $N/10$  thio-sulphate solution, with starch solution as indicator, until the blue colour has disappeared and does not return immediately.

The method is applicable in the presence of ferric, and even of man-ganous salts, but not in the presence of ammonium salts. C. F. B.

**Useful Reaction for Cobalt.** EUGENIO PIÑERUA ALVAREZ (*Ann. Chim. anal.*, 1906, 11, 445—446).—If a drop of a 1% solution of cobalt chloride or sulphate is added to a large excess of boiling, very strong aqueous sodium or potassium hydroxide, a blue solution is obtained. This is no doubt caused by the formation of a compound of the alkali with cobaltous oxide ( $\text{CoO}_2\text{K}_2$ ), for on diluting with water the hydroxide is regenerated and the blue colour vanishes. In presence of much nickel a precipitate is formed having an azure colour, but this must not be confounded with the compound obtained on adding aqueous alkali to a cobalt solution in the cold, for this precipitate, which turns a rose colour on heating, gives a blue solution if heated with a large excess of alkali.

L. DE K.

**Detection and Estimation of Sodium Chloride in [Commercial] Tin Chlorides.** PAUL HEERMANN (*Chem. Zeit.*, 1907, 31, 27—28).—To a portion of the solution, D 1.5—1.7, is added four

times the bulk of alcoholic hydrochloric acid prepared by saturating 99.5% alcohol with hydrogen chloride. As little as 0.1% of sodium chloride may thus be detected, and when the amount exceeds 1% the liquid gives a copious crystalline precipitate. If aqueous hydrochloric acid is used no precipitate is formed unless the sodium chloride exceeds 1%; if 96% alcohol is employed no deposit is obtained until the sodium chloride present is about 6–8%.

The precipitate formed by the alcoholic acid may be collected and washed free from chlorides with absolute alcohol, then dissolved in water and titrated as usual.

L. DE K.

**Direct Estimation of Antimony.** HERBERT W. ROWELL (*J. Soc. Chem. Ind.*, 1906, 25, 1181–1183).—The method depends on the oxidation of antimonious to antimonic chloride by potassium bromate in the presence of hydrochloric acid, and is a modification of a process described previously by Nissenson and Siedler (*Abstr.*, 1903, ii, 697). One gram of the finely-divided alloy is dissolved in 25 c.c. of concentrated hydrochloric acid and 5 c.c. of a saturated solution of bromine in hydrochloric acid, and the excess of bromine is expelled by heating the mixture. Three or 4 grams of sodium sulphite are next added to reduce the antimony and the solution is evaporated to a volume of about 10 c.c. If more than 3% of arsenic is present, 20 c.c. of concentrated hydrochloric acid and 5 c.c. of saturated sulphurous acid are added, and the liquid is boiled down again. To the concentrated solution, 20 c.c. of concentrated hydrochloric acid and 40 c.c. of hot water are added, and the whole is boiled for one minute to remove traces of sulphur dioxide. The solution is then titrated with  $N/20$  potassium bromate solution, using methyl-orange as indicator. The bromate solution is standardised on arsenious chloride solution. During the titration, the solution should be kept at a temperature of not less than 60°, and the bromate solution must be run in drop by drop with constant stirring. Lead, zinc, tin, silver, and chromium have no influence on the estimation, but the presence of large quantities of calcium and ammonium salts tends to make the results too high. If copper is present, it must be removed before carrying out the titration; for this purpose the alloy is evaporated with nitric acid, the mixed oxides of antimony and tin are collected on a filter, dried, and fused with sodium hydroxide. The fused mass is then dissolved in hydrochloric acid and the estimation continued as described.

W. P. S.

**Estimation of Columbium and Tantalum in the Presence of Titanium.** CHARLES H. WARREN (*Amer. J. Sci.*, 1906, [iv], 22, 520–522).—The author confirms Noyes's statement that repeated fusion with potassium pyrosulphate does not only dissolve titanium, but also notable traces of columbium and tantalum oxides. Osborne's process, oxidation of the lower oxides of titanium and columbium with permanganate and subsequent colorimetric estimation of the titanium by means of hydrogen peroxide, was found to be very unsatisfactory. Up to the present no satisfactory process is known to the author.

L. DE K.

**Estimation of Small Amounts of Ethyl Alcohol.** MILAN J. ŠTRITAR (*Zeit. physiol. Chem.*, 1906, 50, 22—29. Compare Abstr., 1904, ii, 686; Nicloux, Abstr., 1905, ii, 181; Landsberg, Abstr., 1904, ii, 499).—The ethyl alcohol contained in solutions of about 1 to 1·5% may be estimated by the iodide method (Abstr., 1904, ii, 686). The method may also be used for determining the ethoxy-groups in esters; these are hydrolysed with potassium hydroxide, the ethyl alcohol distilled over and diluted to the required strength. When the percentage of alcohol is below 0·5, the experimental error is greater.

J. J. S.

**Determination of the Densities of Alcohols by means of their Critical Temperatures of Solution.** LÉON CRISMER (*Bull. Soc. chim. Belg.*, 1906, 20, 294—305. Compare Abstr., 1903, ii, 10).—Vandam has proposed to apply the results obtained by the author (*loc. cit.*) to the determination of the critical temperature of solutions of butters in alcohol having  $D^{15.5^\circ}$  0·7967. In the present paper the data employed by Vandam are criticised, since they are not in accordance with those previously recorded by the author, and the precautions which must be taken in preparing alcohol and light petroleum to be used in making determinations of this kind are described. It is shown that (1) unless recourse is had to the use of a thermostat, the results obtained in determining the density of alcohol by means of a Westphal balance or a pycnometer are unsuitable for use in standardising a light petroleum to be employed for the determination of the critical solution temperature of an alcohol; (2) the best and simplest method of determining the density of a commercial alcohol is to ascertain its critical solution temperature in light petroleum, previously standardised by means of anhydrous alcohol; (3) in each case it is safer to determine a second point on the curve of critical solution temperature in order to verify its concordance with the data previously recorded; and (4) light petroleum, once standardised, may be preserved unchanged for several years in stoppered flasks kept in the dark.

T. A. H.

**The Allen-Marquardt Process for the Estimation of Higher Alcohols.** EDWARD A. MANN and C. E. STACY (*J. Soc. Chem. Ind.*, 1906, 25, 1125—1129).—The results of an investigation of this method show that in order to obtain complete oxidation of the amyl alcohol and the recovery of the valeric acid, it is necessary to perform the oxidation in pressure bottles; the use of a reflux apparatus tends to cause loss of valeric acid through incomplete condensation. Trustworthy results are obtained only when the extraction with carbon tetrachloride is carried out at temperatures below 15·5°. Above this temperature, the solubility of ethyl alcohol in carbon tetrachloride, and subsequent formation of acetic acid during the oxidation, render it impossible to calculate the amount of the higher alcohols from the titration. Since serious loss of valeric acid occurs in drying the barium salts for the estimation of the combining weights of the acids, the higher alcohols must be estimated by titration, all the acidity being

calculated as valeric acid. The titration for "mineral acids" is unnecessary, and introduces errors. W. P. S.

**New Method for the Estimation of Glycerol in Wines.** CH. BILLON (*Rev. intern. falsif.*, 1906, 19, 57—58).—A mixture of alcohol and ethyl acetate is employed in place of the usual alcohol-ether solvent for extracting the glycerol from the wine residue. Fifty c.c. of the wine are rendered alkaline with milk of lime and evaporated to the consistency of a paste. The latter is transferred to a 100 c.c. flask by the addition of several successive small quantities of alcohol, using not more than 20 c.c. altogether, and the whole is made up to a volume of 100 c.c. with ethyl acetate. After mixing, the solution is filtered and a known volume of the filtrate evaporated, the residue being then dried at a temperature below 70° and weighed. In the case of sweet wines, 50 c.c. are evaporated with lime, the residue is extracted with boiling alcohol so as to obtain 100 c.c. of alcoholic solution. This is again evaporated, the syrupy residue is taken up with 10 c.c. of alcohol and sufficient ethyl acetate to make the volume 50 c.c., the solution is filtered, and a portion of the filtrate evaporated, as described previously. W. P. S.

**The Values of Different Colour Reactions of Pentoses.** FRITZ SACHS (*Biochem. Zeit.*, 1906, 1, 383—398).—Various methods for the detection of pentose in urine were compared; the principal difficulty appears to be that glycuronic acid gives similar reactions. Salkowski and Blumenthal's orcinol reaction is recommended for clinical use, if prolonged boiling is avoided. Jolles' method with sodium acetate and phenylhydrazine appears to be of little value, and Neumann's modified orcinol test is regarded as of value only as a confirmatory test. W. D. H.

**Detection of Pentoses in Urine.** ADOLF JOLLES (*Biochem. Zeit.*, 1906, 2, 243—244. Compare Abstr., 1906, ii, 203).—The author gives details of his method which make it certain, and defends it from Sach's criticisms (preceding abstract). FRITZ SACHS (*ibid.*, 245—246) replies; he adheres to his opinions. W. D. H.

**A Colour Reaction of Reducing Sugars with Alkaline *m*-Dinitrobenzene.** CHAVASSIEU and ALBERT MOREL (*Compt. rend.*, 1906, 143, 966—967).—*m*-Dinitrobenzene gives a violet coloration with aldoses and ketoses in moderately alkaline solution. The reagent, prepared by adding 35 c.c. of a 33% sodium carbonate solution to a solution of 1 gram of *m*-dinitrobenzene in 100 c.c. of alcohol, is slightly rose-coloured in consequence of the presence of dinitrothiophen (compare Meyer and Stadler, Abstr., 1885, 141). The violet coloration is formed in fifteen minutes if 10 c.c. of the reagent is added to 20 c.c. of a 1% aqueous solution of maltose, lactose, galactose, or arabinose, or in two and a half hours with a 0.1% solution of these carbohydrates. Lævulose gives the violet coloration in two to three minutes in a 1%, or in less than ten

minutes in a 0.1% solution; hence by this reaction lævulose can be detected in the presence of other carbohydrates.

Sucrose, glycogen, the albumins, the albumoses, amides, including carbamide, and creatine do not give colorations with alkaline *m*-dinitrobenzene, but the aldehydes and ketones which are not alcohols and which give a red coloration (Bittó, Abstr., 1897, ii, 468), as also uric acid which gives a violet coloration, must be removed before the aldoses and ketoses are tested for.

This reaction, which is as delicate and characteristic as those usually employed for the detection of the reducing sugars, serves also for the approximate colorimetric estimation of these substances.

G. Y.

**Estimation of Reducing Sugars.** GABRIEL BERTRAND (*Bull. Soc. chim.*, 1906, [iii], 35, 1285—1299).—Four solutions are used, each of which, for the quantities of salt named below, is made up to one litre: (a) cupric sulphate, 40 grams; (b) sodium potassium tartrate, 200 grams, and sodium hydroxide, 150 grams; (c) ferric sulphate, 50 grams, and sulphuric acid, 200 grams; (d) potassium permanganate, 5 grams. The quantity of sugar solution used should be 20 c.c. and contain from 0.01 to 0.09 gram of the sugar; to this 20 c.c. each of solutions *a* and *b* should be added and the mixture boiled for three minutes, reckoned from the time that the first bubbles of steam appear. The cuprous oxide is collected in a Soxhlet tube, dissolved in a known quantity of solution *c*, and the ferrous sulphate, thus produced, titrated by means of solution *d* (compare Wolff, Abstr., 1906, ii, 57).

Tables showing the quantities of copper equivalent to integral amounts (between 10 and 100 mg.) of the principal reducing sugars are given in the original.

T. A. H.

**Gravimetric Estimation of Sugar by Means of Fehling's Solution.** W. KELHOFER (*Zeit. anal. Chem.*, 1906, 45, 745—746).—A number of experiments are communicated to show the accuracy of the author's recent tables (Abstr., 1906, ii, 311) for the estimation of invert sugar.

L. DE K.

**Estimation of Sugar.** IVAR BANG (*Biochem. Zeit.*, 1906, 2, 271—290).—A comparison is made of the author's method with others. He claims that his titration method is as accurate as gravimetric methods, and much more expeditious. The method is titration with a copper solution to which a small amount of hydroxylamine is added; at the end point the mixture becomes colourless.

W. D. H.

**Estimation of Dextrose with Fehling's Solution containing large excess of Alkali.** FRANCISCO P. LAVALLE (*Chem. Zeit.*, 1906, 30, 1301—1302).—Objection has been made to the author's method (Abstr., 1905, ii, 588) on account of the reoxidation of the alkaline cuprous oxide solution. This may, however, be prevented by working in an atmosphere of ammonia generated in the Erlenmeyer flask itself by the addition of a little ammonium chloride. The flask is fitted

with a doubly-perforated cork; through one hole passes the tube connected with the burette containing the dextrose solution, and through the other a tube connected to a U-tube containing pumice moistened with sulphuric acid to absorb the ammonia. L. DE K.

**The Value of Almén's Bismuth Test, and the Worm-Müller Copper Test for Sugar in Urine.** OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1906, 50, 36—72).—The recent remarks of Pflüger on the comparative uselessness of tests for sugar, except that of Worm-Müller, have led the author to a complete and critical examination of the bismuth test, with the result that the value of the latter is largely vindicated. W. D. H.

**The Usefulness of the Hammarsten-Nylander and Worm-Müller Sugar-tests.** EDUARD PFLÜGER (*Pflüger's Archiv*, 1907, 116, 265—282).—Polemical against Hammarsten (preceding abstract). W. D. H.

**Use of Polarised Light for the Microscopical Detection of Rice Starch and Maize Starch in Wheat Flour.** G. GASTINE (*Compt. rend.*, 1907, 144, 35—37. Compare Abstr., 1906, ii, 587).—A small quantity of the flour is moistened with a drop of water, spread on a glass plate, dried at a low temperature, and the drying finished by a few moments' exposure at 120—130° or longer at 100° only. The preparation is then mounted in Canada balsam and examined in simple polarised light, and in polarised light modified by a plate of gypsum giving the red of the first order. In both cases the starch cells have a characteristic appearance. In the dark field of simple polarised light the amylaceous grains or fragments of rice flour, including several cells, appear brilliantly illuminated with a granite-like texture. In chromatically polarised light, the blue and clear orange tints formed at the edge of the hilum in crossed positions form a characteristic linear network. Maize flour gives a reticular appearance of much larger mesh. Millet, buckwheat, darnel, and many other starches, even the smallest, such as exists in the beet-seed, have an analogous appearance. The lenticular grains of wheat starch do not show this appearance.

The method has the advantage over that previously described of allowing the use of objectives of lower power.

The statement, made in many micrographical works, that rice starch does not polarise light, is contradicted. E. H.

**Nessler's Reagent as a Test for Gums.** JEAN VAMVAKAS (*Ann. Chim. anal.*, 1907, 12, 12—13).—The author has obtained the following results. *Almond tree gum*.—A concentrated solution of this gum gives with Nessler solution in the cold a cream-coloured, gummy precipitate. The same reaction is also obtained at the boiling heat. Tartaric acid prevents the precipitation.

*Gum arabic*.—A 30% solution gives in the cold a dirty grey emulsion and a grey deposit is formed after some time. This precipitate is formed immediately on boiling, but tartaric acid almost completely prevents the reaction.



*Gum tragacanth.*—This gives no reaction whatever with Nessler solution. On adding tartaric acid before the Nessler solution and then boiling, a slight, dirty, orange-coloured deposit is formed after some time.

L. DE K.

**A New Apparatus for the Estimation of the Volatile Acids in Wine.** HANS BOETTIGHER (*Zeit. anal. Chem.*, 1906, 45, 755—758).—The distilling flask has the form of an elongated cylinder, thus forcing the steam to traverse a deeper column of liquid than is the case with the apparatus usually employed. The vapours before entering the worm condenser pass first through a bulb connected with a slanting, bent tube. The wine (50 c.c.) is introduced into the cylinder by means of a side tubulus with a ground stopper, and to prevent frothing a few drops of olive oil are added. Steam is now passed through, and the wine is vigorously boiled until the 200 c.c. of distillate required are collected. The bottom of the cylinder is placed in a semi-spherical wire gauze of 25 c.c. content; a special mark thus becomes superfluous.

L. DE K.

**Differentiation of the Two Pharmaceutical Benzoic Acids.** H. CORMIMBOEUF and L. GROSMAN (*Ann. Chim. anal.*, 1906, 11, 462—464).—A reply to Belloni (*ibid.*), who states that there is nothing novel in the process recommended by the authors (*Abstr.*, 1906, ii, 636). The authors admit that various pharmacopœias recommend testing the samples for chlorine by heating with calcium carbonate, but this is by no means so efficacious as the author's process with anhydrous sodium carbonate, which, moreover, is carried out on a much larger quantity of the substance.

Contrary to Belloni's statement, the authors have also never met with a natural benzoic acid which gives the organic chlorine reaction.

In no pharmacopœia, however, is mention made of the characteristic odour noticed on heating the natural product with solution of sodium carbonate.

L. DE K.

**Separation of Salicylic Acid and "Saccharin" from Food Materials.** GIUSEPPE BONAMARTINI (*Rev. intern. Falsif.*, 1906, 19, 39—43).—Bromine precipitates salicylic acid quantitatively from its solution, but as the precipitate has not a definite composition, it is impossible to calculate the amount of salicylic acid from the weight of the bromine precipitate. On the other hand, "saccharin" is not precipitated by bromine, and consequently can be tested for in the filtrate from the bromine-salicylic acid precipitate. In cases where it is desired to test for both salicylic acid and "saccharin" in liquids containing other substances which are precipitated by bromine, as, for instance, in beer and wine, it is necessary to evaporate the liquid and extract the residue with a mixture of ether and light petroleum. The residue obtained on the evaporation of the solvent is then dissolved in water and treated with bromine to separate the salicylic acid from the "saccharin."

W. P. S.

**Occurrence of Salicylic Acid in Tomatoes.** HENRI PELLET (*Ann. Chim. anal.*, 1907, 12, 10—12).—The author agrees with Ferreira da Silva that the presence of 10 mg. of salicylic acid in 1 kilo. of tomatoes should not be regarded as indicating adulteration, as it occurs naturally, although only in traces. L. DE K.

**Optical Behaviour and some other Properties of the most important Animal Fats.** M. A. RAKUSIN (*Chem. Zeit.*, 1906, 30, 1247—1249. Compare Abstr., 1905, ii, 619, 802; 1906, i, 951. Neuberg, Abstr., 1906, i, 923).—The results of measurements of the sp. gr. by means of the Gintl-Rakusin pyknometer or, in the case of solid fats, by the apparatus previously described (Abstr., 1905, ii, 303), and of the optical activity of twenty-four fats of animal origin are tabulated and discussed. The sp. gr. of animal fats rarely exceeds 0.930 at 15°; the high results obtained with butter and commercial lanolin are caused by the presence of water. When dried by the action of anhydrous sodium sulphate in ethereal solution, butter has  $D_{15}^{15}$  0.9200, lanolin,  $D_{15}^{15}$  0.9289. Spermaceti has  $D_{15}^{15}$  0.8922.

Most animal fats are optically inactive, but cod liver oil is laevorotatory and lanolin, dextrorotatory. In concentrations greater than 1 in 1600, *oleum cornu cervi* and *oleum animale Dippeli* are opaque to polarised light. G. Y.

**Detection of Cocoanut Oil and Margarine in Butter.** LUCIEN ROBIN (*Ann. Chim. anal.*, 1906, 11, 454—462).—Five grams of the butter-fat are boiled in the reflux apparatus with 25 c.c. of alcoholic potassium hydroxide for five minutes, 17 c.c. of water are added, and the excess of alkali titrated with alcoholic  $N/2$  hydrochloric acid. A blank experiment having already been made, the saponification number is calculated as usual. A sufficient quantity of the acid is now added to liberate completely the fatty acids and 56.5 vol. % alcohol is added until the volume occupies nearly 150 c.c. The whole is then cooled with constant shaking so as to prevent the formation of a solid fatty cake. After making up exactly to 150 c.c., the liquid is filtered and 50 c.c. are titrated as usual; the result is *fatty acids soluble in 56.5 vol. % alcohol*.

Another 50 c.c. are heated in a water-bath until 15 c.c. are left. The acids insoluble in water float and are washed four times with water at 60°. The acids are then dissolved in a mixture of 2 parts of alcohol and 1 part of ether and titrated with  $N/10$  potassium hydroxide; the result is *fatty acid insoluble in water*, but soluble in dilute alcohol.

The water-soluble acids are then found by difference.

A large number of experiments with pure and adulterated butters are recorded. These show that a butter is undoubtedly adulterated with cocoanut oil if (1) the water-soluble figure is below 5.92, and if the relation insoluble/soluble  $\times 10$  equals at least 13. (2) If, when this figure is above 5.92, the sum of the relation figure and the alcohol-soluble figure exceeds 30. The amount of adulteration may be calculated approximately as follows. A relation figure of 13—15 = 10% of cocoanut oil; 15—20 show 15%; 20—25, 20%, and 25—30, 25%.

If a butter is adulterated with margarine the water-soluble figure is

below 5.92 and the relation figure below 13. For purposes of calculation the standard 6.15 may be employed.

If both margarine and coconut oil are present, the table in the original article will give valuable information. L. DE K.

**The Constants of Bog-Butter found in the Peat in Ireland.** LIONEL G. RADCLIFFE and W. H. MADDOCKS (*J. Soc. Chem. Ind.*, 1907, 26, 3).—The specimen to which the following figures refer was found about 4 ft. below the surface and was probably some hundreds of years old. It was a crumbly, cheese-like substance, and numerous cows' hairs were interspersed throughout the mass, leading to the conclusion that the substance was originally butter which had been placed in the peat water to preserve it. The figures obtained were: m. p. 46.5—49.5°; total fatty matter, 98%;  $D_{15}^{100}$  0.8390; butyrometer number, 23.5 at 50°; acid number, 201.9; saponification number, 324.1; acetyl number, 2.2; Reichert-Meissl number, 1.2; insoluble fatty acids, 98.5%; iodine number (Wijs), 10.0. The non-fatty matter contained nitrogen, and was most probably casein. W. P. S.

**Estimation of Formaldehyde in Milk.** FREDERIC W. RICHARDSON (*J. Soc. Chem. Ind.*, 1907, 26, 3—4).—The method is based on the formation of a violet colour when sulphuric acid is added to milk containing formaldehyde, a qualitative test devised originally by Hehner. Four c.c. of concentrated sulphuric acid containing 0.05% of ferric sulphate are added, drop by drop with constant stirring, to 5 c.c. of the milk. The mixture is then diluted to a volume of 50 c.c. by the addition of 50% sulphuric acid, when a solution is obtained which is sufficiently clear to be examined in a colorimeter. W. P. S.

**Estimation of Preservatives in Milk.** HERBERT S. SHREWSBURY (*Analyst*, 1907, 32, 5—13).—*Formaldehyde*.—The method proposed is based on that described previously by Liverseege (*Abstr.*, 1901, ii, 483). Ten c.c. of the milk and 7 c.c. of dilute ferric chloride-sulphuric acid are mixed in a stoppered tube and left for about fifteen hours. The dilute acid is prepared by mixing 3.5 c.c. of 5.4% ferric chloride, 40 c.c. of water, and 100 c.c. of concentrated sulphuric acid. The coloration produced is compared with that obtained in comparison tubes containing known quantities of formaldehyde, these standards being also left overnight.

*Boric acid*.—Seventy c.c. of the milk, after the addition of 7 c.c. of 12% sodium hydroxide solution, are evaporated to dryness, and the residue is ignited to a white ash. The latter is dissolved in hot water and a few drops of hydrochloric acid, and the solution is transferred to a 100 c.c. flask. Phenolphthalein is now added, and then alternately sodium hydroxide solution and 5.6% calcium chloride solution until a slight excess of both is present. The whole is made up to a volume of 100 c.c. and filtered. The filtrate is acidified with hydrochloric acid, using methyl-orange as indicator, boiled, neutralised with sodium hydroxide, glycerol is added, and the solution titrated with *N*/10 sodium hydroxide, using phenolphthalein as indicator. If the filtrate requires more than 1.5 c.c. of *N*/10 sodium hydroxide, the phosphate precipitate

is redissolved in hydrochloric acid, the solution is diluted, rendered just alkaline with sodium hydroxide, filtered, and the boric acid in the filtrate titrated as described above. This process is repeated until the filtrate requires less than 1.5 c.c. of *N*/10 sodium hydroxide. The number of c.c. of *N*/10 sodium hydroxide required to neutralise all the filtrates, when multiplied by the factor 0.0062, expresses the quantity of boric acid in grams.

W. P. S.

**Estimation of Methylfurfuraldehyde.** KONRAD FROMHERZ (*Zeit. physiol. Chem.*, 1906, 50, 241—249. Compare Jäger and Unger, *Abstr.*, 1903, ii, 187, 456).—Methylfurfuraldehyde yields a precipitate,  $C_{10}H_8O_4N_2$ , with barbituric acid, in the form of minute, yellow needles and plates, which dissolve sparingly in water, cold alcohol, ether, or acetone, but readily in dilute alkalis yielding colourless solutions. It decomposes at about 260°. Its solubility in 100 c.c. of 12% hydrochloric acid is 2.29 mg. The amount of methylfurfuraldehyde (*M*) in a solution may be calculated from the formula  $M = \frac{1}{2}(B + n \times 0.000023)$ , where *B* = the weight of precipitated methylfurfuraldehydebarturic acid, and *n* = the total number of c.c. of solution. A mixture of furfuraldehyde and its methyl derivative may be estimated by means of barbituric acid.

For the separation of the two aldehydes by Ellett and Tollens' method (*Abstr.*, 1905, ii, 210) it is advisable to filter fourteen to sixteen hours after precipitating. After twenty-four hours the methylfurfuraldehyde-glucoside can no longer be completely removed by alcohol.

J. J. S.

**Some Methods of Estimating Nitriles and Carbylamines.** H. GUILLEMARD (*Compt. rend.*, 1906, 143, 1158—1160).—Metallic cyanides react with alkyl iodides to form a mixture of the corresponding alkyl nitrile and carbylamine (*isocyanide*), and in the present paper various methods of estimating each isomeride are described. The carbylamines (*isocyanides*) are readily decomposed in the cold by the action of bromine water or alkali hypobromites with the formation of one equivalent of carbon dioxide; further, the carbylamines decompose aqueous solutions of oxalic acid in the cold with the formation of equal volumes of carbon dioxide and carbon monoxide, and either of these reactions can be employed for the estimation of carbylamines in the presence of the isomeric nitrile, as neither bromine water nor oxalic acid have any action on the alkyl nitriles. In practice the author employs the following method, whereby the nitrile and the carbylamine resulting from the action between an alkyl iodide and a metallic cyanide in a sealed tube are each estimated. The contents of the tube are distilled in the presence of a concentrated solution of potassium cyanide made alkaline with potassium carbonate, the distillate, which contains ammonia and a little hydrocyanic acid in addition to the nitrile and carbylamine, is again distilled in the presence of potassium carbonate, which removes the hydrocyanic acid; the second distillate is treated with a known volume of standard sulphuric acid, whereby the ammonia is neutralised and the carbylamine decomposed into the corresponding formamide; the ammonia is

determined by estimating volumetrically the excess of sulphuric acid; the nitrile is separated from the mixture by distillation, hydrolysed by heating in a sealed tube at 150° for three hours with 50% sulphuric acid and the resulting ammonium salt estimated in the usual way; and the formamide in the residual liquid is similarly estimated after hydrolysis by boiling with concentrated sulphuric acid.

M. A. W.

**Folin's Method for the Estimating of Urea.** E. PROVAN CATHCART (*Proc. physiol. Soc.*, 1906, viii—ix; *J. Physiol.*, 35).—Folin's method gives accurate results, and is expeditious. Uric acid- and hippuric acid-nitrogen are not affected. Allantoin appears to be the only substance in urine likely to give rise to an error, but, as it only occurs in traces, the error is negligible.

W. D. H.

**Estimation of Urea in Urine.** A. CHRUSTALEFF (*Chem. Centr.*, 1906, ii, 1361—1362; from *Bull. Akad. St. Petersburg*, [v], 22, 121—123).—The Folin-Mörner process is recommended as it is not influenced by the presence of other nitrogenous substances.

L. DE K.

**Estimation of Guanidine Carbonate and its Application in Analysis.** HERMANN GROSSMANN and BERNHARD SCHÜCK (*Chem. Zeit.*, 1906, 30, 1205—1206).—Guanidine carbonate, now easily procurable, is a strong, alkaline carbonate which can be titrated with standard acid. Solutions of copper, nickel, and cobalt are precipitated in the cold, but on heating they are slightly redissolved. Aluminium solutions give a precipitate soluble in large excess of the reagent; the alumina is reprecipitated on adding ammonium chloride, but not by ammonia. In the absence of ammonium salts, guanidine carbonate makes a convenient reagent for the quantitative precipitation of cadmium, zinc, and manganese, less so for magnesium. The precipitates are readily washed and collected. Aluminium sulphate and guanidine sulphate form a double salt which, however, is not identical with an ammonia alum.

L. DE K.

**Reactions of Boric Acid with Opium Alkaloids.** C. REICHARD (*Chem. Centr.*, 1906, ii, 1290—1291; from *Pharm. Zeit.*, 51, 817—818).—A mixture of boric acid and narceine moistened with water and evaporated to dryness turns yellow; on adding hydrochloric acid and again evaporating, the mass turns brown. Papaverine behaves like narceine, but narcotine, although at first giving the yellow colour, turns a dark grey. Thebaine gives a green colour, gradually changing to grey or black. Codeine gives a green colour, changing to a dirty brown; morphine behaves very similarly.

L. DE K.

**Microscopic Reactions of Pyramidone.** F. WEEHUIZEN (*Chem. Centr.*, 1906, ii, 1628—1629; from *Pharm. Weekblad*, 43, 1105—1106).—When a solution of iodine in potassium iodide is added to a 1% solution of pyramidone, which has been cautiously acidified with dilute sulphuric acid, a reddish-brown precipitate is formed, the colour

of which changes after a time, or on agitation to dirty yellow. The precipitate appears under the microscope to consist of yellow prisms and more slender needles. When a dilute solution of bromine in potassium bromide is added drop by drop to a solution of a small quantity of pyrimidone in a few drops of dilute sulphuric acid, a green coloration is formed which changes successively to violet, red, and yellow. After shaking the solution and allowing it to remain for some time, it becomes colourless, and a white precipitate is formed which consists of irregularly arranged needles which are longer and more slender than those of the iodine-potassium iodide precipitate. A solution of 1 part of pyrimidone in 400 of water, which has been made acid with dilute sulphuric acid, gives a white precipitate with Mayer's reagent; the precipitate, after remaining for some time, appears to consist of triangular crystals. A white precipitate is also formed by adding potassium cadmium iodide to a 1% solution of pyrimidone; it is made up of rosette-like aggregates of crystals and of 4- and 6-sided plates. The white precipitate formed by mercuric chloride consists of feathery needles. A solution of sodium-palladium chloride forms a yellow precipitate which consists of needles arranged in some cases in X- or Y-shaped clusters.

E. W. W.

**Colour Reactions of some Organic Compounds.** EUGENIO PIÑERUA ALVAREZ (*Ann. Chim. anal.*, 1907, 12, 9—10).—0.05—0.1 gram of the substance and 0.2—0.3 gram of sodium peroxide are put into a porcelain capsule with 5 c.c. of alcohol, and after four to six minutes 15 c.c. of water are added. The following colorations are produced. *Emodin* gives an intense rose colour, turning yellow on addition of a few drops of acetic acid. *Chrysarobin*, a wine-lees colour, not destroyed by dilution with water, but turning yellow on addition of acetic acid. 1:2-*Dihydroxyanthraquinone*, a very beautiful bluish-violet colour, not destroyed by addition of water; with acids, the liquid turns intensely yellow. *Alizarin* from madder turns very strongly violet, and becomes orange on adding acids. 1:2:4-*Trihydroxyanthraquinone* gives an intense reddish-violet colour turning cherry-red on adding water. *Chrysophanic acid* gives a cherry-red colour which becomes brighter on dilution. *Rosolic acid*, an intense purple colour not destroyed by water. *Purpurin*, a beautiful intense rose colour not destroyed by dilution. *Anthragallol*, a persistent, dark blue, nearly black. *Dihydroxybenzoquinone*, a maroon-yellow, turning red on dilution with water. *Ellagic acid* gives a maroon-black, turning yellow on dilution.

L. DE K.

**Detection of Indican in Urine.** FRANCISCO P. LAVALLE (*Chem. Zeit.*, 1906, 30, 1251).—To 10 c.c. of urine are added 2—3 c.c. of hydrochloric acid containing 5 grams of ferric chloride per litre, and, while cooling, 2—3 c.c. of pure sulphuric acid are added drop by drop. The solution is then shaken with a little chloroform, and the blue colour due to sulphindigotic acid is noticed. This reaction is much more delicate than those of Obermayer, Heller, and others.

L. DE K.

**Adsorption Analysis and Chromatographic Methods. Employment for Chlorophyll.** M. TSVET (Chem. Centr., 1906, ii, 1286; from *Ber. deut. bot. Ges.*, 24, 384—393).—Many dyes dissolved in light petroleum, benzene, xylene, carbon tetrachloride, or carbon disulphide are precipitated by powdered substances, from which they may be extracted by alcohol, ether, acetone, or chloroform. There is further an adsorption series in which the substances can replace each other in the adsorption compound. When a mixed solution, as, for instance, chlorophyll dissolved in carbon disulphide, is filtered through a column of precipitated calcium carbonate, the dyes are precipitated, but mutually replace each other and arrange themselves according to the adsorption series in the direction of the stream. If any zone is not pure, it can be extracted and the adsorption repeated until the desired degree of purity is attained. N. H. J. M.

**Preliminary Testing of Urine.** C. J. REICHARDT (Chem. Centr., 1906, ii, 1290; from *Pharm. Zeit.*, 51, 518—519).—After testing for albumin in the usual way by boiling with a few drops of nitric acid, 3 c.c. of pure sulphuric acid and 3 c.c. of saturated ferrous sulphate solution are put into a test tube, and after mixing 6 c.c. of urine are gently poured over it. If dark-coloured rings are formed, the urine contains albumoses, peptones, biliary colouring matters, &c.

L. DE K.

**Tabloid Test for Enzymes for the Rapid Control of Pasteurised Milk.** BRUÈRE (*J. Pharm. Chim.*, 1906, [vi], 24, 488—493).—The reagent consists of tabloids of (a) a mixture of crystallised guaiacol and lactose, and (b) sodium perborate, which are added to the sample of milk under examination. It has an alkaline reaction in solution, and gives with fresh milk a salmon coloration, which immediately changes to garnet red, whereas milk which has been pasteurised above 80°, or boiled, gives no coloration whatever. The coloration is due to the oxydase of the milk, which in the case of cow's milk is at a maximum activity between 40° and 50°, is stopped by cold, and is normal at about 15°. Old milk, after keeping some days, loses its power of giving a coloration, probably owing to the development of lactic acid, as the addition of sodium hydrogen carbonate generally restores the activity of the enzyme. Milk containing vegetable ferments gives an orange or brown coloration, whilst milk preserved by the addition of peroxide yields the red coloration on the addition of the guaiacol and lactose tabloids only. E. F. A.

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## General and Physical Chemistry.

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**Refractive Indices of Gases at the Temperature of the Room and of Liquid Air.** KARL SCHEEL (*Ber. deut. phys. Ges.*, 1907, 5, 24—36).—The refractive index of hydrogen, nitrogen, and air has been measured for a series of wave-lengths by the interference method at 16° and at the temperature of liquid air. The data obtained at 16° are reduced to 0° by means of the formula  $n - 1/d = \text{const.}$  The variation of  $(n - 1)10^7$  with the wave-length  $\lambda$  (expressed in terms of  $\mu$ ) is given by the formulæ: hydrogen,  $1358.3 + 9.05/\lambda^2$ ; nitrogen,  $2906.1 + 22.47/\lambda^2$ ; air,  $2870.5 + 16.23/\lambda^2$ . In order to test the constancy of the expression  $n - 1/d$  over the temperature interval 0° to -190° it is employed to calculate the density of hydrogen and nitrogen at -190°, using the experimentally determined values of the refractive index at 0° and -190°. The calculated values differ from the experimental numbers by 0.4%. Whether this is due to the inconstancy of  $n - 1/d$  or to experimental errors is not known. In any case the formula can be employed to calculate the densities of gases at low temperatures with considerable accuracy.

H. M. D.

**Refraction in Compound Gases.** JULES AMAR (*Compt. rend.*, 1907, 144, 260—261).—Understanding by the refraction  $R$ , the index  $N$  diminished by unity and defining *atomic refraction* as the quotient of the refraction of a simpler substance by its atomicity, the author formulates the rule: *The refraction of a compound gas is the sum of the refractions of the atoms which compose the molecule.* He shows that allowing for the observed refractions having been taken with different rays, for possible polymerisation of the gas and for discrepancies in the refractions observed for the same gas by different authors, the calculated values for hydrogen chloride, nitric oxide, ammonia, and water vapour agree fairly well with those observed.

The same rule gives fairly good results when used to calculate the refraction of one component of a compound gas from the refractions of the gas and of the other component. The value so obtained for carbon in carbon dioxide, when applied to the calculation of the refraction of methane, gives a result agreeing moderately well with that observed. Sulphur vapour gives a value four times as great as that calculated from the refraction of sulphur dioxide, thus indicating that under those conditions sulphur is tetratomic.

E. H.

**Valency, Molecular Refractions, and Volumes.** **Refraction Steres.** I. ISIDOR TRAUBE (*Ber.*, 1907, 40, 130—139).—It is pointed out that when Brühl's values for the molecular refractions (for the  $\alpha$  hydrogen line) of several homologous series of saturated carbon compound are divided by the total number of valencies present in the



molecule, a constant (0.78—0.80 mean 0.787) is obtained which is termed the *refraction stere*. Abnormal values are obtained for compounds which readily associate, for example, methyl alcohol, acetaldehyde, acetone, formic and acetic acids, ethyl formate, methyl acetate, formamide, and various nitro-derivatives.

Compounds with an equal number of valencies, for example, propyl alcohol and propionic acid, ethyl ether and ethyl acetate, *n*-pentane and isovaleraldehyde, have the same molecular refraction.

The method can be used for determining the valency of a particular element in certain of its compounds. Thus oxygen appears to be bivalent and not quadrivalent.

The relationship between atomic volumes, valencies, and the electron theory of matter is discussed.

The values obtained for  $Ma/0.787$  in the case of certain elements and their simple derivative, for example, hydrogen, oxygen, nitrogen, water, hydrogen peroxide, hydrazine, ammonia, &c., are, in all cases except that of nitrogen, higher than the number of valencies present.

The expression valon is introduced to represent the electron or group of electrons present at each valency point.

The conclusion is drawn that in organic compounds composed of carbon, hydrogen, oxygen, nitrogen, &c., the valon volumes are practically proportional to the inner volumes of the atoms, and the atomic and valonic volumes of the different elements are practically multiples in the ratio of the valencies of the atoms. J. J. S.

**Temperature Radiation of Iodine Vapour.** CARL FREDENHAGEN (*Physikal. Zeitsch.*, 1907, 8, 89—91).—A quartz tube containing iodine was heated at about 1250° in an electrical furnace. One end of the tube projected from the furnace into an iron box which was heated by means of a Bunsen burner. By varying the temperature of the projecting portion of the tube the pressure of the iodine vapour could be conveniently increased or decreased. Under these conditions the temperature of the radiating iodine vapour was quite uniform, and in all cases a completely continuous emission spectrum was observed. The banded emission spectra obtained by previous observers are attributable to temperature differences in the radiating vapour. This conclusion is confirmed by the author's own experiments, in which iodine vapour contained in a quartz tube heated by means of a Bunsen burner was examined. The difference between the two emission spectra obtained under these different conditions is supposed to be due to the displacement of the equilibrium in the dissociating iodine vapour when its temperature is not uniform, and the general conclusion is drawn that a system in equilibrium can only give rise to a continuous emission spectrum. H. M. D.

**Temperature of the Incandescent Carbon Particles of Luminous Flames.** RUDOLF LADENBURG (*Chem. Centr.*, 1906, ii, 1707—1708; from *Physikal. Zeitsch.*, 7, 697—700).—In order to determine the temperature of the incandescent particles of a flame by means of the emission curve, the relationship of the absorption of the

particles to wave-length must be known. Experiments made with a Hefner lamp and an acetylene flame burning in a steatite double burner have shown that both flames have strong selective absorption, and that the temperature of the carbon particles is  $1405^{\circ}$  and  $1842^{\circ}$  respectively. The temperature of the flames determined by means of the optical pyrometer and corrected for absorption are  $1421^{\circ}$  and  $1820^{\circ}$  respectively. When the correction for reflection is applied, the value of the temperatures is raised by  $10^{\circ}$  to  $20^{\circ}$ . E. W. W.

**Absorption Spectra of Certain Salts in Aqueous Solution as Affected by the Presence of Certain other Salts with Large Dehydrating Power.** HARRY C. JONES and HORACE S. UHLER (*Amer. Chem. J.*, 1907, 37, 126—195).—The absorption spectra of solutions of cobalt chloride, copper chloride, and copper bromide, and of solutions containing these substances mixed in various proportions with calcium chloride, calcium bromide, or aluminium chloride have been recorded by means of a direct reading spectroscope. Photographic records of the absorption bands and the changes in the position of these bands, when varying amounts of one or another dehydrating agents are added to the coloured solutions, have also been obtained. These changes are illustrated by a number of photographic plates. For a description of the apparatus employed, and the detailed results obtained, the original must be consulted. The general conclusions to be drawn from the study of the absorption spectra will appear in a later paper.

H. M. D.

**Absorption and Fluorescence in Band Spectra and the Ultra-violet Fluorescence of Benzene.** JOHANNES STARK (*Physikal. Zeitsch.*, 1907, 8, 81—85).—From the known facts relative to fluorescence phenomena and spectral absorption bands, the author concludes that fluorescence is always determined by absorption in a band spectrum. The absorption spectrum of all fluorescing substances is a banded spectrum. The generalisation has been tested and confirmed by experiments on benzene which shows seven absorption bands in the ultra-violet region between 271 and 233  $\mu\mu$ . The source of light employed was a mercury lamp of quartz glass, the benzene being contained in a quartz tube, and a spectroscope with quartz lenses was used in the examination of the fluorescence spectra. The absorption bands and the fluorescence bands both decrease in intensity as the wave-length increases. When carbon in the benzene ring is replaced by oxygen, sulphur, or nitrogen, analogous changes are produced in the intensity and position of the bands of the absorption and of the fluorescence spectrum. The question of the connexion between fluorescence and chemical constitution thus appears to be the same as that between absorption and constitution.

H. M. D.

**Variations of the Absorption Bands of Crystals of Tysonite in a Magnetic Field.** JEAN BECQUEREL (*Compt. rend.*, 1907, 144, 132—134. Compare *Abstr.*, 1906, ii, 317).—The absorption spectrum of tysonite, like that of xenotime, is modified by means of a magnetic field. When the crystal has its optic axis parallel

with the magnetic field and the luminous rays are in the same direction, excitation of the magnetic field causes the displacement of some of the bands of the absorption spectrum to an extent independent of the width of the band. The displacement is in opposite sense in the two spectra corresponding with rays circularly polarised in opposite directions, and although smaller than with xenotime is of the same magnitude as the Zeeman effect, and is clearly visible. The explanation suggested previously that certain bands correspond with positively electrified particles and others with electrons is maintained. When the luminous rays are normal to the magnetic field, the extent of the displacements is not independent of, but is lessened by, an increase in, the width of the band. Emphasis is laid on the fact that the second crystalline substance which has been found to give this displacement, like the first, is an exception to the general law for gases and vapours in which all the rays correspond with negative electrons. E. H.

**Designation of Optical Antipodes as *d*- and *l*-Compounds.** EMIL FISCHER (*Ber.*, 1907, 40, 102—106).—An adverse criticism of a paper by Rosanoff (*J. Amer. Chem. Soc.*, 1906, 28, 114).

In those cases where the prefixes *d*- and *l*- refer to compounds which are not dextrorotatory and lævorotatory respectively, but are related in configuration to compounds which are dextrorotatory and lævorotatory, the author proposes the nomenclature *d'*- and *l'*-. Thus lævulose is designated as *d'*-fructose and the naturally occurring dextrorotatory xylose as *l'*-xylose. A. McK.

**Increase and Reversal of Rotation. II. Salts of the Type of Potassium Antimonyl Tartrate.** HERMANN GROSSMAN (*Zeitsch. physikal. Chem.*, 1907, 57, 533—556. Compare Abstr., 1906, i, 799).—Of the corresponding antimonyl, boryl, and arsenyl tartrates the first is the most stable and the last is the least stable. When sodium hydroxide is added to potassium antimonyl tartrate, the specific rotation assumes a large negative value, probably owing to the formation of complexes in which the hydrogen also of the hydroxyl groups is replaced by sodium. The addition of sodium hydroxide to potassium boryl tartrate leads to a marked reduction of the positive rotation, without actually causing reversal of the sign, so that lævorotatory complexes are probably present to a limited extent, especially in concentrated solution. The addition of sodium hydroxide to sodium arsenyl tartrate seems to cause complete resolution into neutral tartrate and optically inactive sodium arsenite. It is noteworthy that sodium and ammonium arsenyl tartrates, examined alone, are both found to exhibit the phenomenon of mutarotation.

The free complex acids,  $\text{Sb}(\text{C}_4\text{H}_5\text{O}_6)_{3/2}\text{H}(\text{AsO})\text{C}_4\text{H}_4\text{O}_6$  and  $\text{H}(\text{BO})\text{C}_4\text{H}_4\text{O}_6$ ,

are markedly hydrolysed on progressive dilution; under these conditions the rotation of the antimony compound increases, that of the arsenyl and boryl compounds falls. The relative stability of these compounds in presence of acids and alkalis is similar to that of the salts. Addition of sodium hydroxide causes reversal of the sign of rotation in the case of the antimony compound only.

The tendency of malic acid to form complexes with antimonious, arsenious, and boric acids is notably weaker than that of tartaric acid. All the complexes formed with malic acid are readily resolved by acids and alkalis. Reversal of rotation occurs in the case of the antimony complex only, and it may be induced by the addition of sodium hydroxide or hydrochloric acid. Aluminium salts are found to have a considerable effect in increasing the laevorotation of malic acid.

J. C. P.

**Some Points of Chemical Philosophy Involved in the Discovery of Radium and the Properties of its Combinations.** HENRY WILDE (*Mem. Manchester Phil. Soc.*, 1907, 51, (1), No. 2, 1—14).—From the constant differences in the atomic weights of the elements in the first and second groups in which mercury and lead are respectively incorporated as the elements of highest atomic weight, and from the regular alternation of light and heavy metals in the two series so obtained, the author concludes that the atomic weight of radium is 184 and its specific gravity about 5.

The radioactive properties of radium are supposed to be dependent on its combination with electronegative elements, and would not be exhibited by metallic radium. Just as calcium, strontium, barium, and zinc in the metallic condition do not exhibit the phosphorescence of their sulphur compounds, so radium plays a similar subordinate part in respect of its radioactivity when combined with electronegative elements. The author does not agree with the view that higher members of different series of elements undergo transformation into each other directly, and doubts whether the distinction made between elementary substances and compounds has a real foundation in nature.

H. M. D.

**Decay of Radium A, B, and C.** PAUL GRUNER (*Ann. Physik.*, 1907, [iv], 22, 399—400).—Polemical. A reply to H. W. Schmidt (this vol., ii, 4).

H. M. D.

**Theory of the Radioactive Disintegration of Matter.** PAUL GRUNER (*Arch. Sci. phys. nat.*, 1907, [iv], 23, 5—25. Compare Abstr., 1905, ii, 367, 368, 666, 792; 1906, ii, 139, 259, 322, 413, 415, 416, 514, 527, 593, 719, 721).—A *résumé* of current theory on the subject.

E. H.

**Composition of Thorianite and the Relative Radioactivity of its Constituents.** ERNST H. BÜCHNER (*Jahrb. Radioakt. Elek.*, 1907, 3, 372—380).—The author has supplemented previous analyses of thorianite by a minute examination of the various group precipitates, and has also determined the distribution of the radioactivity of the mineral amongst its various constituents. A table is given containing the percentage amounts of these constituents, the radioactivity of each, and the fraction of the total activity of the mineral contributed by each constituent. The activity of thorianite is 83.3 when the value for standard uranium oxide is equal to 100. Nearly the whole of the activity is due to the constituents of the mineral

which dissolve in boiling concentrated nitric acid. Whilst the mass ratio of the soluble and insoluble portions is 40 : 1, that of the radioactivity is about 300 : 1. In the case of those constituents which are met with in the soluble and insoluble portions of the mineral, the activity of the soluble fraction is much greater than that of the insoluble fraction. All the separate fractions obtained in the analysis were found to be radioactive with the exception of alumina. This seems to indicate that the active constituent of the iron group is insoluble in excess of alkali hydroxide. One gram of thorianite yields 8.2 c.c. of helium at 0° and 760 mm. H. M. D.

**Radioactive Properties of Uranium.** MAX LEVIN (*Chem. Centr.*, 1906, ii, 1757—1758; from *Physikal. Zeitsch.*, 7, 692—696).—Attempts to obtain a second radioactive product from uranium have failed, but since the experiments were only continued for six months, very slow changes may possibly have escaped observation. Precipitates of silver sulphide, silver chloride, copper sulphide, bismuth sulphide, and lead sulphide did not carry down any active substances from solutions of uranium salts, and precipitation by aniline, toluidine, hydroxides, carbonates, and phosphates failed to extract any new substance. Electrolysis with varicus electrodes and under different electromotive forces also gave negative results, but the radium may be concentrated, however, from solutions of uranium salts by this method. When uranium oxide is placed in a cavity of the anode carbon of an arc, the uranium which is deposited on the cathode shows a constant  $\alpha$ -ray activity and an increasing  $\beta$ -activity, hence it is evident that a state of equilibrium has not been attained; the activity of the residual uranium oxide remains unchanged. Uranium  $X$  may be separated by boiling with soot, and 90% of this substance is also precipitated by animal charcoal; the metal left after calcination is almost pure uranium  $X$ . Radium is not precipitated by boiling with animal charcoal.

Fractional crystallisation also failed to yield a new product, but the activity of the last crystals was found to be abnormal.

E. W. W.

**Radioactivity of the Wiesbaden Thermal Springs.** FERDINAND HENRICH (*Zeitsch. angew. Chem.*, 1907, 20, 49—51. Compare *Abstr.*, 1905, ii, 6, 221).—The gas obtained from the Koch and Schützenhof springs contains radium emanation and helium. Comparative measurements have been made of the radioactivity of a number of different natural waters. P. H.

**Secondary Rays Produced by Very Feeble Röntgen Rays.** WILHELM SEITZ (*Chem. Centr.*, 1906, ii, 1708; from *Physikal. Zeitsch.*, 7, 689—692).—Very feeble Röntgen rays produce secondary rays which have, however, a very slight action on a photographic plate, and are strongly absorbed. The power of penetration of these rays lies between that of the original Röntgen rays, on the one hand, and that of the cathode rays produced by the Röntgen rays, on the other. The secondary rays are but slightly decreased by charging the reflector,

and are not affected by a magnetic field. In addition to the extraordinarily feeble Röntgen rays which constitute the major portion, the secondary rays also contain electrons. The ratio of the energy of the cathode rays to that of the secondary rays has been determined by means of calorimetric and electric measurements and found to increase with the tension.

E. W. W.

**Spectral-analytical Observations on Canal Rays in Compound Gases.** S. KINOSHITA (*Physikal. Zeitsch.*, 1907, 8, 35—38).—The canal rays were produced in cylinders of from 4 to 6 cm. diameter with aluminium electrodes about 16 cm. apart, with a voltage of from 1600 to 3000 volts. It was found that the canal rays cause dissociation of compound gases, those examined being acetylene, nitrous oxide, carbon dioxide, and coal gas. The rays cause the emission of the line or band spectra of the constituent elements, whilst also band spectra of compounds were observed simultaneously. The line spectra exhibit the Doppler effect. The author considers that the canal ray particles are positive ions, and on the assumption that the carbon line 4267.5 is produced by a positive univalent carbon ion, the velocity  $3.06 \times 10^7$  cm./sec. at 7000 volts is deduced. The band spectra exhibit no Doppler effect, and it is, hence, probable that the molecules cannot attain the high velocity of the canal-ray particle without decomposing.

L. M. J.

**Measurement of Inaccessible Potentials by Means of Intermediary Potentials.** L. LOIMARANTA (*Zeitsch. Elektrochem.*, 13, 33—34).—A platinum electrode immersed in a solution containing arsenious and arsenic acids has no definite potential, but in presence of iodine and iodine ions a definite value is quickly attained. The method has already been used by Maitland in the case of solutions of ferrous and ferric ions (*Abstr.*, 1906, ii, 328). The method also yields good results with mixtures of chromic acid and a chromic salt, and of a thio-sulphate and a tetrathionate. Solutions of sulphuric and sulphurous acids and of hydrogen sulphide containing free sulphur gave less definite results.

T. E.

**Intermediary Potentials.** RICHARD ABEGG (*Zeitsch. Elektrochem.*, 1907, 13, 34—35).—Loimaranta (preceding abstract) has observed that it is only necessary to have a considerable quantity of one of the intermediary substances in solution, since it acts as a reservoir from which the other may be produced if necessary. In principle it is possible to use any change occurring at an electrode as an intermediary. For a change such as copper  $\rightarrow$  copper ions, however, the potential to be measured must be near that of copper in a normal solution of its ions, otherwise the copper would dissolve completely or the ions would be almost completely precipitated from the solution. The two cases occur with strong oxidising agents, on the one hand, or strong reducing agents, on the other. In the second case, the electrode would be very easily polarised, especially by currents tending to precipitate the metal. The fact that platinum is not readily polarised even in strongly reducing solutions supports the view that it behaves as a hydrogen electrode.

T. E.

**Electrical Conductivity of Mixtures of Bromine and Ethyl Ether.** WLADIMIR A. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1906, **57**, 502—506).—Solutions of bromine in ethyl ether have a very low conductivity, but solutions of ether in bromine exhibit a conducting power which is not far short of that possessed by concentrated aqueous salt solutions. Ethyl ether and bromine form a crystalline compound, and the conductivity is probably due to the presence of such a compound in solution; the maximum value of the conductivity is found for a mixture containing 11.5% of ether, the composition of which corresponds approximately with the formula  $\text{OEt}_2 \cdot \text{Br}_7$ . Between the solutions of bromine in ether and those of ether in bromine there is a range of concentration over which mixtures of the two substances form two liquid phases. J. C. P.

**Transport Numbers of Potassium Hydroxide in Concentrated Solutions.** GUNNAR NORDSTRÖM (*Zeitsch. Elektrochem.*, 1907, **13**, 35—38).—Calling  $x$  the number of molecules of potassium hydroxide per molecule of water in the solution, the transport number of the potassium,  $(1-n)$ , is  $(1-n) = 0.232 - 0.11x$  at  $18^\circ$ . This formula holds good between  $x = 0.017$  and  $x = 0.14$ , that is between 5 and 30%.

The result is used to calculate the change in the *E.M.F.* of the Edison accumulator due to changes of concentration of the potassium hydroxide during charging and discharging. T. E.

**Migration of the Ions in the Electrolysis of a Fused Mixture of Two Salts.** RICHARD LORENZ and W. RUCKSTUHL (*Zeitsch. anorg. Chem.*, 1907, **52**, 41—47. Compare Abstr., 1904, ii, 699).—The experiments with a fused mixture of lead and potassium chlorides, described in the former paper, have been repeated with practically identical results. It is shown in addition that the tendency to the formation of complex anions containing lead increases with the proportion of potassium chloride present. G. S.

**Temperature of Solid Carbon Dioxide and its Mixtures with Ether and Alcohol at Different Pressures.** JOHN ZELENY and ANTHONY ZELENY (*Chem. Centr.*, 1906, ii, 1723; from *Physikal. Zeitsch.*, **7**, 716—719).—The measurements of the temperatures of the following cooling agents were made by means of a nickel-iron thermocouple, the boiling point of ethylene ( $-103.9^\circ$ ) and the temperature of a mixture of carbon dioxide and alcohol under ordinary pressure ( $-78.34^\circ$ ) being taken as fixed points. When the carbon dioxide gas is continuously removed from pure carbon dioxide snow, the temperature sinks considerably and may even show a decrease of  $15^\circ$ , but the addition of ether or alcohol renders the temperature independent of the removal of gas; alcohol is not, however, so effective as ether. Solid carbon dioxide and the mixtures mentioned have the same temperature at any given pressure. Under normal pressure a difference of 1 cm. pressure causes a difference of temperature of  $0.17^\circ$ , but at 2 cm. pressure the effect is twenty times as great. Measurements were made between pressures of 2 cm. ( $-116.7^\circ$ ) and 84 cm. ( $-77.00^\circ$ ). E. W. W.

**Relation between Development of Heat and Maximum Work in the Case of Condensed Systems.** WALTHER NERNST (*Sitzungsber. K. Akad. Wiss., Berlin*, 1906, 933—940. Compare Abstr., 1906, ii, 727; also van't Hoff, Abstr., 1904, ii, 381; Brönsted, Abstr., 1906, ii, 339, 834).—If the second law of thermodynamics is expressed in the form  $A - Q = T (dA/dT)$ , and the hypothesis is made that the curves representing the variation of  $A$  and  $Q$  with temperature are tangential to each other at the absolute zero, then the following formulæ may be deduced:  $Q = Q_0 + \beta T^2 + \gamma T^3$ ;  $A = Q_0 - \beta T^2 - \gamma/2 \cdot T^3$ . The applicability of these formulæ is tested in several cases with satisfactory results. J. C. P.

**Comparison between Chemical Phenomena Determined by a Heating resulting from purely Calorific Causes and those due to a Heating produced by Electrical Actions [Electricity].** MARCELLIN BERTHELOT. (*Compt. rend.*, 1907, 144, 53—55).—A consideration of the sources of error that may arise by considering as purely thermal in origin the changes that occur in gases, &c., raised to a high temperature by the passage of an electric current through a metallic wire, carbon rod, &c. M. A. W.

**Thermochemistry of Nitrogen.** J. C. THOMLINSON (*Chem. News*, 1907, 95, 50—51).—A theoretical paper in which the heats of formation of hydrogen peroxide, ozone, hydrogen cyanide acid, cyanogen, ammonia, nitrous oxide, nitric oxide, and nitrogen dioxide are discussed, the object being to see if it is possible to deduce thermochemical equivalents for nitrogen in various forms of combination. W. H. G.

**Thermochemistry of Neodymium.** CAMILLE MATIGNON (*Ann. Chim. Phys.*, 1907, [viii], 10, 104—118).—Many of the facts recorded in this paper have been given already (Abstr., 1905, ii, 505; 1906, ii, 675). The heat of solution of  $\text{Nd}_2\text{O}_3$  in dilute hydriodic acid is 106.1 Cal.; that of  $\text{NdI}_3$  in water is 48.9 Cal.; of  $\text{Nd}_2(\text{SO}_4)_3$ , 36.5 Cal.; of  $\text{Nd}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , 8.3 Cal., and that of  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , 5.7 Cal. The heats of formation of the oxides and principal salts of neodymium and of the alkali and alkaline earth metals are tabulated and compared in the original, and the conclusion is drawn that neodymium is intermediate in properties between magnesium and calcium. The data available show that the oxides of the alkali metals should be decomposed when heated with metallic neodymium and, on the contrary, the halogen salts of neodymium should be decomposed by the alkali metals (Abstr., 1901, ii, 602), whilst the haloid salts of magnesium should be decomposed by neodymium. It is possible that this similarity of neodymium to calcium and magnesium may be regarded as supporting Wyrouboff's view that the rare earth metals are bivalent, although the resemblance of lithium to the alkaline earth metals has never been regarded as indicating that lithium is bivalent. T. A. H.

**Van der Waals' Equation and the Liquid State.** PETRU BOGDAN (*Ann. Sci. Univ. Jassy*, 1907, 4, 151—161).—In a previous



paper (*Ann. Sci. Univ. Jassy*, 1906, 3, 35; compare also Abstr., 1906, ii, 274) it has been shown that the lowering of the vapour tension of a solvent, brought about by the solution of a substance in it, is due to association between the molecules of the solvent and those of the solute, and a proof of van't Hoff's formula from the standpoint of the kinetic theory was given. In the present paper this proof is given in a more extended and rigorous form, the only assumption made being that the vapour tension above a solution is less than that above the solvent, which is in accordance with experimentally-ascertained fact. The association hypothesis is introduced only to explain the lowering of the vapour pressure of solutions, osmotic pressure, and to interpret the influence of certain substances on the solubilities of others. The proof is independent of the view taken of the constitution of solutions and is equally applicable whether the liquid is polymerised or not.

T. A. H.

**Exact Calculation of Molecular Weights of Gases.** DANIEL BERTHELOT (*Compt. rend.*, 1907, 144, 76—79. Compare Abstr., 1898, ii, 502; 1899, ii, 207, 404).—In a memoir, "Sur les thermomètres à gaz," published in 1902 in *Travaux du Bureau International des Poids et Mesures* the author showed that the values of  $a$  and  $b$  of

van der Waals' equation are represented by  $a = \frac{1}{273 \cdot 1} \frac{27}{64} R^2 \frac{T_c^3}{p_c} = 0.00000020712 \frac{T_c^3}{p_c}$ ;  $b = \frac{9}{128} \frac{RT_c}{p_c} = 0.00025746 \frac{T_c}{p_c}$ , when the unit of

pressure is that of the atmosphere, the unit of volume that of a gram-molecule of a perfect gas at  $0^\circ$  and 1 atmos.; and that the molecular weight of a gas can be calculated indirectly from the relation  $M = 32(1 - A_0^1)d/(1 - A_0^1)$ , where  $A_0^1 = \epsilon/1 - \epsilon$  and  $\epsilon = (a - b)$  and  $A_0^1$  and  $A_0^1$  refer to the gas under consideration and oxygen respectively. The atomic weights of hydrogen, nitrogen, and carbon, and chlorine obtained by the direct (Abstr., 1898, ii, 502) and indirect methods of calculation are as follows:

	H.	N.			O.		Cl.
		From N <sub>2</sub> .	From NO.	From N <sub>2</sub> O.	From CO.	From CO <sub>2</sub> .	
Direct calculation ...	1.0077	14.007	13.997	13.9995	12.007	12.0025	35.479
Indirect     ,,     ...	1.0076	14.008	13.998	14.002	12.007	11.991	35.486

M. A. W.

**Calculation of the Compressibility of Gases at About Atmospheric Pressure by Means of the Critical Constants.** DANIEL BERTHELOT (*Compt. rend.*, 1907, 144, 194—197).—In order to obtain the "limiting densities" of gases (which give their exact molecular weights) from their normal densities, the latter must be multiplied by the factor  $(1 - A_0^1)$ , where  $A_0^1 = (a - b)/[1 - (a - b)]$ . By means of van der Waals' equation  $a = 0.000005656 \frac{T_c^3}{p_c}$ ,  $b = 0.0004578 \frac{T_c}{p_c}$ .

The author makes use of the values  $a_0 = a/T = 0.000000020712 \frac{T_c^3}{p_c}$ ,

$b = 0.00025746 T_c/p_c$ , and shows that the latter values agree better than the former with those obtained with the experimental number

$$A'_2 = \frac{a-b}{\{1-2(a-b)\}\{1-3(a-b)\}}$$

for  $H_2$ ,  $N_2$ ,  $CO$ ,  $O_2$ ,  $NO$ ,  $CO_2$ ,  $N_2O$ , and  $HCl$ .

The author adversely criticises the corrections applied by Guye to van der Waals' constants. E. H.

**Molecular Weights of Different Gases Calculated by the Method of Limiting Densities.** DANIEL BERTHELOT (*Compt. rend.*, 1907, 144, 269—272. Compare preceding abstracts).—The molecular weights of hydrogen, nitrogen, carbon monoxide and dioxide, nitrous oxide, hydrogen chloride, ammonia and sulphur dioxide are calculated according to the author's method of limiting densities described previously (Abstr., 1898, ii, 502) by help of the densities and compressibilities of the gases observed by different workers. The values obtained for hydrogen chloride and sulphur dioxide place the atomic weight of chlorine between 35.454 and 35.478, and that of sulphur between 32.050 and 32.064, thus agreeing well with the results obtained by chemical analyses. The greater part of the paper is directed to a mathematical discussion of the formulæ to be used in calculating the coefficients of deviation from Boyle's law. E. H.

**Surface Tension of Aqueous Solutions.** II. GÉZA ZEMPLÉN (*Ann. Physik.*, 1907, [iv], 22, 391—396. Compare Abstr., 1906, ii, 728).—The author's view that the temperature coefficient of molecular surface energy has the same value for aqueous solutions as it has for pure liquids is found to be supported by the surface tension numbers recently obtained by Grabowsky and Pann for thirteen aqueous salt solutions of various concentrations at 10° and 30°. When the electrolytic dissociation of the solute is taken into account in the calculation of the molecular weight of the solution, the mean value of the temperature coefficient is 2.09, with a maximum deviation of 0.48; if the dissociation is neglected, the values are 2.54 and 0.74 respectively. The results indicate that the degree of association of water remains unaltered when electrolytes are dissolved in it. H. M. D.

**Adsorption in Solutions.** HERBERT FREUNDLICH (*Zeitsch. physikal. Chem.*, 1906, 57, 385—470).—The author has studied the extent to which various substances dissolved in water and other solvents are adsorbed by charcoal. It is found that well-defined equilibria are reached very rapidly from either side. The adsorption isotherm for dilute solutions, formed from various solvents and various solutes, is given by the formula  $\lambda = v/m \cdot \log_e a/(a-x) = k(a/v)^{-1/n}$ , where  $v$  is the volume of the liquid,  $m$  is the amount of charcoal,  $a$  is the total quantity of dissolved substance,  $x$  is the quantity adsorbed,  $k$  and  $n$  are constants which depend on the temperature and the nature of the dissolved substance. For a given temperature, a given solute, and a given value of  $a/v$ ,  $\lambda$  is a constant, the value of which remains the same for different values of  $m$ . For a given temperature, the exponent  $1/n$  varies only between 0.5 and 0.8, in spite of variation of solvent,

solute, and adsorbing material (silk, cotton, and wool, as well as charcoal). The adsorption isotherm does not apply to aqueous solutions of strong electrolytes, or to solutions of substances which yield hydroxyl ions. In aqueous solution, inorganic salts and acids are but sparingly adsorbed by charcoal; the adsorption of fatty acids, aromatic sulphonic acids, and salts of organic acids generally is considerable, whilst the adsorption of aromatic acids other than sulphonic acids, of chlorine, bromine, and phenylthiocarbamide is very marked indeed. The adsorption in organic solvents is generally slight. When the organic acids are arranged in the order of the extent to which they are adsorbed by charcoal, the order is practically the same as when silk is taken as the adsorbing substance (see Appleyard and Walker, *Trans.*, 1896, **69**, 1334). The extent of adsorption is but little affected by alteration of temperature. Incidentally it was found that a number of reactions are accelerated in presence of charcoal, such as the oxidation of formic, citric, and mandelic acids, and of glycerol, the reaction between chlorine or bromine and water, and the esterification of organic acids in alcoholic solution; a decomposition of phenylthiocarbamide by charcoal was also detected. Hydroxyl ions have the effect of causing a suspension of the charcoal, which is cleared by the addition of electrolytes.

The general relation of adsorption phenomena to other properties of solutions is discussed at length, and the conclusion is reached that these phenomena can be referred back to alterations in the surface tension between solid and liquid, so that substances which lower the surface tension must be adsorbed and *vice versa*. In harmony with this view it is shown that negative adsorption is very rare, and very small when it does occur. Marked adsorption is to be observed only in solvents which have a high value for the surface tension between solid and liquid, and in such cases the extent to which solutes are adsorbed increases as their surface tension diminishes. One notable consequence involved in the adsorption isotherm, namely, the marked increase of the surface concentration while the concentration in the solution is still small, may be referred back to the fact that small quantities of a solute are relatively much more effective than large quantities in lowering the surface tension.

J. C. P.

**Endothermic and Exothermic Dissociation Processes.**  
JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1907, **57**, 633—639).—With any dissociation process, it would be possible at a given temperature to have heat either absorbed or developed by starting with proportions of the reacting substances on one side or the other of the equilibrium point. That is, without some rule as to the direction of the reaction which is considered, the change might be either endothermic or exothermic. If, however, a dissociation process is strictly defined as a process in which simple molecules are produced from more complex ones, then it may be shown that almost all dissociation processes are endothermic. Very few (for example,  $2\text{O}_3 \rightarrow 3\text{O}_2$ ) are exothermic, and these must all become endothermic finally at high temperatures, for, although the absorbed heat of dis-

sociation is negative at the ordinary temperature, it increases with rise of temperature and ultimately becomes positive. J. C. P.

**Substances which Possess more than one Stable Liquid State, and the Phenomena Observed in Anisotropic Liquids.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch., Amsterdam*, 1907, 9, 472—483. Compare this vol., ii, 78).—The substances dealt with are cholesteryl heptate, nonoate, laurate, myristate, palmitate, and stearate, which were prepared by melting together equal parts by weight of cholesterol and fatty acid and then purifying by fractional crystallisation from mixtures of ether and alcohol or ether and ethyl acetate. The heptate and laurate crystallise in long, hard needles; the other esters were obtained as flexible, tabular crystals. Most of these esters have three stable liquid phases, but in the case of the stearate, only labile anisotropic liquid phases may occur. The laurate is interesting, in that it can be heated a few degrees above its melting point without melting, and it is considered probable that in all these peculiar substances phenomena of retardation play a great rôle. The visible changes that accompany alteration of temperature and the appearance of the substances under the microscope are recorded in detail, and the observations show that the spherulite structure of the solid phase is of great importance in the transformation of a supercooled anisotropic liquid into the solid phase. This is further borne out by some observations made with phytosteryl acetate and propionate. J. C. P.

**Irreversible Phase-transitions in Substances which may Exhibit more than One Liquid Condition.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch., Amsterdam*, 1907, 9, 483—492. Compare this vol., ii, 78, and preceding abstract).—There are probably no known substances which exhibit under the microscope the phenomena characteristic of anisotropic liquids so well as  $\alpha$ -phytosteryl butyrate, isobutyrate, valerate, and isovalerate, the second and third of these substances being specially suitable for the purpose. Retardation phenomena are very marked in the various transitions, and the behaviour, particularly of the two valerates, can only be described as a gradual transformation solid  $\rightleftharpoons$  liquid, in which there is intermediate realisation of an indefinite number of anisotropic liquids.

It is pointed out that supercooled ferric chloride hexahydrate, like many of the substances which yield fluid crystals, crystallises in spherulites, the formation of these being preceded by the differentiation of the supercooled liquid into an aggregate of liquid globules.

J. C. P.

**Kinetics of the Formation of Ethers by the Action of Absolute Alcohol on Alkyl Sulphates.** ROBERT KREMANN (*Monatsh.*, 1906, 27, 1265—1273).—The formation of sulphuric acid and ethyl ether by the action of absolute alcohol on ethyl sulphate takes place in two stages, ethyl hydrogen sulphate being formed as the intermediate product. In such reactions, the velocity constants of the two stages usually differ markedly; in this case, at 57° the velocity of the second stage is only 1/10,000 that of the first. The velocity of the

first stage can be measured therefore by determining the increase in the acid titre, which is proportional to the ethyl hydrogen sulphate formed. In the presence of an excess of alcohol, the reaction is unimolecular, and the velocity constant  $k$ , calculated by means of the equation  $k = 1/t \cdot \log a/a - x$ , remains constant during the whole stage. The reaction has been studied with methyl and ethyl sulphates, and methyl, ethyl, and propyl alcohols. At  $55^\circ$ , the reaction of methyl sulphate with methyl alcohol has  $k = 10.9 \times 10^{-3}$ ; the reaction with ethyl alcohol has  $k = 7.7 \times 10^{-3}$ , and with propyl alcohol,  $k = 6.0 \times 10^{-3}$ . At the same temperature, the reaction of ethyl sulphate with methyl alcohol has  $k = 3.5 \times 10^{-3}$ ; with ethyl alcohol,  $k = 2.15 \times 10^{-3}$ , and with propyl alcohol,  $k = 1.9 \times 10^{-3}$ . As was to be expected, the velocity constant diminishes with increasing molecular weights of the reacting substances.

In experiments at other temperatures, the reaction of ethyl sulphate with ethyl alcohol had at  $57^\circ$  the constant  $k = 0.0027$ , and at  $65^\circ$ ,  $k = 0.0046$ , which gives a temperature coefficient of 2.1 for  $10^\circ$ . The reaction of methyl sulphate with methyl alcohol at  $31.5^\circ$  has  $k = 0.00082$ , and at  $44^\circ$ ,  $k = 0.0032$ . From this the temperature coefficient for  $10^\circ$  is calculated by means of the equation  $k_{t+10}/k_t = 10^{10b}$ , to be 3.0, or slightly higher than the normal value. G. Y.

**Esterification of Aminobenzoic Acids by Means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Monatsh.*, 1906, 27, 997—1044. Compare Abstr., 1906, ii, 659).—The rate of esterification of the three aminobenzoic acids by alcoholic hydrogen chloride has been determined in the manner described previously for determining the rate of esterification of benzoic acid, and found, in presence of only traces of water, to increase more rapidly than the total concentration of the hydrogen chloride, and probably also more rapidly than the excess of hydrogen chloride over that necessary for the formation of the hydrochloride of the amino-acid. This behaviour is more marked in the case of *o*- than with *m*- or *p*-aminobenzoic acid, the rate of esterification of these two acids, by means of  $N/3$  to  $2/3N$  alcoholic hydrogen chloride, being approximately proportional to the concentration of the excess of the hydrogen chloride.

On esterification of *m*-aminobenzoic acid in 0.05—0.06*N* solution with aqueous alcoholic hydrogen chloride, the relation of the velocity constant to the amount of water and of the excess of hydrogen chloride present, is represented by the expression:  $1/k = 0.87 + 21.35/c' + 0.6088/c'^2 + (75.62 - 43.09/c' + 22.66/c'^2)w + (-223.0 + 190.5/c' - 6.713/c'^2)w^2$ , when the molecular concentration of the water lies between  $w = 0.02$  and  $w = 1.15$ , and that of the excess of hydrogen chloride is between  $c' = 0.1$  and  $c' = 0.6$ ; with  $c' = 0.6$ , the expression applies also to solutions with  $w = 2.5$ .

The relation of the velocity constant to the concentration of the excess of hydrogen chloride, and to the amount of water present is represented in the case of *p*-aminobenzoic acid by the similar expression:  $1/k = 10.10 + 16.27/c' + 0.6692/c'^2 + (-155.5 + 111.13/c' + 3.077/c'^2)w + (-33.05 + 55.8/c' + 8.136/c'^2)w^2$ , which applies to solutions with  $w = 0.02 - 1.34$ , and  $c' = 0.1 - 0.6$ , or with  $c' = 0.6$  and

$w = 2.4$ . With about  $N/3$  hydrogen chloride and absolute alcohol, the concentration of the *p*-aminobenzoic acid may be  $0.09N$ .

The hydrolysis of ethyl *o*- and *p*-aminobenzoates takes place so slowly as to be negligible in comparison with the rate of esterification.

When the action of only the excess of the hydrogen chloride is taken into account, the esterification of the aminobenzoic acids resembles closely that of benzoic and the nitrobenzoic acids. G. Y.

**Boric Acid, Amyl Alcohol, and Water.** PAUL MÜLLER and RICHARD ABEGG (*Zeitsch. physikal. Chem.*, 1907, 57, 513—532).—The existence of polyborates in concentrated solutions of boric acid and sodium hydroxide is confirmed, but the relationships of these are complicated, and it is probable that even in dilute solutions several complexes exist side by side. Addition or removal of boric acid seems to affect chiefly the amount of polyborate, and only slightly the amount of free boric acid in the solution.

By partition experiments in which sodium chloride solutions of various concentrations were shaken up with amyl alcohol, it has been shown that in amyl alcohol charged with water there exists a hydrate of the alcohol, and it is probable that the hydrate contains 3 molecules of water to 1 molecule of alcohol. In reaching this conclusion the authors suppose that the active masses of the free components of the hydrate are negligibly small in comparison with that of the compound. In aqueous amyl alcohol saturated with boric acid there exists not only the aforementioned hydrate, but also a compound containing 2 molecules of alcohol and 1 molecule of boric acid.

The influence of hydroxy-compounds, such as lactic acid, glycerol, and mannitol, on the solubility of boric acid in water has been studied, and the results obtained throw light on the chemical nature of this influence. When the solubility of boric acid in mixtures of water and methyl alcohol, water and ethyl alcohol, &c., is determined, it is found that the curves representing the variation in solubility with changing composition of the solvent mixture all exhibit a minimum. When a  $C_n$  alcohol is part of the solvent, the minimum occurs at a smaller percentage of water than when the alcohol present contains  $n + 1$  atoms of carbon.

In the case of alcohols not completely miscible with water, the temperature coefficients of the reciprocal solubility are opposite in sign for the two phases. J. C. P.

**Solubilities in Mixed Solvents. IV. Solubilities of Certain Mercury Salts.** WALTER HERZ and G. ANDERS (*Zeitsch. anorg. Chem.*, 1907, 52, 164—172. Compare Abstr., 1904, ii, 709; 1905, ii, 510, 709; Sherrill, 1903, ii, 534).—The solubilities of mercury halides and cyanide have been determined at  $25^\circ$  in the following binary solvents containing the components in varying proportions: methyl alcohol and water, ethyl alcohol and water, and ethyl acetate and water.

The solubility in methyl alcohol and water increases with the proportion of alcohol for the bromide, iodide, and cyanide, but shows a

maximum for the chloride at 1 mol. water to 2 mols. alcohol. The observed solubility,  $L$ , is in almost every case less than  $l$ , that calculated from the composition of the solution on the assumption that the components exert their effect independently. Except in the case of the iodide, the values of  $L-l$  attain a maximum at intermediate concentrations.

In mixtures of ethyl alcohol and water, the solubility increases with the proportion of the former except in the case of the cyanide. In this case also  $L-l$  is negative, but attains a maximum only for the chloride.

Owing to the limited mutual solubility of ethyl acetate and water, only a few experiments were carried out with this mixture, but in some instances a small change in the composition of the solvent greatly altered the solvent power.

With the object of determining whether there is a connexion between the positions of the maxima of the viscosity curves of the systems and those of  $L-l$ , several series of viscosity measurements were made, but no simple relation between the two properties was discovered.

G. S.

**Intrinsic Movement of Particles in Colloidal Solutions.** THE SVEDBERG (*Zeitsch. Elektrochem.*, 1906, 12, 909—910).—The author's observations (this vol., ii, 17) led him to the conclusions that the amplitude of vibration of a particle is proportional to the time of vibration, that is, the particles move with constant mean speed, and that the curve representing the amplitude as a function of the viscosity of the solution is hyperbolic. He now finds that both these results have been deduced from purely theoretical considerations by Einstein (*Ann. Phys.*, 1905, [iv], 17, 549; 1906, 19, 289). T. E.

**New Apparatus for Sublimation.** V. SCHWOROZOFF (*Zeitsch. angew. Chem.*, 1907, 20, 109).—The apparatus consists of a small test-tube provided with a porous stopper made of chalk, unglazed porcelain, or parchment. The substance to be sublimed is placed in this tube, which is then introduced into a wider tube the lower end of which can be immersed in an oil or metal bath of known temperature; the upper part of the outer tube is surrounded by a water jacket. The apparatus can be used for subliming very small quantities of material, and, since the outer tube can be exhausted, the sublimation can be carried out under diminished pressure.

P. H.

**Improved Liebig's Condenser.** HENRY R. ELLIS (*Chem. News*, 1907, 95, 52).—A simple device for improving the efficiency of a Liebig's condenser when used as a reflux for very volatile liquids. It consists in the insertion of a second smaller condenser within the middle tube of a Liebig's condenser.

W. H. G.

**A New Desiccator for the Drying of Gases.** M. I. KUSNETZOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, ii, 453—454).—The apparatus resembles an ordinary potash gas pipette without a side tube, but the reservoir is connected to the pipette by means of a removable indiarubber

cork. Phosphoric oxide is first introduced into the pipette ; it is then connected with the reservoir which contains mercury, and, after exhausting the last traces of air by means of a pump, the gas to be dried is introduced. Z. K.

**Apparatus for Crystallising and Filtering in Indifferent Gases.** WILHELM STEINKOPF (*Ber.*, 1907, 40, 400—403. Compare Beckmann, *Annalen*, 1892, 266).—An apparatus is described in which substances can be crystallised and filtered, by means of a Gooch crucible, in an atmosphere of hydrogen or any other gas. J. J. S.

**A New Centrifugal Apparatus for Laboratory Use.** TH. KÖRNER (*Chem. Rev. Fett. Harz. Ind.*, 1907, 14, 34—35).—The apparatus consists of a circular drum having a capacity of from 150 to 500 c.c., and mounted so as to be capable of being rotated at a high speed. A hole is provided at the top of the drum through which, while the contents are being submitted to centrifugal action, is lowered one limb of a siphon made of narrow brass tubing. This end of the tube is bent at a right-angle so that the velocity of the liquid forces a portion of it through the siphon, whence it is discharged into a receptacle. The siphon is only lowered into the drum when it is considered that separation of solid substances has been attained. The apparatus is suitable for the clarification of solutions of tanning materials, &c. W. P. S.

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## Inorganic Chemistry.

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**The Constitution and Configuration of Inorganic Compounds.** ALFRED WERNER (*Ber.*, 1907, 40, 15—69).—A lecture delivered before the German Chemical Society. A. McK.

**Decomposition of Hydrogen Peroxide Solutions.** AUGUST FISCHER (*Pharm. Centr.-h.*, 1907, 48, 57—65, 79—84).—An investigation of the decomposition of aqueous solutions containing 1 to 25% of hydrogen peroxide at 15°, 20°, and 25°. The solutions were prepared by dilution of a 30% solution (Merck's Perhydrol), and it is shown that this is accompanied by a slight decomposition (0.1 to 0.3%); further, that under the above conditions, at 15° and 20°, solutions containing 6 to 8% of hydrogen peroxide decompose most rapidly (roughly 50% in ten days); at 25° these containing 2 to 10% of hydrogen peroxide with approximately equal rapidity (roughly 55% after ten days). Increase of concentration above 6% at 15° and 20°, and above 10% at 25° is accompanied by an increase in stability. Various factors, such as the presence of dust, the quantity of solution in the bottle, &c., influence the rate of decomposition. Decomposition apparently ceases when the pressure of oxygen within the bottle is

sufficiently great. The decomposition is prevented to a large extent and to about the same degree by the presence of very small quantities of hydrochloric and sulphuric acids; phosphoric acid is not quite so effective, but is better than boric acid. Contrary to Arth's statement (*Chem. Zeit.*, 1901, 568), oxalic acid does not decompose hydrogen peroxide, but when present in quantities varying between 0.1 and 2% prevents decomposition to a greater degree than either hydrochloric or sulphuric acid.

W. H. G.

**Dry Method for the Generation of Oxygen from Sodium Peroxide.** HAROLD J. TURNER (*Amer. Chem. J.*, 1907, 37, 106—107).—In reactions depending on the action of water and apt to become violent, salts containing water of crystallisation may with great advantage be used in place of water. When a mixture of fused sodium peroxide and crystalline sodium sulphate or carbonate is gently warmed, oxygen is evolved in a steady stream. The preparation of small quantities of the gas for laboratory or lecture purposes can be conveniently effected in this way.

A similar method has been adopted recently for the decomposition of calcium carbide on a large scale.

E. G.

**Continuous Apparatus for Preparing Pure Oxygen for Use in Organic Analysis.** ALPHONSE SEYEWETZ and POIZAT (*Compt. rend.*, 1907, 144, 86—87).—A steady evolution of oxygen under sufficient pressure for use in organic combustions is obtained when a solution of 25 grams of potassium permanganate in 500 c.c. of water and 50 c.c. of concentrated sulphuric acid is allowed to flow from a dropping funnel into a litre flask containing 500 c.c. of hydrogen peroxide (10 vol.). The longer limb of a siphon passes through the cork of the flask and is bent in such a way that the permanganate solution drops on to the tube instead of directly into the peroxide solution; by this means a steadier flow of oxygen is obtained. The siphon serves to empty the flask and to introduce a fresh charge. The oxygen thus obtained contains traces of chlorine from the hydrochloric acid, which is a common impurity of hydrogen peroxide, and of ozone.

M. A. W.

**Preparation of Ozone by Electrolysis.** FRANZ FISCHER and KARL MASSENEZ (*Zeitsch. anorg. Chem.*, 1907, 52, 202—218. Compare McLeod, *Trans.*, 1886, 49, 591; Kremann, *Abstr.*, 1904, ii, 24).—The paper contains the description of an electrolytic method by which oxygen containing a very high proportion of ozone can be obtained without destruction of the electrodes.

The apparatus is made of glass and consists of two side cathode compartments and a middle anode compartment. The latter contains two glass tubes, bent towards each other at their lower ends and joined by a narrow platinum tube which serves as electrode and is kept cool by a continuous current of water being passed through the interior. The arrangements for collecting and analysing the gases are given in detail.

In agreement with McLeod (*loc. cit.*), it was found that sulphuric

acid, D 1.075—1.1, gave the best results, and a current density of 58 amperes per sq. cm. proved most efficient. The chief improvement in the method is as to the best size and shape of the anode, and in the observation that when the anode surface is rendered smooth or "polished" by electrolysis for a short time with strong acid it gives much higher yields of ozone. In the final form the platinum tube was sealed over completely, and then a thin strip 6 mm. long and 0.4 mm. broad exposed. In this way long contact of the ozone with the platinum surface (which decomposes the gas) is avoided, and a gas containing a little over 17% of ozone by weight is obtained, the electrode remaining unaffected even after long use. G. S.

**Thermal Relationships between Ozone, Nitric Oxide, and Hydrogen Peroxide.** II. FRANZ FISCHER and HANS MARX (*Ber.*, 1907, 40, 443—458. Compare Abstr., 1906, ii, 845).—In continuation of former work (*loc. cit.*), the authors have studied the influence of the temperature of the Nernst filament used, the influence of the form of the aperture through which the air was passed, and the influence of the temperature of the air passed through the slit.

With increase of the temperature of the filament, the concentration of ozone in the air increases in the manner demanded by theory. The temperature of the filament on the side on which the air was blown was determined by the light emission per square millimetre.

When moist air is used, the temperature of the filament has a similar effect on the yield of hydrogen peroxide, so that it is experimentally established both for ozone and hydrogen peroxide that the concentration of these endothermic products increases with the temperature.

The form of the aperture through which the air is blown has an important influence on the yield of gases. A double aperture is most efficient.

The highest concentration of ozone obtained by blowing air on the filament was 0.03% by weight, calculating on air, and 0.13% by weight, calculating on the oxygen contained in the air.

The influence of the temperature of the air blown on to the filament is slight up to 60°. When warm air at about 60° is used, the ozone yield falls to about 80% of the value obtained by using air at about 5°.

If 96% oxygen is blown on to the filament instead of air, the influences of the experimental conditions are analogous to those which obtain in the case of air.

If the oxygen is moist, the yield of ozone is very considerably diminished, whilst hydrogen peroxide is formed.

The maximum yield of ozone in the cases where oxygen is used is attained when the rate of flow of the oxygen is slow.

A. McK.

**Synthesis of Hydrogen Sulphide.** JAROSLAV MILBAUER (*Ann. Chim. Phys.*, 1907, [viii], 10, 125—129).—Hydrogen was passed over melted sulphur (alone, or mixed with a catalytic agent), maintained at a constant temperature, and the amount of hydrogen sulphide formed

per hour was estimated by means of standard iodine solution. It was found that the rate of formation of hydrogen sulphide was not accelerated by the presence of the sulphide of any one of the following metals: silver, gold, mercury, thallium, arsenic, molybdenum, platinum, or by metallic mercury or palladium, but was increased by platinum black, or red phosphorus. The acceleration in the latter case is possibly due to the occurrence of the following reactions:  $P_2S_5 + 8H_2 = 2PH_3 + 5H_2S$  and  $2PH_3 + 4S_2 = P_2S_5 + 3H_2S$ .

The rate of formation of hydrogen sulphide by the action of hydrogen on sulphur alone increases continuously with rise of temperature, but in presence of red phosphorus the maximum rate is attained at  $218^\circ$ , after which it diminishes up to  $278^\circ$ . The rate of formation in the case of sulphur and hydrogen alone is greater when the sulphur has been heated almost to boiling and then cooled to  $278^\circ$ , which indicates, as Bodenstein has shown (Abstr., 1899, ii, 638), that the transformation  $S_8 \rightleftharpoons 4S_2$  takes place more slowly than  $S_2 \rightleftharpoons 2S$ .

T. A. H.

**Preparation of Hydrogen Sulphide.** HENRI FONZES-DIACON (*Bull. Soc. chim.*, 1907, [iv], 1, 36—37. Compare Abstr., 1900, ii, 405).—Aluminium sulphide,  $Al_2S_3$ , is prepared by closely packing a mixture of powdered aluminium and sulphur in a crucible lined with magnesium and igniting the mixture by means of lighted magnesium ribbon. The sulphide is placed in a dry flask, provided with a stopper carrying (1) a tap funnel from which water can be allowed to drip slowly on the sulphide; (2) a mercury manometer, and (3) a leading tube with a stop-cock. The evolution of hydrogen sulphide can be stopped almost at once by cutting off the supply of water and closing the delivery tube.

T. A. H.

**Formation of Hyposulphites.** EUGÈNE GRANDMOUGIN (*Bull. Soc. ind. Mulhouse*, 1906, 76, 351—356).—The use of iron for the reduction of sodium hydrogen sulphite on a commercial scale (Schützenberger, *Compt. rend.*, 1869, 69, 200) is not very successful. The action of sodium on sulphur dioxide in presence of ethyl ether or alcohol (Abstr., 1904, ii, 250) is very slow and gives a very bad yield. Sodium at its melting point does not appreciably combine with dry sulphur dioxide, and does not act on liquid sulphur dioxide at  $-10^\circ$ , but when kept for fifteen days in liquid sulphur dioxide in a sealed tube at  $20^\circ$  a small quantity of sodium hyposulphite is formed. Sodium acts on concentrated solutions of sodium hydrogen sulphite with explosive violence, and more slowly on more dilute solutions, but in neither case is any hyposulphite formed. Sodium amalgam readily reduces solutions of sodium hydrogen sulphite to the hyposulphite, but the method is not valuable industrially.

Calcium has no action on liquid sulphur dioxide, but readily reduces solutions of the hydrogen sulphite to the hyposulphite. The stability of sodium hyposulphite solutions is increased by adding alkali hydroxides, sodium sulphide, or reduced indigo (compare Meyer, Abstr., 1903, ii, 285).

E. H.

**Colloidal Selenium.** P. I. KHOLODNY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, ii, 127—147).—The solutions of colloidal selenium used by the author were prepared by dissolving in water the red selenium precipitated on reducing selenium dioxide by means of sulphur dioxide (compare Schulze, *Abstr.*, 1886, 302). Such solutions are blood-red, but if sufficiently diluted with water assume an orange tint. They are moderately stable and only slightly opalescent and are considerably more transparent than silver solutions of corresponding concentration. The precipitation of the selenium from a 1.5% solution by means of various acids, alkalis, and salts was investigated. The density of colloidal selenium was determined by taking advantage of the observation that, when its solution is treated with carbon disulphide, the latter removes the whole of the selenium from solution. If then  $A$  represents the weight of the colloidal selenium solution,  $B$  the weight of the solution, of the same volume, of the impurities alone,  $M$  the weight of the colloidal selenium,  $\delta$  the density of the solution of the impurities, and  $x$  the required density of the colloidal selenium,  $A = B + M - M\delta/x$ . The application of this method to colloidal solutions containing from 5 to 10% of selenium gives a constant value,  $D_4$  4.26—4.27 for colloidal selenium. The constancy of this value for solutions of different concentrations indicates that the solution of the selenium occurs without diminution of the total volume of solvent and solute. The above value for the density of colloidal selenium agrees with that given by various authors for the density of amorphous selenium.

T. H. P.

**Absorption of Nitrogen and Hydrogen by Aqueous Solutions.** GUSTAV VON HÜFNER (*Zeitsch. physikal. Chem.*, 1907, 57, 611—625).—The absorption coefficients of nitrogen and hydrogen in solutions of dextrose, lævulose, arabinose, erythritol, aminoacetic acid,  $\alpha$ -aminopropionic acid, carbamide, and acetamide have been determined. On the whole, the extent to which the absorption coefficient falls away from the value for pure water is proportional to the absolute weight of the solute present. The chief exceptions to this rule occur in the cases of acetamide and the two amino-acids.

J. C. P.

**Hydrazoic Acid [Azoimide].** LOUIS M. DENNIS and HELEN ISHAM (*Ber.*, 1907, 40, 458—468).—The authors describe the preparation of anhydrous azoimide by the action of sulphuric acid on potassium trinitride. The various precautions taken to minimise the danger from explosion are given in detail. The azoimide so obtained, which is practically pure (99.94%), has m. p.  $-80^\circ$  and b. p.  $37^\circ$ , the latter value being in accordance with that quoted by Curtius and Radenhausen (*Abstr.*, 1891, 524). It is a colourless, mobile liquid at the ordinary temperature and may be kept in a sealed tube for several days without undergoing decomposition. The authors did not find that azoimide exploded spontaneously on any occasion. The explosion is extremely violent when the acid is shaken or when it is strongly heated.

The vapour density, determined at a temperature  $25^{\circ}$  above the boiling point, indicated the unimolecular formula  $\text{HN}_3$  for azoimide.

A. McK.

**Products Formed from Carbon, Nitrogen, and Carbonates of the Alkaline Earths.** OTTO KÜHLING (*Ber.*, 1907, 40, 310—319).—An examination of the relative quantities of cyanide and cyanamide obtained by heating sugar charcoal (3 atoms) with the pure carbonates of barium, strontium, and calcium (1 mol.) in a stream of moist or dry nitrogen free from carbon dioxide and oxygen at temperatures varying from  $900^{\circ}$  to  $1400^{\circ}$ . The results obtained show that the tendency to take up nitrogen falls with decreasing atomic weight. At  $1050$ — $1100^{\circ}$  barium carbonate gives 23.4% of cyanide and 1.6% of cyanamide; strontium carbonate at  $1200$ — $1250^{\circ}$ , 1.4% and 0.8% respectively, and calcium carbonate at  $1350$ — $1400^{\circ}$  does not form a trace of either. The effect of adding the corresponding chloride to the mixture is to increase the percentage of the cyanide and cyanamide. The paper contains a summary of the patent literature bearing on the subject.

W. R.

**Solubility of Carbon in Barium and Strontium Carbides.** H. MOREL KAHN (*Compt. rend.*, 1907, 144, 197—199. Compare Abstr., 1906, ii, 538).—When barium carbide in a charcoal crucible is subjected to a current of 550—600 amperes at about 90 volts for six minutes, it takes up from 1.25% to 1.50% of carbon, and the amount increases with time until after eleven minutes from 5.40% to 6.20% of carbon is dissolved. On longer heating, the variations in the amount of carbon dissolved are considerable and do not depend on the solubility of the carbon. Under the same conditions, strontium carbide dissolves 1.3% to 1.5% of carbon in six minutes and 6.15% to 6.25% in ten minutes. The results are entirely similar to those obtained with calcium carbide.

E. H.

**Methods of Investigation of Silicate Fusions.** CORNELIUS DOELTER (*Centr. Min.*, 1907, 1—2).—An answer to the remarks of Day and Shepherd (Abstr., 1906, ii, 770) on the methods employed for the determination of the melting points of silicates. It is maintained that the optical method leads to as accurate results as the thermal method.

L. J. S.

**Preparation of Pure Helium by Filtration of the Gases from Cleveite through a Quartz Diaphragm.** ADRIEN JAQUEROD and F. LOUIS PERROT (*Compt. rend.*, 1907, 144, 135—136. Compare Abstr., 1905, ii, 10).—Quartz is quite impermeable to all gases except hydrogen, helium, and, perhaps, carbon monoxide up to  $1067^{\circ}$ . This is the basis of a method of obtaining pure helium from the cleveite gases. The latter, together with about 5% of oxygen (for the oxidation of hydrogen and carbon monoxide), is introduced into the annular space between a platinum cylinder and a quartz bulb placed within it, at rather more than atmospheric pressure. When the apparatus is heated to about  $1100^{\circ}$  and the quartz bulb evacuated, helium

diffuses through. The method, although very slow, effects almost complete purification, spectroscopic examination of the gas showing the red hydrogen line only faintly, and the nitrogen bands not at all.  
E. H.

**Two Chemical Compounds, each containing Three Metals.** ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1906, 57, 507—510).—A study of freezing-point curves for systems of three metals has led to the recognition of the compounds  $\text{NaKHg}_2$  (m. p.  $188^\circ$ ) and  $\text{NaCdHg}$  (m. p.  $325^\circ$ ).  
J. C. P.

**Lithium Subchloride.** ANTOINE GUNTZ (*Ann. Chim. Phys.*, 1907, [viii], 10, 13—23. Compare Abstr., 1896, ii, 299, 359).—The product obtained by heating lithium chloride with lithium in a current of hydrogen is not, as previously supposed by the author, lithium subchloride,  $\text{Li}_2\text{Cl}$ , but a mixture of lithium hydride and chloride. Attempts to prepare the subchloride have been made (1) by heating a mixture of lithium hydride and chloride at  $880^\circ$  under reduced pressure; (2) by heating a mixture of lithium chloride and lithium in presence of argon, and (3) by heating a mixture of lithium and lithium chloride in a hermetically sealed steel crucible plunged in a bath of melted calcium chloride. The products obtained were analysed, and in no case could the formation of the subchloride be definitely established although the results obtained are compatible with the view that small quantities of the salt may have been formed.

Similar results have been obtained by Guntz and Bassett in the case of calcium (Abstr., 1906, ii, 540). Bunsen's failure to obtain rubidium by the electrolysis of the chloride was probably due to the formation of rubidium hydride and not to the production of rubidium subchloride as he supposed. The dissociation of an alkali hydride when dissolved in the chloride of the same metal may, under certain conditions, give rise to a finely-divided deposit of the metal and the formation of a coloured product which may be mistaken for the subchloride (compare Wöhler and Kasarnowski, Abstr., 1906, ii, 22).  
T. A. H.

**Solubility of Alkaline Earths in their Molten Chlorides.** KURT ARNDT (*Ber.*, 1907, 40, 427—431).—The experiments were carried out in an Heräus crucible electric furnace for 110 volts and 2 amperes provided with a Le-Chatelier pyrometer and a rheostat. The determinations were made in two ways, by heating the chloride and its corresponding oxide in a platinum or porcelain crucible and estimating the % of alkali in the saturated fused mass, or by studying the cooling curves and so obtaining the equilibrium between solvent and solute. In round numbers, 1 molecule of calcium, strontium, and barium oxides are dissolved by 7, 3, and 2 molecules of their respective chlorides. In the case of the barium chloride, mixed crystals containing 17.7%  $\text{BaO}$  were isolated. Fluorspar has practically no influence on the solubility of lime in calcium chloride.  
W. R.

**Bleaching Powder.** EUGEN SCHWARZ (*Zeitsch. angew. Chem.*, 1907, 20, 138—143).—The author discusses the views recently published on

the composition of bleaching powder (compare Ditz, Abstr., 1899, ii, 26 ; 1901, ii, 239 ; 1902, ii, 656 ; Winteler, Abstr., 1903, ii, 145, 291 ; Tiesenholt, Abstr., 1902, ii, 562 ; 1906, ii, 163). Strontium hydroxide in the solid state and in solution is shown to be analogous with calcium hydroxide in its behaviour towards chlorine. A strontium bleaching powder cannot be obtained containing such a high proportion of "bleaching" chlorine as ordinary bleaching powder, but in other respects the products are practically identical.

The action of chlorine monoxide on calcium chloride has been studied. The amount of water present influences the reaction to a great extent, anhydrous calcium chloride not being attacked, whereas with 30% of water, calcium hypochlorite is first produced, which under prolonged action of the chlorine monoxide is converted into chlorate. A sample of the product containing a high percentage of hypochlorite is stable in dry air, is not decomposed readily by carbon dioxide when dry, but fairly readily when moist. A "synthetic" bleaching powder, prepared by mixing some of this product with calcium chloride and containing roughly the same percentage of "bleaching" chlorine as commercial bleaching powder, when treated with moist carbon dioxide gives off slowly an amount of chlorine corresponding with that present as hypochlorite only, whereas under the same treatment, the commercial product parts with 80% of its bleaching chlorine. The author therefore concludes that bleaching powder is not a mere mixture of calcium chloride and calcium hypochlorite, but consists principally of the compound  $\text{CaOCl}_2$ ; carbon dioxide acts on this, liberating hypochlorous acid, which in the nascent state reacts with the chloride portion of the molecule, converting this into hypochlorite, which is susceptible to further decomposition by the carbon dioxide.

W. H. G.

**Two New Ammonium Calcium Sulphates.** JOH. D'ANS (*Ber.*, 1907, 40, 192—194. Compare Abstr., 1906, ii, 751 ; Ditte, this journal, 1877, i, 440 ; Bell and Taber, Abstr., 1906, ii, 352).—*Ammonium pentacalcium sulphate*,  $\text{Ca}_5(\text{NH}_4)_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$ , prepared by boiling calcium sulphate with 30% aqueous ammonium sulphate in a reflux apparatus, crystallises in strongly refracting prisms, and closely resembles the analogous potassium salt (van't Hoff, Abstr., 1904, ii, 561). On boiling calcium sulphate with 40% aqueous ammonium sulphate, *ammonium dicalcium sulphate*,  $\text{Ca}_2(\text{NH}_4)_2(\text{SO}_4)_3$ , is formed ; this crystallises in pentagonal dodecahedra and decomposes on prolonged boiling with the mother liquor, forming syngenite and ammonium pentacalcium sulphate, or, in contact with the cooled mother liquor, forming syngenite. Both of these new double salts are decomposed by water.

G. Y.

**Reversible Action of Oxygen on Magnesium Chloride.** FRITZ HABER (*Zeitsch. anorg. Chem.*, 1907, 52, 127—128).—A comparison of the papers published simultaneously by Moldenhauer (this vol., ii, 85) and by Haber and Fleischmann (*ibid.*, ii, 84) on the equilibrium between magnesium chloride and oxygen has made it clear that the partial pressures and constants in the table given by the



latter observers do not correspond. Although the general results of the investigation are not thereby affected, a recalculation of the observations and, if necessary, a repetition of some of the experiments are rendered necessary; the proper values will be communicated later.

It is pointed out that the so-called "concentrations" of the reacting gases given in Moldenhauer's paper are really partial pressures expressed in hundredths of an atmosphere. G. S.

**Solubility of the Hydrates of Magnesium Bromide and Iodide.** BORIS N. MENSCHUTKIN (*Zeitschr. anorg. Chem.*, 1907, 52, 152—158. Compare Abstr., 1906, i, 131, 132, 552, 943).—Magnesium bromide hexahydrate was obtained pure by decomposing the dietherate with water, and its solubility in water determined from 0° to its melting point, 164°. The solubility at 18° agrees exactly with that found by Mylius and Funk (Abstr., 1897, ii, 442), but not with the value obtained by Étard (Abstr., 1894, ii, 442). The solubility curve is compared with those of the corresponding alcoholates (*loc. cit.*).

Magnesium iodide octahydrate,  $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ , was obtained by the action of water on the corresponding dietherate, and its solubility in water determined from 0° to its melting point, 43·5°. The solubility of the hexahydrate, the stable solid phase above 43·5°, has been determined from the latter temperature to 215°.

Of the three hexahydrates, the chloride is the least and the iodide the most soluble. G. S.

**Behaviour of Magnesium Hydrogen Carbonate when its Solution is Boiled.** R. RINNE (*Chem. Zeit.*, 1907, 31, 125—126).—Magnesium hydrogen carbonate was prepared by the action of carbon dioxide on pure magnesia suspended in distilled water. Aqueous solutions of this magnesium carbonate were found not to deposit all their dissolved magnesia even on boiling for some time. P. H.

**Solvent Action of Water on Zinc in Brass.** JOHANNES H. ABERSON (*Chem. Weekblad*, 1907, 4, 32—34).—The solvent action of soft water on the zinc in the brass gauzes and their supports in the reservoir-filters at Wageningen was investigated. The corrosion rendered the supports very brittle, due to their transformation into an outer crust and an inner core, which were only feebly united. Sometimes the core was wanting. The brass gauze was also corroded. Analysis of the outer crust showed a deficiency in zinc of about 6%, and of the gauze a deficiency of about 27%, and a corresponding increase in the percentage of copper in each case. The zinc was estimated as oxide and the copper electrolytically. The author attributes the action to the softness of the water, the surface of the alloy not being coated with carbonate. The oxygen present, continually renewed by pumping, converted the zinc into oxide, which then dissolved as zinc hydrogen carbonate. The solution of the zinc was also facilitated by electrolytic action, due to soldered joints. The author has noticed the solvent action of this water on zinc and lead, and considers that filters for very soft water should be constructed without brass. A. J. W.

**Zinc-Thallium and Zinc-Iron Alloys.** A. VON VEGESACK (*Zeitsch. anorg. Chem.*, 1907, 52, 30—40. Compare Heycock and Neville, *Trans.*, 1897, 71, 383).—Zinc and thallium have only a limited mutual solubility. At its melting point, zinc dissolves about 2.5% of thallium, the melting point of the former metal being thus lowered about 3°; at the melting point of thallium the latter metal dissolves about 5% of zinc, and its melting point is lowered about 4°. The mutual solubility curves could not be determined owing to the thermal effects on admixture being very slight.

There is no indication of chemical combination between the two metals, and they show practically no tendency to form mixed crystals.

The freezing points of alloys of zinc and iron up to about 24% of zinc have been determined, and indications of the existence of the compounds  $\text{FeZn}_3$  and  $\text{FeZn}_7$  have been obtained.

From alloys containing 11—24% of iron, there is a primary separation of crystals of unknown composition which react at 777° with the fused mass to form the compound  $\text{FeZn}_3$ . The latter separates primarily from alloys containing 4—11% of iron, but when the temperature falls to 662° it reacts with the fused mass to form the compound  $\text{FeZn}_7$ . The two compounds seem to be miscible to a slight extent in the solid form. The compound  $\text{FeZn}_7$  forms a series of mixed crystals which are saturated when 7.3% of iron is present. Below 442°, the saturated mixed crystals react with the fused mass to form another series of mixed crystals extending from 0.7—7.3% of iron. The results were confirmed by microscopic examination.

Alloys containing 0.7—11% of iron become harder and more brittle with increase in the amount of the latter metal; those containing over 5% of iron are porous. The compounds  $\text{FeZn}_3$  and  $\text{FeZn}_7$  are also porous and very brittle.

G. S.

**Action of Carbon Dioxide on Metallic Hydroxides.** PAUL N. RAIKOW (*Chem. Zeit.*, 1907, 31, 55—57, 87—89. Compare Abstr., 1905, ii, 85).—Carbon dioxide is passed into the mixture obtained by adding to a normal solution of metallic salt a quantity of potassium hydroxide sufficient to convert about one-fifth of the metal into hydroxide; the increase in weight due to combination of carbon dioxide with the metallic hydroxide is then observed. Under these conditions, magnesium hydroxide is converted completely into the hydrogen carbonate, zinc and cadmium hydroxides into normal carbonates, mercuric oxide chiefly into the normal carbonate, a small quantity of an acid carbonate also being formed; neither mercurous oxide nor glucinum hydroxide combines with carbon dioxide, in the latter case probably owing to the formation of a soluble basic glucinum sulphate stable towards carbon dioxide. Freshly precipitated glucinum hydroxide suspended in water is, however, under the same treatment, apparently converted into the basic carbonate  $\text{BeCO}_3 \cdot 3\text{Be}(\text{OH})_2$ . Aluminium, chromium, and ferric hydroxides do not combine with carbon dioxide under this treatment, whereas zirconium, lanthanum, cerous and ceric hydroxides are converted into the respective normal carbonates; although cerous carbonate is usually described as being white, that obtained under these conditions is yellow; thalious hydr-

oxide is converted completely into the hydrogen carbonate; yttrium hydroxide into the basic carbonate,  $3Y_2(CO_3)_3 \cdot 2Y(OH)_3$ , and not into the normal carbonate obtained by Cleve by passing carbon dioxide into water containing yttrium hydroxide in suspension; ferrous and manganous hydroxides are converted chiefly into their respective normal carbonates, a small quantity of an acid carbonate also being formed in each case. Freshly precipitated aluminium, chromium, and ferric hydroxides when suspended in water do not combine with carbon dioxide.

W. H. G.

**Action of Carbon Dioxide on Metallic Hydroxides.** PAUL N. RAIKOW (*Chem. Zeit.*, 1907, 31, 141—143. Compare preceding abstracts).—An excess of carbon dioxide converts nickel hydroxide into a carbonate of the formula  $Ni_3H_2(CO_3)_4$ ; this substance is fairly soluble in a solution saturated with carbon dioxide, but as this gas escapes from the solution the carbonate is thrown out. An analogous experiment carried out with a cobalt salt led to no definite result. Freshly precipitated copper hydroxide suspended in water is not acted on by carbon dioxide in the absence of air. Cuprous hydroxide is first converted into a carbonate of the formula  $Cu_3H(CO_3)_2$ , which, however, subsequently decomposes completely. Silver only gives a normal carbonate. Freshly precipitated lead hydroxide is converted by an excess of carbon dioxide into normal lead carbonate. The investigation has brought to light the existence of new types of carbonates, namely, the  $1/4$  saturated nickel carbonate,  $Ni_3H_2(CO_3)_4$ , and the  $3/4$  saturated copper carbonate,  $Cu_3H(CO_3)_2$ .

P. H.

**Cadmium-Sodium Alloys.** NICOLAI S. KURNAKOFF and A. N. KUSNETZOFF (*Zeitsch. anorg. Chem.*, 1907, 52, 173—185. Compare Abstr., 1900, ii, 277; Heycock and Neville, *Trans.*, 1889, 55, 673).—The investigation of the system cadmium-sodium by thermal and microscopic methods shows that the metals form two compounds of the respective formulæ  $NaCd_2$  and  $NaCd_6$ .

The freezing-point curve of the system shows two maxima at  $384^\circ$  and 33.2 atom. % and  $363^\circ$  and 14.25 atom. % of sodium respectively, corresponding with the compounds  $NaCd_2$  and  $NaCd_6$ , as well as three eutectic points at  $95.4^\circ$  and 99.3%,  $351^\circ$  and 19.2%, and  $291^\circ$  and 5.5 atom. % of sodium respectively. From 14.3 to 17% of sodium a series of mixed crystals separates.

The compound  $NaCd_2$  occurs in well-formed octahedral crystals, has  $D_4^{20} 5.669$ , and is only slowly acted on by water; its crystallographic constants have also been determined. The compound  $NaCd_6$  occurs in cubic crystals.

G. S.

**Preparation of Pure Praseodymium Compounds.** N. A. ORLOFF (*Chem. Zeit.*, 1907, 31, 115).—A method for separating praseodymium completely from lanthanum. The praseodymium compound containing lanthanum only as impurity is boiled with a solution of potassium permanganate and mercuric oxide, to which a solution of cerium chloride is then gradually added. The precipitate obtained consists of the higher oxides of cerium and praseodymium, whilst the

lanthanum remains in solution. The praseodymium is then separated from the cerium by any of the usual methods. W. H. G.

**Separation of the Earths of the Yttrium Group.** ANTON BETTENDORFF (*Annalen*, 1907, 352, 88—110).—After separating the oxides of the cerium group from the mixed oxides, obtained from orthite, the residue is treated with formic acid and the formates so produced are separated by repeated fractional crystallisation into three principal fractions which give oxides possessing the equivalents  $RO = 120.0$ ,  $91.7$ , and  $80.5$  respectively.

The earth,  $R''O = 120.0$ , dissolved in nitric acid and freed from traces of didymium and samarium by using potassium sulphate (compare Bettendorff, *Abstr.*, 1890, 851) gave by partial precipitation with dilute ammonia a brown oxide ( $RO = 121.57$ ) and a very light yellow oxide ( $RO = 119.90$ ), in other words, the nearly pure oxides of terbium and gadolinium. By repeated partial decomposition of the nitrates of the oxide ( $RO = 91.7$ ), two fractions,  $RO = 82.0$  and  $RO = 103.4—105.0$ , were finally obtained; the chloride of the fraction  $RO = 82.0$  gave an intense yttrium spark-spectrum; the concentrated solution of the nitrates of the oxides,  $RO = 103.4—105.0$ , gave by treatment with sodium sulphate sparingly soluble double sulphates of a yellow oxide,  $RO = 119—120$ , practically identical with that obtained above from the formates least soluble in water ( $RO = 120.0$ ). From the fraction,  $RO = 80.5$ , by using Rowland's method, namely, systematic precipitation from the acidified solution of the nitrates, a white oxide,  $RO = 75.17$ , was obtained finally; since a solution of its nitrate did not show any absorption band in its spectrum, it is probably pure yttrium oxide.

The mixture of oxides obtained from gadolinite after separation of the oxides of the cerium group could not be further separated by fractional crystallisation of the double sulphates; by employing von Welsbach's oxide method of separation, however, the following fractions were obtained: ytterbium material, erbium material, and yttrium material. From the ytterbium material ( $RO = 130.75—131.8$ ) by fractional precipitation with ammonia were obtained three fractions,  $RO = 131.0$ ,  $131.5$ ,  $131.8$ ; it is at present impossible to say which represents the purest ytterbium compound.

From the erbium material, using von Welsbach's method, the following fractions were obtained:  $RO = 129.0—127.0$ ;  $126.5$ ,  $123.0$ , and  $120.0$ . As the ytterbium is gradually separated by fractional precipitation with ammonia from the fraction  $RO = 127.—129.0$ , the oxide loses its rose-red colour, becoming yellowish-brown,  $RO = 126.5$ ; the author therefore concludes that the rose-red oxide ( $RO = 126.63$ ,  $R''' = 166.0$ ), usually supposed to be erbium oxide, is an impure ytterbium oxide coloured red by an oxide of smaller equivalent weight and stronger basic properties, probably thulium oxide; thulium is present in large quantities in the fraction  $RO = 127—129$ .

The oxides,  $RO = 126.5$ , were not further separated. The oxides,  $RO = 119—124$ , gave what appeared to be an oxide with the constant value  $RO = 124.7$ , but this could not be further investigated owing to the small quantity obtained. Since the absorption spectrum of the

nitrate solution of this fraction,  $RO=119-124$ , shows not only the presence of erbium but also of holmium, whereas the absorption spectrum of the solution of the nitrate of the terbium oxide, obtained from orthite, shows the presence of holmium and not erbium, it follows that holmium is separated much more readily from erbium by means of a supersaturated solution of sodium sulphate than by partial precipitation with ammonia. By using Rowland's method (Abstr., 1894, ii, 449) it was possible to obtain from the yttrium material ( $RO=81.4$ ) a yttrium oxide,  $RO=76.0$ , containing, however, traces of didymium; by treating the nitrate of this oxide with potassium sulphate, it was possible to free it from didymium; the oxide then had the value  $RO=75.33$ ; this value remained unchanged even after further treatment by Rowland's method. The spectrum of the sulphate of the yttrium oxide ( $RO=75.16$ ) from orthite, although very similar, is not identical with that of the sulphate of the yttrium oxide ( $RO=75.33$ ) from gadolinite; this latter oxide appears to contain the oxide of a yet unknown element.

W. H. G.

**Double Ammonium Lead Chlorides.** HARRY W. FOOTE and L. H. LEVY (*Amer. Chem. J.*, 1907, 37, 119—123).—The ammonium lead chlorides which crystallise from aqueous solutions at  $25^\circ$  have been examined by heating weighed quantities of ammonium chloride and lead chloride with a known quantity of water, allowing to crystallise at  $25^\circ$ , and then, to ensure equilibrium, shaking for several days in a thermostat at the same temperature. The solubility data indicate that the only double salt has the composition  $NH_4Cl, 2PbCl_2$ . No evidence was obtained of the existence of the double salts,  $2NH_4Cl, PbCl_2$  and  $NH_4Cl, PbCl_2, H_2O$ , which have been described previously.

H. M. D.

**Double Cæsium Lead Bromides.** HARRY W. FOOTE (*Amer. Chem. J.*, 1907, 37, 124—126).—The conditions of formation of the known double bromides of cæsium and lead have been determined at  $25^\circ$  by solubility measurements. The following are mean values for the composition of the aqueous solutions saturated with respect to the compounds in the first column:

	% CsBr in solution	% PbBr <sub>2</sub> in solution
$PbBr_2 + CsBr, 2PbBr_2$ .....	0.28	0.32
$CsBr, 2PbBr_2 + CsBr, PbBr_2$ .....	17.75	—
$CsBr, PbBr_2 + 4CsBr, PbBr_2$ .....	36.80	—
$4CsBr, PbBr_2 + CsBr$ .....	54.43	—
$CsBr$ .....	55.23	—

H. M. D.

**Action of Carbon Dioxide on Aqueous Solutions of Lead Acetate.** ARTUR ALTMANN (*Zeitsch. anorg. Chem.*, 1907, 52, 219—228).—Solutions of lead acetate from  $N/50$  to  $2N$  were precipitated by excess of carbon dioxide at intervals of temperature from  $0-100^\circ$  and the precipitates analysed. The proportion of the salt precipitated (as normal carbonate) decreases with rise of temperature and increased concentration of the acetate.

From solutions heated at  $100^{\circ}$  for some time in a reflux apparatus the normal carbonate is precipitated, but when the heating is carried out in such a way that the acetic acid set free by hydrolysis, according to the equation:  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O} = \text{OH} \cdot \text{Pb} \cdot \text{C}_2\text{H}_3\text{O}_2 + \text{C}_2\text{H}_4\text{O}_2$ , is allowed to escape, the precipitate obtained with carbon dioxide from dilute solutions consists of the basic salt,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , whilst from strong solutions mixtures of the latter salt and normal carbonate are precipitated. G. S.

**Alloys of Copper and Nickel.** W. GUERTLER and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, 52, 25—29. Compare Gautier, Abstr., 1896, ii, 646).—The freezing-point curve of copper-nickel alloys falls regularly from the melting point of nickel to that of copper, indicating that the metals form a continuous series of mixed crystals; the curve is slightly concave to the axis of composition.

Pure nickel has a transition point at  $320^{\circ}$ , above which it is no longer magnetic; the transition temperature is progressively lowered by addition of copper and occurs at about  $30^{\circ}$  when 42% of the latter element is present.

The deductions from the freezing-point observations are borne out by a microscopic examination of etched surfaces; even in slowly-cooled alloys, however, the mixed crystals are not quite homogeneous. G. S.

**Electrolytic Formation of Copper Peroxide.** ERICH MÜLLER and FRITZ SPITZER (*Zeitsch. Elektrochem.*, 1907, 13, 25—27).—When a solution of cupric oxide in a very concentrated solution of sodium hydroxide is electrolysed, a yellow substance is formed at the anode which behaves like a peroxide. The same substance is produced when 12*N* sodium hydroxide is electrolysed with a copper anode at low temperatures with a current density of about 0.2 ampere per sq. cm. The substance decomposes into oxygen and copper oxide and cannot be obtained in a pure state. By comparing the loss of weight of the anode with the quantity of electricity used and the quantity of oxygen evolved, it is found that the copper dissolves in the tervalent condition; the substance may therefore be  $\text{Cu}_2\text{O}_3$ . T. E.

**Cuprous Metaphosphate.** VICTOR AUGER (*Compt. rend.*, 1907, 144, 199—200).—When metaphosphoric acid heated to dull redness is added to excess of copper turnings contained in a platinum capsule provided with a lid and heated to a similar temperature, the copper dissolves with evolution of hydrogen and the mass becomes brown.

The latter is immediately oxidised by air, but if the mass is poured off from the unattacked copper into a platinum crucible and protected from air, on cooling it deposits lamellæ of copper in weight equal to that subsequently found in the residual mass in the form of cupric phosphate. The cuprous metaphosphate formed is thus stable at a red heat, but decomposes on cooling into cupric metaphosphate and copper.

If the fused mass of cuprous metaphosphate dissolved in excess of metaphosphoric acid is allowed to fall in small drops into methyl

chloride, transparent vitreous, pale yellow beads of cuprous metaphosphate dissolved in excess of metaphosphoric acid are obtained. These can be kept in a sealed tube for some days, but gradually become reddish-brown and opaque. The change occurs immediately on warming. E. H.

**A New Silicide of Manganese Described by Gin.** PAUL LEBEAU (*Compt. rend.*, 1907, 144, 85—86).—Polemical against Gin. The crystalline manganese silicide described by Gin (this vol., ii, 92) is probably an impure specimen of the compound  $\text{SiMn}_2$ , discovered by Vigouroux (*Abstr.*, 1896, ii, 249) and reproduced by the author (*Abstr.*, 1904, ii, 343). M. A. W.

**Colloidal Ferric Hydroxide. IV. Preparation of Colloidal Ferric Hydroxide in Presence of Barium Nitrate, Potassium Chloride, and Potassium Nitrate.** A. V. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 595—596. Compare *Abstr.*, 1905, ii, 714).—The author regards colloidal solutions of ferric hydroxide as emulsions of very small bubbles, the walls of which consist of the colloidal substance, and the contents either of the solution used or, in some cases, of water. Where the walls of the bubbles are impermeable to the salt in solution, they are pressed together and so precipitated by the increased osmotic pressure caused by raising the concentration of the salt. If, however, these colloidal membranes are pervious to the salt, no such precipitation occurs, the added salt being distributed between the solutions inside and outside of the bubbles. The author has, indeed, prepared colloidal ferric hydroxide solutions containing, per litre, 8.69 grams of barium nitrate, or 2.152 grams of potassium chloride, or about 4 grams of potassium nitrate. T. H. P.

**Preparation of Small Quantities of Chromium for Lecture Experiment, &c.** J. OLIE, JUN. (*Chem. Centr.*, 1906, ii, 1755; from *Chem. Weekblad*, 3, 662—663).—In order to demonstrate the preparation of chromium, 50 grams of potassium dichromate, which has been melted and powdered, is mixed with 18 grams of well-dried aluminium powder and 20 grams of this powder incorporated with 100 grams of a mixture of 160 grams of dry aluminium powder with 450 grams of calcined chromium oxide. The mass is ignited by means of a mixture of barium peroxide and aluminium powder and magnesium ribbon. The yield varies from 50 to 75%, and is better when larger quantities are used. In the latter case the proportion of the first mixture may be reduced to 10 to 15 grams. E. W. W.

**Chromium Boride.** EDGAR WEDEKIND and K. FETZER (*Ber.*, 1907, 40, 297—301. Compare Moissan, *Abstr.*, 1894, ii, 454; Binet du Jassoneix, *ibid.*, 1907, ii, 30; Tucker and Moody, *Trans.*, 1902, 81, 16).—This is an extension of the inquiry into the synthetic use of the aluminothermic process for the combination of metals and metalloids (*Abstr.*, 1905, ii, 322). Whereas pure chromium boride cannot be prepared from a mixture of boron and chromium oxide in an electric furnace as the carbon cannot be removed, it is obtained as a silver

white, crystalline powder when boron and chromium thermite are caused to interact. The excess of chromium is removed from the powdered regulus by treatment with dilute hydrochloric acid, followed by nitric acid, and, finally, aqua regia.

*Chromium boride*,  $\text{CrB}$ , is more difficult to fuse than chromium, and has  $D^{17}$  5.4, and hardness 8. Acids or alkalis have no action on the boride, even hydrofluoric acid alone, or when mixed with nitric acid. It is only slightly attacked by molten sodium hydroxide, potassium nitrate, or potassium chlorate; sodium peroxide, however, oxidises it with incandescence to borate and chromate. When heated in oxygen to a red heat, the boride only undergoes a very slight change in colour. Chromium boride has weak magnetic properties. W. R.

**Action of Silicon Tetrachloride on Chromium.** ÉMILE VIGOUROUX (*Compt. rend.*, 1907, 144, 83—85. Compare Abstr., 1906, ii, 32, 287, 451).—Silicon chloride is decomposed by prolonged heating in contact with pure chromium at  $1200^{\circ}$ , yielding chromous chloride and the chromium silicide,  $\text{Cr}_3\text{Si}_2$  (compare Lebeau and Figueras, Abstr., 1903, ii, 486), 60 grams of chromium yielding 15 grams of the silicide. M. A. W.

**Proportion of Chlorine Precipitated by Silver Salts from Solutions of the Green Hydrate of Chromium Chloride.** J. OLIE, JUN. (*Zeitsch. anorg. Chem.*, 1907, 52, 48—61).—The paper consists mainly of a discussion of the results of Weinland and Koch (Abstr., 1904, ii, 488) on the influence of the nature and concentration of the silver salt and the nature of the free acid on the proportion of chlorine precipitated by silver salts from solutions of the green hydrate of chromium chloride, with some additional observations.

According to Werner, only one-third of the chlorine should be precipitated by silver salts, whereas Weinland and Koch, who always used at least 3 equivalents of the silver salt in neutral solution, found that more than 2 equivalents of chlorine were precipitated. The author has used smaller proportions of silver salts and finds that even 2.11 equivalents of silver nitrate precipitate 2 equivalents of chlorine. Whereas the silver salts of strong acids only partially precipitate the chlorine, the silver salts of weak acids precipitate the 3 equivalents almost completely; this is ascribed to the action of the latter class of salts in removing hydrogen ions.

The action of neutral salts, such as sodium and ammonium nitrates on precipitation by silver nitrate, is slight in small concentration, but a large amount of these salts greatly increases the proportion of chlorine thrown down.

Strong acids at first cause a decrease in the proportion of chlorine precipitated until in certain concentrations only 1 equivalent is affected; stronger solutions cause an increase in the amount precipitated. Weak acids have a much smaller effect. It is suggested that the great effect of strong acids and neutral salts when present in considerable concentration is due to direct exchange of the chlorine in the positive nucleus for other groups. G. S.



**Dehydration of the Isomeric Hydrates of Chromium Chloride.** J. OLIE, JUN. (*Zeitsch. anorg. Chem.*, 1907, 52, 62—67).—According to Werner, the green hydrate of chromium chloride has 4 molecules of water of constitution and 2 of water of crystallisation, whereas the  $6\text{H}_2\text{O}$  of the violet chloride is water of constitution. Werner's dehydration experiments have been repeated at the ordinary temperature and the results confirmed.

Further, the green salt was heated in a vacuum over sulphuric acid, the temperature being gradually raised to  $100^\circ$ . Under these circumstances the salt did not melt; on long continued heating it lost rather more than  $4\text{H}_2\text{O}$  as well as a little hydrogen chloride, and left a dark violet residue of the approximate composition,  $\text{Cr}_2\text{Cl}_5\text{OH}\cdot 4\text{H}_2\text{O}$ , which dissolved in water to form a solution almost identical in appearance and behaviour with that of the original green salt.

The violet salt, heated under the same conditions, lost rather less than  $4\text{H}_2\text{O}$ , and left a residue of approximately the same composition as that obtained from the green salt. G. S.

**A Chromium Sulphate in which the Acid is Entirely Masked, and the Equilibrium of Chromic Solutions.** ALBERT COLSON (*Compt. rend.*, 1907, 144, 79—81).—When a slightly acid solution of commercial chromium sulphate is allowed to evaporate spontaneously after several months' exposure to sunlight (Abstr., 1906, ii, 74), a mixture of violet and green salts is obtained, from which the sulphate,  $\text{Cr}_2(\text{SO}_4)_3\cdot 6\text{H}_2\text{O}$ , can be isolated by the action of alcohol in the form of transparent, green leaflets, insoluble in absolute alcohol, and sparingly soluble in 70% alcohol; it is identical with the sulphate obtained from a chromic acid solution saturated at  $-4^\circ$  with sulphur dioxide (Abstr., 1906, ii, 233).

A cold solution of chromium sulphate is therefore an equilibrium mixture of the violet sulphate and the three green sulphates,  $\text{Cr}_2(\text{SO}_4)_3\cdot 6\text{H}_2\text{O}$ ;  $\text{Cr}_2(\text{SO}_4)_2(\text{OH})(\text{SO}_4\text{H})$ , and  $\text{Cr}_2\text{SO}_4(\text{OH})_2(\text{SO}_4\text{H})_2$ . M. A. W.

**Condensed Chromic Sulphates.** ALBERT COLSON (*Compt. rend.*, 1907, 144, 206—208. Compare Abstr., 1905, ii, 94; Recoura, Abstr., 1896, ii, 27).—The equilibrium indicated in the following equation,  $2\text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Cr}_4\text{O}(\text{SO}_4)_5$ , is only relatively stable, and the pentasulphate,  $\text{Cr}_4\text{O}(\text{SO}_4)_5$ , is acted on by boiling water with momentary production of a fresh quantity of acid, thus:  $\text{Cr}_4\text{O}(\text{SO}_4)_5 + \text{H}_2\text{O} = \text{Cr}_4\text{O}_2(\text{SO}_4)_4 + \text{H}_2\text{SO}_4$ . This is proved by the repeated boiling of a  $N/10$  solution of the normal green sulphate,  $\text{Cr}_2(\text{SO}_4)_3\cdot 10\text{H}_2\text{O}$ , cooling very rapidly, and then adding baryta solution. Measurement of the heat developed shows that each successive boiling after the first liberates sulphuric acid according to the second equation.

From its exceedingly slow rate of dissolution in cold water and from its cryoscopic behaviour, the author considers that the green sulphate obtained by Wyrouboff (Abstr., 1902, ii, 565) by drying the violet sulphate at  $110^\circ$  has not the formula,  $\text{Cr}_2(\text{SO}_4)_3\cdot 5\text{H}_2\text{O}$ , attributed to it by that author, but is a condensed sulphate. By drying the powdered violet sulphate at  $90^\circ$  for twelve hours, it loses  $11\text{H}_2\text{O}$ , and the pro-

duct is much more rapidly dissolved by cold water than is the sulphate dried at  $110^{\circ}$ . A cryoscopic determination showed that the lowering of the freezing point of the solution obtained is approximately half that given by the normal sulphate containing the same amount of chromium. The formula  $\text{SO}_4 \cdot \text{Cr} \cdot \text{SO}_4 \cdot \text{Cr} \cdot \text{SO}_4$  is suggested for the green sulphate.

E. H.

**Dichromate and Chromate.** JULIUS SAND and K. KAESTLE (*Zeitsch. anorg. Chem.*, 1907, 52, 101—103. Compare Abegg and Cox, Abstr., 1904, ii, 662; Sand and Eisenlohr, following abstract).—Abegg and Cox consider that a dichromate solution contains mainly  $\text{CrO}_4^{''}$  ions and undissociated chromic acid, the proportion of  $\text{Cr}_2\text{O}_7^{''}$  ions being small. The authors adduce evidence to show that the acid resulting from the hydration of chromium trioxide is at least of medium strength, and suggest that in dichromate solutions there is a hydrolytic equilibrium,  $\text{Cr}_2\text{O}_7^{''} + \text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{''} + 2\text{H}$ . The experiments have, however, not led to a conclusive result.

If the above equilibrium exists in solution, the expression  $k = [\text{CrO}_4^{''}]^2[\text{H}]^2/[\text{Cr}_2\text{O}_7^{''}]$  must be constant. To test this point, the concentration of hydrogen ions in solutions of potassium dichromate, and in solutions of the same salt partially neutralised with potassium hydroxide, have been measured by their action on a mixture of potassium iodide and iodate, as already described. The reaction will be represented by the ionic equation,  $3\text{Cr}_2\text{O}_7^{''} + 5\text{I}^- + \text{IO}_3^- = 6\text{CrO}_4^{''} + 3\text{I}_2$ , and is accelerated by  $\text{H}^+$  ions.

The "constant," calculated on the above assumptions, gave values which were not even approximately equal. This deviation is not due to the direct action of dichromate on potassium iodide, as the rate of reaction between these substances is much slower than the main reaction. The disturbance is probably due to the catalytic effect of some product formed during the reaction.

For this reason the equilibrium constant cannot be accurately determined, but an approximate estimate gives  $k = 1.5 \times 10^{-13}$  at  $25^{\circ}$ , from which it can be calculated that a 0.1*N* solution of potassium dichromate is hydrolysed to the extent of 0.18%.

The constant,  $k_1$ , of the equation  $d[\text{I}_2]/dt = k_1[\text{H}]^2[\text{I}^-]^2[\text{IO}_3^-]$ , required for the determination of  $k$ , was determined directly; it has the value  $1.6 \times 10^{11}$  at  $25^{\circ}$ .

G. S.

**Polymolybdates. I. Progressive Neutralisation of Commercial Ammonium Molybdate.** JULIUS SAND and F. EISENLOHR (*Zeitsch. anorg. Chem.*, 1907, 52, 68—86).—Junius (Abstr., 1905, ii, 825) has shown that commercial ammonium molybdate has the formula  $(\text{NH}_4)_{10}\text{Mo}_{12}\text{O}_{41}$ . The authors in the course of an investigation of the progressive neutralisation of the salt by sodium hydroxide have obtained evidence that at least one intermediate polymolybdate ion,  $\text{Mo}_6\text{O}_{22}^{8-}$ , is formed before the bivalent orthomolybdate ion,  $\text{MoO}_4^{2-}$ , is reached.

Ammonium molybdate seems to undergo ionisation normally,  $(\text{NH}_4)_{10}\text{Mo}_{12}\text{O}_{41} = 10\text{NH}_4^+ + \text{Mo}_{12}\text{O}_{41}^{10-}$ . On progressive neutralisation

there are two possibilities: (1) in the original solution there may be a hydrolytic equilibrium,  $\text{Mo}_{12}\text{O}_{41}^{10'} + 7\text{H}_2\text{O} \rightleftharpoons 12\text{MoO}_4^{''} + 14\text{H}^+$ , in which case the gradual addition of sodium hydroxide will remove the  $\text{H}^+$  ions, and in all stages of the process there will be equilibrium between  $\text{Mo}_{12}\text{O}_{41}^{10'}$ ,  $\text{MoO}_4^{''}$  and  $\text{H}^+$  ions in varying proportions; (2) there may be one or more intermediate polymolybdate ions. Experiment shows that the second alternative is correct and the composition of one polymolybdate has been determined by an electrochemical method (this abstract) and by a kinetic method (succeeding abstract).

It is pointed out that if a simpler polymolybdate is formed during neutralisation, the curve representing the hydrogen ion concentration plotted against the amounts of sodium hydroxide added must show a break. To test this point, the *E.M.F.* of a polymolybdate solution in which the hydrogen ion concentration remained constant throughout the experiment was measured against a corresponding solution, to which gradually increasing amounts of sodium hydroxide were added, and a distinct break in the curve was observed. From the position of the break, it was estimated to occur when one of the two equations,  $\text{Mo}_{12}\text{O}_{41}^{10'} + 6\text{OH}' = 2\text{Mo}_6\text{O}_{22}^{8'} + 3\text{H}_2\text{O}$  or  $\text{Mo}_{12}\text{O}_{41}^{10'} + 6\text{OH}' = 4\text{Mo}_3\text{O}_{11}^{''''} + 3\text{H}_2\text{O}$ , is satisfied. The form of the curve is in favour of the first equation, and this view was confirmed by a kinetic method (see succeeding abstract).

There are indications that a second polymolybdate ion is formed in the course of neutralisation, and the matter is being further investigated. G. S.

**Polymolybdates. II. Action of the Iodide-Iodate Mixture on Ammonium Molybdate.** JULIUS SAND and F. EISENLOHR (*Zeitsch. anorg. Chem.*, 1907, 52, 87—100. Compare preceding abstract).—In the former paper, evidence has been adduced to show that the complex ion of ammonium molybdate is partially hydrolysed in solution according to the equation  $\text{Mo}_{12}\text{O}_{41}^{10'} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{Mo}_6\text{O}_{22}^{8'} + 6\text{H}^+$ ; in the present paper this view is confirmed, and the determination of the numerical value of  $k = [\text{Mo}_6\text{O}_{22}^{8'}]^2[\text{H}^+]^6 / [\text{Mo}_{12}\text{O}_{41}^{10'}]$  described.

Dushman (Abstr., 1904, ii, 718) has shown that the rate at which iodine is liberated from a mixture of potassium iodide and iodate in acid solution is proportional to the iodate ion concentration and to the square of the iodine and hydrogen ion concentrations. As this affords a convenient means of measuring hydrogen ion concentrations, the rate at which iodine was liberated from mixtures of potassium iodide and iodate with ammonium molybdate was determined. Whilst no constant value for  $k$  is obtained on the assumption that  $\text{Mo}_3\text{O}_{11}^{''''}$  ions are present (compare previous abstract), good constants are obtained on the view that  $\text{Mo}_6\text{O}_{22}^{8'}$  ions take part in the equilibrium. The numerical value of  $k$  at  $25^\circ$  is  $3.80 \times 10^{-31}$ , from which it can be calculated that a 0.01 molar solution of ammonium molybdate is hydrolysed to the extent of 0.19% and is  $1.17 \times 10^{-4}$  normal with regard to hydrogen ions. G. S.

**Thorium Chloride, Oxychloride, Hydride and Nitride.** CAMILLE MATIGNON and MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1907, [viii], 10, 130—144).—This paper gives a fuller account of work

already partly recorded (Abstr., 1901, ii, 106 ; compare also Abstr., 1901, ii, 60 ; Krüss, *ibid.*, 1897, ii, 456 ; Rosenheim, Samster, and Davidsohn, *ibid.*, 1903, ii, 601 ; Matignon and Bourion, *ibid.*, 1904, ii, 340 ; Moissan and Martinsen, *ibid.*, 1905, ii, 531). Anhydrous thorium tetrachloride may be prepared by heating thoria strongly in a porcelain tube and passing over it a current of carbon monoxide and chlorine, but more rapidly by heating the oxide to a temperature below that of the melting point of thorium tetrachloride in the vapour of carbon tetrachloride. The principal by-product of the reaction is carbonyl chloride, but small quantities of hexachloroethane and tetrachloroethylene are also produced, probably due to the decomposition of the carbon tetrachloride under the influence of heat.

In the foregoing reaction, *thorium oxychloride*,  $\text{ThOCl}_2$ , appears to be produced as an intermediate product, and may be isolated by stopping the reaction when the product contains thorium tetrachloride and thoria in the ratio 8 or 9 : 1, and treating this with absolute alcohol, when a residue of the oxychloride in small, colourless needles is obtained. It is soluble in water without decomposition, but is slowly attacked by alcohol with the elimination of a small quantity of chlorine. The anhydrous oxychloride on exposure to air absorbs moisture and is converted into the hexahydrate described by Rosenheim, Samster, and Davidsohn (*loc. cit.*). The latter, under reduced pressure, forms the *pentahydrate*,  $\text{ThOCl}_2 \cdot 5\text{H}_2\text{O}$ , and this dehydration appears to proceed further with the eventual formation of a *trihydrate*. It was found impossible to prepare pure thorium by reducing thoria with sodium (compare Moissan and Hönigschmidt, Abstr., 1906, ii, 678).

Thorium hydride,  $\text{ThH}_4$ , is not rapidly decomposed by water or hydrochloric acid in the cold ; it is completely dissociated at  $390^\circ$  under atmospheric pressure. The heat of formation, deduced indirectly (compare Matignon, 1899, ii, 273 ; 1905, ii, 235), is 21.4 Cal., whence it appears that it is more easily dissociated than the hydrides of barium, lithium, and calcium.

Thorium nitride,  $\text{Th}_3\text{N}_4$ , prepared by heating thorium strongly in a current of nitrogen, is a yellowish maroon powder, infusible at a red heat, and is decomposed slowly by cold and immediately by warm water, liberating ammonia. It is not dissociated even at a red heat in a vacuum, but burns in the air with incandescence, but without the sparkling brilliance of thorium. The nitride described by Kohlschütter (Abstr., 1901, ii, 598) is not decomposed by water or acids, and his suggestion that it is a polymeride of the foregoing is scarcely tenable as it is lighter in colour, and since it has not been obtained free from thoria it is probably an oxynitride of the formula  $\text{Th}_4\text{N}_2\text{O}_5$ .

T. A. H.

**Decomposition of Antimony Hydride.** ALFRED STOCK, FRANZ GOMOLKA, and HANS HEYNE MANN (*Ber.*, 1907, 40, 532—570. Compare Stock and Guttmann, Abstr., 1904, ii, 246).—The rate of decomposition of antimony hydride in glass vessels in the presence of an antimony mirror has been determined from the increase of pressure at constant volume, a correction being applied for the molecular attraction of the hydride, which causes a deviation from

Boyle's law of 12.6 mm. at 25° and 760 mm. With a given vessel and a mirror deposited at 150° the initial velocity of reaction is fairly constant, but in successive experiments in the same vessel the initial velocity is constant only after the superposition of three mirrors upon one another.

The authors confirm Stock and Guttman's observation that the activity of an antimony mirror is determined largely by the nature of the surface, but deny that the activity is dependent on the concentration of the hydride from which the mirror is produced.

The authors contend that their measurements are those of a chemical reaction and not of diffusion phenomena, because the temperature coefficient is 2.050 between 15° and 25°, and 1.909 between 25° and 35°; the temperature coefficients of chemical reactions lie between 2 and 3 at the ordinary temperature. The addition of hydrogen does not affect the rate of decomposition, and under given conditions, the relative velocity of the reaction is nearly proportional to the square root of the concentration of the antimony hydride.

In the presence of oxygen, the antimony mirror is poisoned completely for several hours; then it recovers and the reaction proceeds with increased velocity. The mirror is unaffected by oxygen in the complete absence of antimony hydride; hence the poisoning is due to oxidation, not of the mirror itself, but of the hydride or of some compound formed intermediately, by which a layer of oxide is formed and destroys contact between the hydride and the catalyst. The "revivifying" of the mirror may be due to the reduction of this oxide by the antimony hydride; the increased velocity of the reaction is not due to the water so produced, but may be consequent on changes in the surface of the catalyst caused by successive oxidation and reduction.

Black antimony (compare Stock and Siebert, *Abstr.*, 1906, ii, 34) is not poisoned by oxygen, and is changed into the ordinary metallic mirror after the decomposition of the antimony hydride has been in progress for a few minutes.

Photographs of antimony mirrors, produced under different conditions, are given. C. S.

**Theory of the Decomposition of Antimony Hydride.** ALFRED STOCK and MAX BODENSTEIN (*Ber.*, 1907, 40, 570—575. Compare preceding abstract).—The results (*loc. cit.*) agree with those calculated by means of the equation  $M = aC^p$ , where  $M$  is the quantity adsorbed,  $C$  the concentration of the hydride, and  $a$  and  $p$  constants dependent on the nature of the substance and the temperature. The decomposition of antimony hydride is probably a slow chemical reaction, modified by adsorption phenomena. C. S.

**Peroxides of Bismuth.** V. ALEXANDER GUTBIER and R. BÜNZ (*Zeitsch. anorg. Chem.*, 1907, 52, 124—126. Compare *Abstr.*, 1906, ii, 174, 234, 551, 678).—Lorch (*Inaug. Diss., Munich*, 1893) claims to have obtained sodium metabismuthate by the action of sodium peroxide and chlorine on bismuth hydroxide at the temperature of a freezing mixture. The authors have repeated his experiments, and find that

the products are brown in colour, completely soluble in concentrated nitric acid, continue to lose alkali on washing, and contain comparatively little active oxygen. They consider that derivatives of "bismuthic acid" cannot be obtained in the presence of sodium hydroxide.

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G. S.

## Mineralogical Chemistry.

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**Fumarole Action. II.** FERDINAND HENRICH (*Zeitsch. angew. Chem.*, 1907, 20, 179—181. Compare Abstr., 1906, ii, 685).—In extension of his previous experiments, the author has found that on passing a slow current of steam over a mixture of sand and sodium or potassium chloride heated to bright redness, an appreciable quantity of these salts is volatilised. This fact serves to account for the presence of sodium or potassium chloride on the surface of fumaroles. P. H.

**Cinnabar from Sonoma Co., California ; Gypsum and Calcite from Terlingua, Texas.** ARTHUR SACHS (*Centr. Min.*, 1907, 17—19).—Crystallographic descriptions are given of these minerals.  
L. J. S.

**Uranium Ores from German East Africa.** WILLY MARCKWALD (*Centr. Min.*, 1906, 761—763).—Enclosed in sheets of mica from Lukwengule in the Uruguru Mountains, Morogoro district, are crystals of pitchblende, which are largely altered to a yellow uranyl carbonate. Analysis I is of the pitchblende, and II of the uranyl carbonate for which the name *rutherfordine*, after E. Rutherford, is proposed (not to be confused with rutherfordite from Rutherford Co., North Carolina)

	U <sub>3</sub> O <sub>8</sub> .	UO <sub>3</sub> .	PbO.	FeO.	CaO.	SiO <sub>2</sub> .	H <sub>2</sub> O.	CO <sub>2</sub> .	Gangue.	Total.	Sp. gr.
I.	87.8	—	7.5	1.0	2.1	0.3	0.5	0.2	99.4	8.84	
II.	—	83.8	1.0	0.8	1.1	—	0.7	12.1	0.8	100.3	4.82

Analysis II corresponds with the formula UO<sub>2</sub>CO<sub>3</sub>.

The carbon dioxide is not expelled below a temperature of 300°. Anhydrous uranyl carbonate has not before been met with in nature, nor has it been prepared artificially ; attempts to obtain it from the ammonium double salt were unsuccessful. The radioactivity of this pitchblende and of the rutherfordine is about 20% higher than that of pitchblende from Joachimsthal.  
L. J. S.

**Apatite and Milarite from Switzerland.** KARL BUSZ (*Centr. Min.*, 1906, 753—761).—A crystallographic description is given of adularia, quartz, milarite, and apatite from a new occurrence on the Rhone Glacier.

The perfectly developed crystals of the apatite are pale violet in colour ;  $a : c = 1 : 0.7335$ . The following analysis, by K. Walter, proves

the material to be an almost pure fluor-apatite. Determinations of the refractive indices are given :

Total, less										
P <sub>2</sub> O <sub>5</sub> .	(Al,Fe) <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	F.	Cl.	O for F. Sp. gr.
41·44	0·94	0·39	54·80	0·14	0·45	0·53	0·22	2·93	trace	100·61 3·195

L. J. S.

**Constitution of Biotite.** KARL DALMER (*Centr. Min.*, 1907, 51—58. Compare Abstr., 1898, ii, 440).—Tschermak's theory, which explains the composition of biotite by assuming mixtures of muscovite and olivine molecules, is discussed; the author finds it necessary to consider the olivine to be hydrated. Biotites are divided chemically into (1) normal biotites (mixtures of muscovite and olivine molecules), including anomite, haughtonite, protolithionite, meroxene, and lepidomelane; (2) acid biotites or phengite-biotites (mixtures of phengite and olivine, or of phengite, muscovite, and olivine molecules), including phlogopite and zinnwaldite.

L. J. S.

**Tourmaline from Brazil.** GUSTAV REIMANN (*Jahrb. Min.*, 1907, *Beil.-Bd.*, 23, 91—162).—Detailed descriptions are given of the forms of 160 crystals. The optical and pyro-electrical characters were also investigated.

L. J. S.

**Order of Separation in Silicate Fusions.** RUDOLF FREIS (*Jahrb. Min.*, 1907, *Beil.-Bd.*, 23, 43—90).—Mixtures of two or three of the minerals diopside, anorthite, olivine, nepheline, orthoclase, and magnetite were fused, and the melting points of the glasses and of the crystallised products were determined. In the latter, the order of separation of the minerals was: magnetite, olivine, diopside, anorthite, diopside, nepheline, orthoclase; this being the same order as given by Rosenbusch for igneous rocks, except that in the fusions diopside separated after as well as before anorthite. An accumulation of certain materials in the fusions is suggestive of magmatic differentiation. In these silicate fusions dissociation takes place, and the laws of dilute solutions are not applicable.

L. J. S.



### Physiological Chemistry.

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**Artificial Parthenogenesis by Momentary Elevation of Temperature.** RALPH S. LILLIE (*Proc. Amer. physiol. Soc.*, 1906, xvi—xvii; *Amer. J. Physiol.*, 18).—Exposure of star-fish eggs to 34—38° for from 30 to 120 seconds is followed by apparently normal development. W. D. H.

**Chemistry of Cell Division, Maturation, and Fertilisation.** ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1907, 18, 89—111).—The paper is highly speculative. The chemical basis of cell division is

probably a process of respiration, the astral figure being a localised region at the centre, of which there is intense reduction; an oxydase and free oxygen are other factors concerned. W. D. H.

**Temperature and Carbon Dioxide Excretion in Rats kept in Very Moist or Very Dry Atmospheres.** JOHN J. R. MACLEOD (*Amer. J. Physiol.*, 1907, 18, 1—13).—The harmful effect of a warm, humid atmosphere on man, as compared with dry air of the same temperature, is well known to experience, but has never been accurately investigated to any extent. The present research on rats showed that in these animals which do not depend greatly for heat regulation on evaporation from the body surface, little or no deleterious effect of humidity could be observed. Such animals, however, are not able to withstand hot, dry atmospheres so well as man can.

W. D. H.

**Contact Action in Biological Chemistry. Enzyme and Plasma.** THOMAS BOKORNY (*Chem. Zeit.*, 1907, 31, 139—141).—A variety of reactions which are effected by organised ferments or by enzymes may also be brought about by means of inorganic catalysts. The efficiency of an inorganic catalyst may be impaired by certain substances, but can, as a rule, be restored by suitable treatment, whereas a ferment once poisoned is completely destroyed. The phenomena of respiration and assimilation are regarded as examples of enzyme action. P. H.

**The Sugar in Blood and Tissues.** EDWARD S. EDIE and D. SPENCE (*Bio-chem. J.*, 1907, 2, 103—111).—The blood with aseptic precautions is dialysed against saline solution for 40—50 hours in an ice chamber, and the sugar in the dialysate estimated by a gravimetric copper method. The sugar is present (1) as free sugar, (2) in combination with proteid or lecithin, and (3) as polysaccharide. The method, although lengthy, is regarded as more trustworthy than others, such as the mercury precipitation method. The corpuscles are devoid of sugar. W. D. H.

**Oxydases in Blood.** WALTHER EWALD (*Pflüger's Archiv*, 1907, 116, 334—346).—A discussion of the work of others on the three oxydases described in blood precedes the experimental portion of the paper. The three enzymes are  $\alpha$ -oxydase, which oxidises easily oxidisable substances; peroxydase, which activates intermediate peroxides and so oxidises substances difficult of oxidation; and superoxydase (catalase or hæmase), which serve as a protective means of the body cells against the too great activity of peroxydases. This is the view of Bach and Chodat, which is regarded as untenable by the author. Cyanide poisoning is shown to lessen the amount of catalase, and to increase the readiness with which oxyhæmoglobin is reduced.

W. D. H.

**Action of Serum and Tissue Extracts on Blood Coagulation.** LEO LOEB (*Proc. Amer. physiol. Soc.*, 1906, xvii; *Amer. J. Physiol.*, 18).—Both the coagulin of tissue extracts and the thrombin

of serum are believed to act independently on fibrinogen. This conclusion is drawn mainly from observations on invertebrate blood, but it is unlikely that there is any essential difference between this and vertebrate blood, although in the latter case complications arise from the presence of substances in the serum which accelerate or hinder the action of tissue coagulins. W. D. H.

**Influence of Lecithin on Digestive Ferments.** SIEGMUND KÜTTNER (*Zeitsch. physiol. Chem.*, 1907, 50, 472—496).—The results obtained by the addition of lecithin emulsion to an artificial gastric digest appear to be very varying; the methods adopted were numerous, and included that with Mett's tubes. The general conclusion is drawn that the influence of lecithin below certain limits is beneficial; above these it hinders protein-hydrolysis. The same conclusion is drawn in reference to trypsin. The favouring influence of lecithin on the fat-splitting enzyme of pancreatic juice is more marked. W. D. H.

**Occurrence of Indole in Human Gastric Contents.** HERMANN STRAUSS (*Biochem. Zeitsch.*, 1907, 3, 26—29).—In reference to the discovery of indole in the gastric contents by Albu and Neuberg in cases of gastric cancer, the author points out that he once found it in a case of stenosis, in which the putrefactive process occurred in the stomach. He has since searched for it, but never found it in similar cases. In the author's case, as in cancer, there was subacidity of the gastric juice. W. D. H.

**The Occurrence of Erepsin in the Pancreas.** HORACE M. VERNON (*Zeitsch. physiol. Chem.*, 1907, 50, 440—441).—Polemical against K. Mays (this vol., ii, 38). W. D. H.

**The Lipase of Intestinal Juice.** W. BOLDYREFF (*Zeitsch. physiol. Chem.*, 1907, 50, 394—413).—Lipase is present in pure intestinal juice. It acts better on emulsified than on non-emulsified fats. It is weaker than pancreatic lipase; its action is not favoured by the presence of bile, and but little weakened by the presence of antiseptics. W. D. H.

**The Value of Betaine in the Sheep.** W. VÖLTZ (*Pflüger's Archiv*, 1907, 116, 307—333).—If betaine is given to a dog, the total nitrogen in it is excreted the same day. In herbivora (sheep), it is retained longer in the body. In these animals, contrary to what is found in carnivora, betaine is split up in the body, and some of the non-nitrogenous portion is not excreted in the urine; it is possible that this is harmful. W. D. H.

**Katabolism of Glycine in Badly Nourished Conditions of the Infant.** LUDWIG F. MEYER and HANS RIETSCHEL (*Biochem. Zeitsch.*, 1907, 3, 31—44).—In normal conditions, glycine is completely burnt in the body. In the present investigation, it was added to the food of infants suffering from malnutrition. They show a diminution of the power to utilise glycine; in some cases, acidosis and glycosuria occurred also. The condition is regarded as one in which the oxidative energy of the body is lessened. W. D. H.

**Creatine and Creatinine in Human Metabolism.** KJ. OTTO and KLERCKER (*Biochem. Zeitsch.*, 1907, 3, 45—87. Compare Abstr., 1906, ii, 295).—Any biological relationship between these two bases is questionable. If given to an animal they are excreted in the urine unchanged, and of the two creatinine is the more readily eliminated. Urinary creatinine is wholly of endogenous origin; its relationship to the muscular creatine has not been proved, and is considered uncertain. Folin has come to much the same conclusions.

W. D. H.

**The Mechanism of Proteid Assimilation.** CH. INAGAKI (*Zeitsch. physiol. Chem.*, 1907, 50, 449—471).—Nucleo-histone unites with proteoses in a salt-like way, so long as it is in a free or dissociated condition, so that it is possible that proteoses introduced into the blood stream may be fixed by the cell substance in this way. No evidence of any such fixation was found in the blood itself.

W. D. H.

**Sparing Action of Gelatin.** J. R. MURLIN (*Proc. Amer. physiol. Soc.*, 1906, xii—xiii; *Amer. J. Physiol.*, 18).—Lusk and Nolan showed that, in diabetes, gelatin may yield up to 60% of its weight as dextrose. The present research was made to determine to what extent this carbonaceous part of the gelatin molecule will account for its proteid-sparing action, but the conclusion is arrived at that this action is entirely accounted for by its nitrogenous constituents.

W. D. H.

**The Replacement of Proteid by Gelatin.** PETER RONA and W. MÜLLER (*Zeitsch. physiol. Chem.*, 1907, 50, 263—280).—The sparing-action of gelatin is one of the oldest known facts in reference to metabolic investigations. Its power to replace other proteids is limited, and this is now explicable because it lacks the tyrosine and tryptophan groups. Kaufmann (Abstr., 1905, ii, 735) is one of the latest to determine the extent of sparing-action, and the present experiments, like his, were made on dogs, but in this case the addition of the missing groups did not increase the value of the gelatin.

W. D. H.

**Action of Vegetable Cathartics on the Isolated Centre of a Jelly-Fish.** JOHN B. MACCALLUM (*J. Biol. Chem.*, 1907, 2, 385—390).—Various vegetable purgatives stimulate the isolated central portion of *Polysorchis* to contract rhythmically. There is, however, no proof that this region is free from nerves, and so no conclusion can be drawn that the purgatives act on the muscular tissue alone.

W. D. H.

**Nutrition of the Excised Mammalian Heart.** CHARLES C. GUTHRIE and F. H. PIKE (*Amer. J. Physiol.*, 1907, 18, 14—38).—Defibrinated blood and serum were found superior to saline solutions for keeping the excised heart beating. A certain degree of capillary pressure appears also to be essential. A strip of cat's aorta behaves very like a strip of ventricle.

W. D. H.

**Cause of the Staircase Phenomenon.** FREDERIC S. LEE (*Proc. Amer. physiol. Soc.*, 1906, xviii—xix; *Amer. J. Physiol.*, 18).—The staircase phenomenon in muscle is due to the accumulation of fatigue products, namely, carbon dioxide, mono-potassium phosphate, and sarcolactic acid.

W. D. H.

**Creatinine and Creatine in Meats and their Products.** HARRY S. GRINDLEY and H. S. WOODS (*J. Biol. Chem.*, 1907, 2, 309—326).—Folin's colorimetric method was employed. Contrary to C. S. Johnson's statement, fresh meat contains only the faintest trace of creatinine. The results of creatine estimation in various fresh meats are given in tabular form. Similar determinations are given for various meat extracts; in these the proportion of the two substances varies very much.

W. D. H.

**Formation of Fat in Animals Fattened for Slaughter.** GEORGE T. KEMP and L. D. HALL (*Proc. Amer. physiol. Soc.*, 1906, xix; *Amer. J. Physiol.*, 18).—The fat was never found microscopically within the sarcolemma; still very lean flesh yields more fat by extraction than can be accounted for by the adipose tissue revealed by the microscope. No support was found in favour of the view that toughness of meat is due to the thickening of the sarcolemma.

W. D. H.

**Chemical Examination of Human Bone-Marrow under different Pathological Conditions.** JULIUS WOHLGEMUTH (*Chem. Centr.*, 1906, ii, 1770; from *Arbeit. Path. Inst. Berlin*).—The presence of albumoses, and principally of deutero-albumoses and a nucleo-proteid which contained a considerable quantity of phosphorus, has been detected in a number of samples of human bone-marrow. When the aqueous extract was made faintly acid with acetic acid, a precipitate was formed which after washing, dissolving in sodium carbonate, and reprecipitating formed a snow-white powder which gave a moderately strong reaction with orcinol-hydrochloric acid; it contained 45.01% C, 5.91% H, 14.21% N, 1.78% P, and 0.315% S.

E. W. W

**The Change Produced in Milk by Sodium or Potassium Hydroxide.** FRIEDRICH KRÜGER (*Zeitsch. physiol. Chem.*, 1907, 50, 293—302).—Gautier and Morel have recently pointed out that the addition of potassium or sodium hydroxide to milk causes a red coloration. The present paper points out that the reaction was described by the author twelve years ago. The best result is obtained when the milk contains 1—2% of sodium hydroxide. All attempts to separate the colouring matter have failed, but the presence of both caseinogen and lactose is necessary for its production. An elevated temperature increases the rapidity of its appearance.

W. D. H.

**Bile in Human Milk.** J. L. B. VAN DER MARCK (*Pharm. Weekblad*, 1907, 44, 153—155).—The author has detected bile in a sample of human milk from a patient who developed jaundice after

each confinement. The milk was a deep yellow colour with a green fluorescence. After thirty minutes, it had separated into a deep yellow, fatty layer, and an almost colourless aqueous liquid. The percentage of solid residue was 13.1, including 7.14% of fat, 2.09% of lactose, 0.124% of ash, and 3.746% of proteids. The fat contained urobilin and a smaller amount of bilirubin, but the aqueous liquid was wholly free from them.

A. J. W.

**[Alleged] Formation of Free Nitrogen During Intestinal Putrefaction.** AUGUST KROGH (*Zeitsch. physiol. Chem.*, 1907, 50, 289—292. Compare Schittenhelm and Schröter, *Abstr.*, 1904, ii, 139; Oppenheimer, *ibid.*, 361).—Free nitrogen is not found in intestinal putrefaction.

W. D. H.

**The Effect of Amino-Acids on the Elimination of Acetone Derivatives.** L. BORCHARDT and F. LANGE (*Beitr. chem. Physiol. Path.*, 1907, 9, 116—133. Compare Borchardt, *Abstr.*, 1906, ii, 312; Embden, Salomon, and Schmidt, *Abstr.*, 1906, ii, 375).—Glycine, alanine, and asparagine tend to reduce the amount of acetone eliminated from the organism both in the urine and in the breath. Glutamic acid does not tend to increase the amount of acetone, whereas leucine produces a considerable increase in the acetone eliminated. In all cases the amount in the breath was less than that in the urine.

J. J. S.

**Phenolglycuronic Acid.** ERNST SALKOWSKI and CARL NEUBERG (*Biochem. Zeitsch.*, 1907, 2, 307—311).—Neuberg and Naimann's synthetic phenolglycuronic acid (*Abstr.*, 1905, i, 412) is identical with the acid obtained from the urine of a sheep to which 500 grams of phenol had been administered, at the rate of 5 grams per day. The phenolglycuronic acid may be separated from the benzoic and hippuric acids which are also formed by means of cold water, in which it is readily soluble.

J. J. S.

**Occurrence of Bile Acids in Fæces under Normal and Pathological Conditions.** HANS URY (*Chem. Centr.*, 1906, ii, 1682; from *Arb. Path. Inst., Berlin*).—Normal fæces do not contain taurocholic or glycocholic acid, and cholic acid, if present, occurs only in extremely small traces. The bile acids, and in some cases their decomposition products, can be detected, however, in pathological excrements which have an abnormal consistency, but the quantity is small.

E. W. W.

**Influence of Work in Phloridzin Diabetes.** GRAHAM LUSK (*Proc. Amer. physiol. Soc.*, 1906, xii; *Amer. J. Physiol.*, 18).—Mechanical effort in a fasting dog made diabetic by phloridzin only slightly increases proteid metabolism, but leads to a slight increase in the sugar output, which may be derived from the residue of glycogen present in the animal.

W. D. H.

**Diastatic Ferment in the Tissues in Diabetes.** FRANCIS A. BAINBRIDGE and ARTHUR P. BEDDARD (*Bio-chem. J.*, 1907, 2, 89—95).—The liver and muscles of diabetic men and depancreatized cats contain a diastatic ferment, but whether in greater amount than usual was not ascertained. Sometimes it is present in the blood also. Its activity is not increased by the addition of a boiled extract of pancreas.

W. D. H.

**Treatment of Diabetes by Secretin.** NELLIS B. FOSTER (*J. Biol. Chem.*, 1907, 2, 297—304).—No benefit was observed in treating cases of diabetes with secretin. This coincides with the statements of Bainbridge and Beddard (*Abstr.*, 1906, ii, 786) as opposed to those of Moore and his colleagues (*ibid.*, ii, 186, 787).

W. D. H.

**Treatment of Diabetes by Secretin.** HENRY D. DAKIN and C. C. RANSOM (*J. Biol. Chem.*, 1907, 2, 305—307).—One case only is described; the use of secretin lessened the output of sugar slightly, but this was not permanent, nor so great as in Moore's cases.

W. D. H.

**Pharmacological "Action at a Distance."** ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1907, 18, 39—46).—Metallic silver and copper in the neighbourhood of echinoderm eggs cause them to put on fertilisation membranes. Mercury (when the eggs are sensitive), iodine, and bromine cause the same result. Iron, nickel, lead, tin, platinum, gold, and probably hydrogen were ineffective. Membrane formation is followed by liquefaction; this occurs only on the side toward the metal and away from the metalloid. This is explained on an electrical hypothesis, positive ions being driven away from, and negative ions attracted to, the metallic wire.

W. D. H.

**Pharmacological Action of Ammonium Salts.** ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1907, 18, 58—63).—Although the pharmacological action of most salts is ionic, in the case of ammonium salts, their characteristic stimulating action is due to the amount of undissociated ammonium hydroxide present, and probably to the nascent ammonia formed from the latter. In this case, there has therefore to be taken into account non-ionic or rather twin-ionic action such as that caused by  $\pm > \text{NH}_3$  particles. Perhaps the activity of free alkaloids is due to similar causes.

W. D. H.

**Rhythm of Turtle's Sinus Venosus in Isotonic Solutions of Non-Electrolytes.** HAROLD E. EGGERS (*Amer. J. Physiol.*, 1907, 18, 64—70).—Isotonic solutions of sugar, urea, and glycerol stimulate the turtle's sinus venosus, as they do the heart of *Limulus*. They act depressingly on the cardiac muscle of *Limulus*, and this is regarded as support to the neurogenic theory for the vertebrate heart. The action of these substances on heart tissue is through the osmotic factor.

W. D. H.

**Relation of Antitoxin to the Globulin of Blood-Serum. The Leucocyte Reaction during Immunisation with Diphtheria-Toxin.** J. C. G. LEDINGHAM (*J. Hygiene*, 1907, 7, 65—91, 92—100).—During the immunisation with diphtheria-toxin of a horse which finally failed to yield high-grade antitoxic serum, the globulin of the blood showed no tendency to increase. A slight rise in total proteid was due to albumin. The failure of the horse was probably related to the initial high globulin-content of its blood. In a goat, the rise in total proteid affected mainly the albumin fraction. In the case of a horse which yielded a high-grade serum, the globulin, and especially the euglobulin fraction, progressively increased. The pseudoglobulin contains most of, if not all, the antitoxin, but it is possible this holds good when the antitoxin content is steadily rising. In the goat, the antitoxin in the two kinds of globulin may vary at different periods in the course of immunisation.

The increase in polynuclear leucocytes which follows the injection of large and increasing amounts of diphtheria-toxin is merely an evidence of efficient cell-stimulation, and is not necessarily accompanied by increased formation of antitoxin. W. D. H.

**Tetanus-Toxin, Antitoxin, and Brain Emulsions.** L. NOON (*J. Hygiene*, 1907, 7, 101—104).—The affinity of brain matter for tetanus-toxin is specific, as is that of antitoxin. A solution of pure toxin is easily rendered innocuous by treatment with brain matter, but if a small dose of antitoxin has been added to the toxin some hours beforehand, treatment with brain matter no longer suffices to render the solution atoxic. The free toxin is removed, and a toxic compound of toxin and antitoxin was isolated. Both brain-toxin combinations and antitoxin-toxin compounds dissociate with more or less rapidity, unless in the presence of enough free toxin (and free brain or antitoxin) to maintain the state of equilibrium. Consequently, to obtain a neutral mixture, a large excess of brain or antitoxin must be added beyond the combining equivalent. The dissociation is thus reduced until free toxin is no longer recognisable. W. D. H.

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### Chemistry of Vegetable Physiology and Agriculture.

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**Bacteria which form Creatinine.** NINA AUTONOFF (*Centr. Bakt. Par.*, 1907, 43, i, 209—212).—Various bacilli of the Coli group were found to cause the formation of creatinine when grown in peptone broth. Subsequently it was found that the same property was possessed by micro-organisms of widely differing groups; a list of cases where positive and negative results were obtained is given. The bacteria which gave a positive result are usually also efficacious in forming acids.

W. D. H.

**Bacterial Decomposition of "Sulphocyanide."** RENATO PEROTTI (*Chem. Centr.*, 1906, ii, 1777—1778; from *Staz. sper. agrar. ital.*, 39, 406—412).—Solutions of "sulphocyanide," either alone or mixed with nutritive substances such as dipotassium hydrogen phosphate or dextrose, after remaining in water for twenty-four hours, were sterilised by heating in autoclaves for ten minutes at 120° on two successive days, and after filtering were again sterilised; the composition of the thiocyanate was not affected by this treatment. After impregnating with active bacteria, complete decomposition of the ammonium thiocyanate with formation of ammonia was found to take place only when dipotassium hydrogen phosphate and dextrose were present, hence ammonium thiocyanate doubtless yields ammonia when used as a manure. E. W. W.

**The Synthesis of Organic Phosphorus Compounds in Killed Yeast Cells.** LEONID IWANOFF (*Zeitsch. physiol. Chem.*, 1907, 50, 281—288).—If zymin is added to a solution of cane-sugar and inorganic phosphates and fermentation allowed to take place, the phosphoric acid is combined with an organic compound, being contained in an aldo- or keto-group. W. D. H.

**Intermediate Products of Alcoholic Fermentation.** ARTHUR SLATOR (*Ber.*, 1907, 40, 123—126. Compare *Trans.*, 1906, 89, 141; Büchner and Meisenheimer, *Abstr.*, 1904, ii, 199; 1905, ii, 274; 1906, ii, 790).—The addition of a small amount of lactic acid to a mixture of yeast and water has much the same effect as the addition of acetic acid; it increases the amount of gas evolved, but to a far less extent than dextrose. Lactic acid, when added to a fermenting solution of dextrose, retards fermentation to much the same extent as an equivalent quantity of acetic acid; the acid is used up, but very slowly during the fermentation; after four hours at 25°, 92% of the acid was still present. The author is of the opinion that lactic acid is not an intermediate but a by-product of alcoholic fermentation.

J. J. S.

**Absence of Nutrition in the Formation of Leduc's "Artificial Plants."** ALBERT CHARRIN and GOUPILO (*Compt. rend.*, 1907, 144, 136—137).—The authors have prepared Leduc's "artificial seeds" by means of copper sulphate and sugar syrup, and have sown them in a medium containing equal parts of a 1% solution of salt and a 3½% solution of potassium ferrocyanide, but they have observed neither an appreciable variation in weight nor any alteration in the sugar content, and conclude that nutrition does not take place.

E. H.

**Osmotic Strength of Cell Sap in Plants.** ERIC DRABBLE and HILDA DRABBLE (*Bio-chem. J.*, 1907, 2, 117—132).—The osmotic pressure in the sap of the turgid cell varies between 1495 and 3389 mm. of mercury. It is least in submerged water plants and greatest in salt-marsh plants. It is increased by drought and by inadequate anatomical provision for checking loss of water by transpiration. The

rate of absorption of water is proportional to the osmotic pressure of the sap, and rises with increase of temperature. W. D. H.

**The Occurrence of Ammonia during Germination and Autolysis of Plants.** NICOLA CASTORO (*Zeitsch. physiol. Chem.*, 1907, 50, 525—534).—The occurrence of ammonia during germination was discovered by Schulze. The present experiments made with various plants, but chiefly lupins, confirm this and give estimations of the amount formed. Ammonia is also a product of autolysis of the plant tissues. W. D. H.

**Fermentative Fat-splitting.** EMIL HOYER (*Zeitsch. physiol. Chem.*, 1907, 50, 414—435).—In the germination of castor oil seeds a formation of acid takes place; this is due to a ferment, and leads to the activation of the lipolytic enzyme of the seeds and a splitting of the oil present, and so enables the plant to utilise its reserve-fat. A method for the isolation of the enzyme is described. W. D. H.

**The Rôle of Phenols, Tannic Acids, and Hydroxybenzoic Acids in Cork Formation.** ERIC DRABBLE and MAXIMILIAN NIERENSTEIN (*Bio-chem. J.*, 1907, 2, 96—102).—Condensation products giving reactions similar to those of cork are precipitable by hydrochloric, phosphoric, acetic, and formic acids, and by carbon dioxide on a mixture of formaldehyde and a phenol, tannic acid, or hydroxybenzoic acid. The condensation product of gallic acid yields diphenylmethane when reduced with zinc dust. Tannic and hydroxybenzoic acids are present in the plant in close association with the cork. Gallic acid and a substance resembling the artificial condensation products were extracted from cork; the latter yields diphenylmethane when reduced with zinc dust. Probably the condensation products are formed in the plant and precipitated at an early stage in the cell-walls of the cork. W. D. H.

**Poisons of *Amanita Phalloides*.** JOHN J. ABEL and WILLIAM W. FORD (*J. Biol. Chem.*, 1907, 2, 273—288).—Immunity can be established towards the two poisonous principles in this fungus, and the serum of immunised animals is antihæmolytic and antitoxic. The hæmolytic substance in the *Amanita* is not a toxalbumin, but a nitrogenous glucoside. Whether it is present in all varieties of *Amanita* is doubtful, and its properties preclude it from playing the rôle of a blood poison in cases of poisoning by the fungus. W. D. H.

**Catalase Topography in Sugar Beet Roots.** VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhmen.*, 1907, 31, 207—217).—The roots were cut up into several pieces and the activity of each towards hydrogen peroxide determined. The results show that the amounts of catalase vary considerably in the different parts, increasing towards the head and towards the surface. The highest amounts are therefore in the rind of the upper parts and the lowest amounts in the middle. Seed roots which had been stored during the winter were employed, and it is

probable that other results would be obtained with roots at different periods of growth.

The catalytic power of beet pulp is best maintained under neutral conditions, and is much diminished in presence of acids and less by alkalis.

N. H. J. M.

**Glucosides of Frangula Bark.** TUNMANN (*Pharm. Centr.-h.*, 1907, 48, 99—103).—From a number of microchemical and gravimetric analyses it appears that the amount of anthraglucosides contained in Frangula bark varies at different times of the year and reaches a maximum in the month of April. The substances contained in the bark which go to form the anthraglucosides are valuable reserve materials.

The paper contains a summary of the present state of knowledge regarding these compounds.

P. H.

**Cyanogen-producing Glucosides in Plants and the using up of Reserve Substances.** MARCO SOAVE (*Chem. Centr.*, 1906, ii, 1726—1727; from *Staz. sper. agrar. Ital.*, 39, 428—437).—Seeds of *Mespilus japonica* contain total N 0.508; N as amygdalin, 0.035; N as proteids, 0.464%. During germination hydrogen cyanide is produced in considerable quantity, amounting to 1.93% of the total nitrogen, whilst the nitrogen as amygdalin, or other glucoside, rises to 7.22% of the total nitrogen. It must therefore be assumed that at least a part of the reserve nitrogen may acquire the form of a glucoside.

N. H. J. M.

**Inositol in Plants.** MARCO SOAVE (*Chem. Centr.*, 1906, ii, 1726; from *Staz. sper. agrar. Ital.*, 39, 413—427).—Inositol does not occur in resting seeds of *Helianthus annuus* and *Lathyrus sativus*, but is produced, no doubt from Posternak's anhydro-oxymethylenediphosphoric acid (*Abstr.*, 1903, ii, 680), when the seeds are boiled for some hours with dilute sulphuric acid. It is also produced during germination, but disappears when all the reserve substances are used up.

N. H. J. M.

**Pharmacodynamic Action of a New Alkaloid contained in Fresh Valerian Root.** J. CHEVALIER (*Compt. rend.*, 1907, 144, 154—157).—Fresh valerian root, as distinguished from the dried substance, is shown to contain an alkaloid, a glucoside, and a resinous compound all physiologically active. The presence of the alkaloid was first pointed out by Worlizewski and it has now been isolated, but in quantity too small for the establishment of its chemical identity. A description of its very energetic physiological and therapeutic action is given.

E. H.

**Organic Phosphorus in Wine.**—MARCO SOAVE (*Chem. Centr.*, 1906, ii, 1726; from *Staz. sper. agrar. Ital.*, 39, 438—443).—Unripe grapes, must, and wines contain inositol which seems to be produced, at least in part, from Posternak's anhydro-oxymethylenediphosphoric acid. Four red wines, which did not contain any inositol, yielded inositol when boiled with dilute sulphuric acid.

N. H. J. M.

## Analytical Chemistry.

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**Improved Apparatus for Gas-analyses.** OTTO PFEIFFER (*Zeitsch. angew. Chem.*, 1907, 20, 22—24).—In order to prevent the slight errors due to "dead space" in the connexions, the author has furnished both burette and pipettes with a funnel and a three-way stop-stock with small inlet tube. If two such tubes are to be connected with a short rubber tube, the air contained therein may be readily expelled by means of water from the funnels, and after each absorption the gas contained in the connexion may be driven back similarly into the burette. The usual U-shaped capillary tube in the phosphorus pipette has been done away with, as it serves no useful purpose.

L. DE K.

**Possibility of Determining the Composition of a Mixture by Indirect Analysis.** J. P. WUITE (*Chem. Weekblad*, 1907, 4, 19—24).—A theoretical paper, in which the author concludes, from examples cited, that no general rule can be laid down as to the applicability or inapplicability of the method of indirect analysis to the determination of the composition of a mixture, and that the possibility of a solution depends on the special circumstances of each case. The views of De Haas (*Abstr.*, 1896, i, 122) are criticised, and it is pointed out that his conclusions are derived from too narrow premises.

A. J. W.

**Application of the Pycnometric Method to the Determination of the Weight and Volume of Precipitates Suspended in Liquids.** J. J. HAZEWINDEL (*Chem. Centr.*, 1906, ii, 1732—1733; from *Bull. Assoc. Chim. Sucr. Dist.*, 24, 301—304).—In Gillot and Grosjean's formula,  $k = p/(D - d')V$  (*Abstr.*, 1906, ii, 488),  $k = d/d - d'$ , and the error is therefore very small if the density of the precipitate is large and the variations of  $d'$  insignificant. The extent to which the analytical error affects the accuracy of the determination of  $k$  is greater the less the difference  $D - d'$ . It is advisable, therefore, to use a sufficiently large quantity of precipitate, and in every case to calculate the real value of  $k$  from the formula given above.

E. W. W.

**Standardisation of Acids and Alkalis.** ERWIN RUPP (*Chem. Zeit.*, 1907, 31, 97).—Crystallised borax is again recommended for the standardisation of mineral acids or alkalis on account of its unalterable composition. When used for acids, with methyl-orange as indicator, it acts like a known weight of sodium oxide, and therefore represents a known amount of the acid; when mixed with glycerol half of the boric acid is set free, which, with phenolphthalein as indicator, represents a definite quantity of alkali. Mannitol may be used instead of glycerol, but is less convenient.

L. DE K.

**A New Method for the Estimation of Halogens in Organic Compounds by Means of Metal-ammoniums.** E. CHABLAY (*Compt. rend.*, 1907, 144, 203—205).—Organic compounds containing halogen are found to react with metal-ammoniums with conversion of all the halogen present into metallic halide. On this reaction is based the method of determining halogen. Ammonia is liquefied on to a weighed quantity of the substance (if liquid or soluble in liquid ammonia) contained in a large test-tube cooled by immersion in a mixture of solid carbon dioxide and acetone, and then small pieces of clean sodium added until a blue coloration indicates presence of excess. The ammonia is then allowed to evaporate, the excess of sodium oxidised by a current of moist air and the halogen estimated as silver halide. If the substance is solid and insoluble in liquid ammonia, it is dissolved in ether, benzene, or toluene, and the solution treated with sodammonium. The method is as accurate as that of Carius, or heating with lime, and the advantages over the latter are rapidity and ease of manipulation.  
E. H.

**Causes which Modify the Estimation of Fluorine in Mineral Waters.** P. CARLES (*Compt. rend.*, 1907, 144, 201—203. Compare this vol., ii, 129).—Powdered fluorite in contact with hydrochloric acid evolves hydrogen fluoride, and consequently a method of estimating fluorine in water residues, which involves digestion with hydrochloric acid to render silica insoluble, is liable to serious error.

The author's method is open to the same objection in the case of waters containing much silica. With the latter, it is necessary to remove silica after partial evaporation by means of sodium hydrogen carbonate and ammonium carbonate; usually, however, the original method is sufficiently accurate.

Water saturated with carbon dioxide is found to dissolve calcium fluoride. The great majority of mineral waters contain fluorine, the mean amount being 0.007 gram per litre; sea-water contains 0.012 gram fluoride per litre.  
E. H.

**Estimation of Sulphur in Pyrites.** MAX DENNSTEDT and F. HASSLER (*Zeitsch. angew. Chem.*, 1906, 20, 108. Compare Abstr., 1906, ii, 896).—A final reply to Luuge (this vol., ii, 50). The authors still uphold their views on the subject.  
L. DE K.

**Detection of Sulphites in the Presence of Thiosulphates and Thionates.** EMIL VOTOČEK (*Ber.*, 1907, 40, 414—418. Compare Bloxam, *Chem. News*, 1895, 72, 63; Autenrieth and Windaus, Abstr., 1898, ii, 452).—Solutions of normal sulphites readily destroy the colours of dilute solutions of certain triphenylmethane-dyes, whereas solutions of thiosulphates or of di-, tri-, and tetra-thionates do not. Solutions of mono- and poly-sulphides also remove the colour from the dye solutions, and the sulphide ion must be removed by means of zinc or cadmium ions before the test with the dye is made. The best effects are obtained by using a mixture of 3 vols. of magenta solution (0.25 gram in 1 litre) and 1 vol. of malachite-green solution of the same concentration. The colour is restored on the addition of

a small amount of acetaldehyde. If the original solution is alkaline, carbon dioxide is passed in; if acid, an excess of sodium hydrogen carbonate is added. A solution of 0.00006 gram of sulphurous acid in 1 c.c. of water can readily be detected by this method. J. J. S.

**Estimation of Sulphuric Acid by Benzidine.** CARL FRIEDHEIM and OTTO NYDEGGER (*Zeitsch. angew. Chem.*, 1907, 20, 9—22).—Raschig estimates sulphuric acid by precipitation with benzidine, and then titrating the compound with standard alkali. In a lengthy article the authors describe a full investigation of the most favourable conditions for the precipitation. The acid or the acidified sulphate is diluted so as to contain 0.1—0.2% of  $\text{H}_2\text{SO}_4$ , and to this is added an equal volume of benzidine solution, prepared by dissolving 0.7 gram of benzidine in 20 c.c. of hydrochloric acid, D 1.12, and diluting to 1 litre.

The process may be employed in presence of some other substances, if not present in large quantities. For every mol. of sulphuric acid there should not be more than 10 mols. of hydrogen chloride, 10 mols. of nitric acid, 20 mols. of acetic acid, 5 mols. of alkali salts, or 1 to 2 mols. of ferric iron. Reduction of the iron is not necessary.

For further particulars, and for the correction for solubility, &c., the tables in the original article should be consulted. L. DE K.

**Iodometric Estimation of Ammonia.** PAUL ARTMANN and ANTON SKRABAL (*Zeitsch. anal. Chem.*, 1907, 46, 5—17).—The ammonia or the ammonium salt is mixed with an excess of sodium hypobromite solution of known strength, and the undecomposed hypobromite estimated as usual by adding potassium iodide and dilute sulphuric acid and titrating with standard thiosulphate with starch as indicator. The decolorisation should be permanent for five minutes, the non-return of the blue colour within that time affording a most delicate test as to the accuracy of the titration. L. DE K.

**Detection of Nitric and Nitrous Acids.** H. W. WAGNER (*Pharm. Centr.-h.*, 1907, 48, 5—7).—A slight modification of Sprengler's phenol test. A little of the nitrate is added to some phenol-sulphuric acid and heated gently in a test-tube. The liquid is then poured into a beaker containing water and neutralised with ammonia, when it will turn a permanent green. If thymol is substituted for phenol, a yellow coloration will be observed, and with resorcinol, a reddish-blue is noticed.

Nitrites are tested for as follows. A little of the nitrite is heated in a test-tube with phenol for a few moments, and 1 c.c. of sulphuric acid is added. The liquid is then poured into water and rendered alkaline with ammonia, when it will turn dark blue. L. DE K.

**Rapid Estimation of Phosphoric Acid by Weighing as Ammonium Phosphomolybdate.** J. GRAFTIAU (*Chem. Centr.*, 1906, ii, 1737—1738; from *Bull. Assoc. Chim. Sucr. Dist.*, 24, 315—320).—An aliquot part of the solution (0.1—0.4 gram of sample) is neutralised with ammonia, the precipitate is redissolved in a few drops of nitric acid, and 10 c.c. of Petermann's ammonium citrate solution are added.

Two to three c.c. of nitric acid, 10—15 c.c. of saturated ammonium nitrate solution, and 50—75 c.c. of water are added, the liquid is heated to boiling and 100 c.c. of the usual molybdic acid solution are added, and the precipitate is allowed to settle for ten to fifteen minutes at 70°. It is then collected on a disc of filtered paper contained in a Gooch crucible into which has been introduced also 2 c.c. of an emulsion of filter paper fibre (1—1000), washed with 1% nitric acid, dried at 105—110° for two hours, and weighed. The weight of the yellow precipitate  $\times 0.0375 = P_2O_5$

L. DE K.

**Separation of Arsenic from Lead, Arsenic from Copper, and Bismuth from Lead.** PAUL JANNASCH and E. HEIMANN (*J. pr. Chem.*, 1906, [ii], 74, 488—498. See this vol., ii, 201).—A reply to the criticism of Friedheim (*Abstr.*, 1905, ii, 652). With due precautions, the hydrogen chloride process gives excellent results.

L. DE K.

**Estimation of Carbon Monoxide in Tobacco Smoke.** JULIUS TÓTH (*Chem. Zeit.*, 1907, 31, 98—99).—The smoke (representing that which is actually inhaled) is drawn by means of an aspirator through an elongated bulb containing sulphuric acid, then through a cylinder filled with cotton wool, then through two 2-bulb tubes containing aqueous potassium and barium hydroxides, then again through a bulb containing sulphuric acid, and then through a U-tube filled with calcium oxide. The gases are then passed through a doubly-bent tube containing pure iodic acid, and heated in a glycerol bath at 60—70°. If any carbon monoxide should be present, this reduces the iodic acid with liberation of iodine, which is then collected in a Peligot tube containing a 10% solution of potassium iodide and afterwards titrated, as usual, with *N*/100 sodium thiosulphate. Two atoms of I liberated = 5 mols. of CO.

L. DE K.

**Phosphotungstic Acid as a Test for Potassium.** GEORG C. MEYER (*Chem. Zeit.*, 1907, 31, 158—159).—Phosphotungstic acid gives with potassium salts a finely-divided precipitate, whilst sodium, calcium, and magnesium salts are not affected. In order to apply the test to the detection and even approximate estimation of potassium compounds in rock salt, 20 grams of the sample are dissolved in water and the solution made to 100 c.c., and to 1 c.c. of the clear solution is added 1 c.c. of a 20% solution of sodium phosphotungstate, which will indicate as little as 0.7% of potassium chloride. A 20—10% solution will show 1%, a 10—5% solution 2.5%, and a 5—2.5% solution 4% of potassium chloride. Intermediate quantities may be judged with a fair amount of accuracy.

L. DE K.

**Estimation of Calcium Carbonate in Marl.** M. J. VAN'T KRUIJS (*Chem. Weekblad*, 1907, 4, 29—32).—The presence of ferrous carbonate in marl precludes the estimation of calcium carbonate by measurement of the volume of carbon dioxide evolved by hydrochloric acid. Acetic acid (30%) has been substituted, using a Scheibler's apparatus. The slowness of the reaction, which usually requires some



hours, causes leakage through the rubber connexions of the apparatus, and makes it difficult to judge the end-point. To avoid this, the sample of marl is reduced to a fine state of division by repeated trituration in a mortar with successive small quantities of water, the fine powder in suspension being transferred to the apparatus. Acetic acid is added, and the flask is constantly agitated during the first quarter of an hour. The reaction is complete in  $1\frac{1}{4}$ — $1\frac{1}{2}$  hours. A double series of experiments, in which standard samples of 96.4% calcium carbonate weighing 0.4 gram were treated in a second apparatus in a similar manner simultaneously with the samples of marl, was carried out. The weight of marl taken in each experiment was such as yielded approximately the same volume of carbon dioxide as the standard sample, thus avoiding errors caused by small variations in temperature. Ten samples were estimated by the author, and independently by another worker, the results being concordant. Two samples which had not been powdered as described yielded results which were too low, one giving an error of  $-4.5\%$ , and the other of  $-3\%$  of  $\text{CaCO}_3$ .  
A. J. W.

**Assay of Barium Sulphide.** LEO WESSELY (*Chem. Zeit.*, 1907, 31, 71—72).—Ten grams of the powdered sample are introduced gradually into a flask containing 500 c.c. of boiling water. When cold, the liquid is made up to 1 litre and 25 c.c. of the clear solution are titrated with  $N/10$   $\text{HCl}$ , using methyl-orange as indicator. Into a spacious flask are then introduced 300 c.c. of water, 2 c.c. of hydrochloric acid, and nearly as much  $N/10$  iodine solution as there was acid used in the previous titration. Twenty-five c.c. of the liquid are now run in, to the decolorised solution is added some starch water, and then again iodine solution until the blue colour appears. One c.c. of  $N/10$  iodine = 0.0084745 gram of barium sulphide.  
L. DE K.

**Use of Thioacetic Acid in Qualitative Analysis.** NAZARENO TARUGI and M. MARCHIONNESCHI (*Chem. Centr.*, 1906, 2, 1733—1734; from *Boll. Chim. Farm.*, 45, 629—637).—Thioacetic acid when heated with mineral acids at  $90^\circ$  is decomposed into acetic acid and hydrogen sulphide; it may thus be used conveniently in place of the latter, and precipitation may be effected by it, even in presence of large excess of acid, particularly when under pressure. According to the authors zinc is precipitated from its solutions when heated with thioacetic acid at  $90^\circ$  in a sealed tube; the precipitation is complete when the free acid does not exceed 3.5%, partially only with 4.52%. Cadmium, nickel, cobalt, and iron are also precipitated, but manganese is not. The sulphides of arsenic (antimony and tin) are soluble in excess of the reagent with evolution of hydrogen sulphide and formation of an additive product, arsenious thioacetate. The sulphides of bismuth and mercury also evolve hydrogen sulphide from the reagent, but do not yield a thioacetate. The sulphides of gold and platinum do not react with thioacetic acid.  
L. DE K.

**Estimation of Free Acid, Copper, and Arsenic in [Electrolytic] Copper Lyes.** H. KOCH (*Zeitsch. anal. Chem.*, 1907, 46, 29—37).—*Free Acid.*—Kieffer's process, adding standard solution of

pure cuprammonium sulphate ( $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ ) until a turbidity forms, has not met with approval. The author, however, states that a satisfactory test solution is obtained by the addition of ammonium sulphate (65 grams of the crystallised copper salt and 6 grams of ammonium sulphate made up to 1 litre with water).

**Copper.**—This is successfully titrated in acid solution with standard sodium sulphide when some chloroform is added, which carries with it the sulphide formed. Instead of chloroform, which is unpleasant to use, ether may be used, but as this floats on the surface, the titration should be carried out in an apparatus resembling a non-tubulated retort placed upside down, the neck being provided with a stopper; on inclining the apparatus, the ether and copper sulphide collect on the surface in the body of the retort.

**Arsenic.**—This is estimated as usual by distillation with fuming hydrochloric acid and ferrous sulphate, and titration of the arsenic; weak lyes should be concentrated until acid fumes are evolved. When applying the distillation process to refined metallic copper, it is best to remove the bulk of the copper, and the following plan is recommended.

Thirty grams of copper are dissolved in 300 c.c. of nitric acid, D 1.2, the excess of acid is expelled by evaporation, the residue is dissolved in about 1 litre of water, and mixed with ammonia in excess. Ten c.c. of a cold saturated solution of sodium phosphate, and then 20 c.c. of magnesium mixture are added, and after three or four days the mixed precipitate of magnesium ammonium phosphate and arsenate is collected, washed slightly with ammoniacal water, and dissolved in dilute sulphuric acid. After heating until acid fumes become visible, the whole is distilled with ferrous sulphate and hydrochloric acid.

L. DE K.

### Iodometric Estimation of Potassium Permanganate.

TADEUSZ MILOBENDZKI (*Zeitsch. anal. Chem.*, 1907, 46, 18—29).—A series of experiments conducted with all possible precautions and showing the suitability of Volhard's process (addition of potassium iodide in acid solution, and titrating the liberated iodine with standard thiosulphate).

L. DE K.

### Metallic Iron as Standard for Potassium Permanganate.

H. KINDER (*Chem. Zeit.*, 1906, 31, 69—71. Compare Abstr., 1906, ii, 582).—Traces of hydrocarbons which may be present in the standard iron solution may be oxidised completely by adding excess of potassium permanganate. After some time the iron is again reduced to the ferrous state by hydrogen sulphide, the excess of which is then removed by heating and passing a current of carbon dioxide.

In order to obtain accurate results in the titration of iron or its ores, the amount actually used in the titration should represent as nearly as possible the iron weighed out for the standardisation of the permanganate. For further particulars the tables in the original paper should be consulted.

L. DE K.

**Separation of Cobalt from Manganese and Iron by Means of Potassium Nitrite.** W. FUNK (*Zeitsch. anal. Chem.*, 1907, 46, 1—4).—The time-honoured process of separating cobalt from nickel in

the form of cobalt potassium nitrite may be applied also to its separation from manganese if the latter is not in too large an excess. The metals should be present as sulphates. The method may be also used for separating small quantities of cobalt and ferric iron (about 0.05 gram total). The metals should be present as chlorides. When operating on larger quantities there is a risk of the precipitate being contaminated with iron.

The cobalt precipitate is then dissolved in sulphuric acid and submitted to electrolysis.

L. DE K.

**Electrolytic Estimation of Antimony.** J. M. M. DORMAAR (*Chem. Weekblad*, 1907, 4, 55—66).—The causes of the high results obtained in estimating antimony electrolytically have been investigated. Reference is made to the work of Cooke (*Proc. Amer. Acad.*, 1878, 13, 1; 1880, 15, 251); Parodi and Mascazzini (*Zeit. anal. Chem.*, 1879, 18, 587); Lückow (*Abstr.*, 1880, 282); Classen (*Abstr.*, 1881, 1081; 1885, 190 and 932); Lecrenier (*Abstr.*, 1890, 421); Ditte and Metzner (*Ann. Chim. Phys.*, 1893, [vi], 29, 389); Ost and Klaproth (*Abstr.*, 1900, ii, 692); Hollard (*Abstr.*, 1903, ii, 455), and Henz (*Abstr.*, 1904, ii, 150).

The antimony was dissolved in concentrated sodium sulphide solution, free from sulphite, and potassium cyanide added until the colour was discharged. The solution was electrolysed in a platinum dish as cathode, at 60° and a current density of 0.002 ampere per sq. cm. After fifteen minutes, the current density was gradually raised to 0.006 ampere per sq. cm. The antimony was deposited in a light grey, very adherent layer. In four experiments the excess of antimony obtained was about 3%, using about 0.4 gram of antimony. The surplus was proved to be due partly to oxidation by repeating the experiments with about 2 grams of antimony, and subsequent ignition of the precipitated metal in hydrogen, the water formed being collected and weighed in tubes filled with pumice moistened with sulphuric acid. The residue in the ignition tube contained a very small quantity of orange-coloured antimony sulphide, its formation being probably due to the presence of sodium sulphide in the precipitated antimony.

The author's conclusions are: (1) The excess increases markedly with rise in current density and augmentation of the amount of antimony employed; (2) the excess is principally the result of oxidation; (3) it is partly due to occlusion of sulphur compounds in the precipitate; (4) the oxidation is not atmospheric, but inherent in the electrolytic process itself, as is proved by carrying out the operation in an atmosphere of hydrogen.

A. J. W.

**Volumetric Estimation of Antimony.** J. B. DUNCAN (*Chem. News*, 1907, 95, 49).—The author approves of the process given by Nissenson and Siedler for the estimation of antimony in hard lead (*Abstr.*, 1903, ii, 697) and has now extended it to all kinds of antimony compounds.

Ores not soluble in hydrochloric acid are rendered soluble by fusing 0.3 gram as usual with sulphur and sodium carbonate. The antimony sulphide precipitated on acidifying the aqueous solution is readily

soluble in hydrochloric acid. This solution is oxidised with bromine; the liquid is well boiled and then again reduced to the antimonious state by boiling with sodium sulphite. As soon as the excess of sulphur dioxide has been expelled, the solution is titrated by means of potassium bromate (2.7852 grams per litre). In presence of sufficient free hydrochloric acid, this oxidises the antimony and when the end is approaching a few drops of methyl-orange are added as indicator, the end-reaction being known by the disappearance of the colour. The bromate solution may be checked by dissolving 0.3 gram of pure metallic antimony in 20 c.c. of hydrochloric acid and a few drops of bromine, and reducing with sodium sulphite.

L. DE K.

### Separation of Metals by means of Dry Hydrogen Chloride.

PAUL JANNASCH and E. HEIMANN (*J. pr. Chem.*, 1906, [ii], 74, 473—487).—The alloy is treated in a boat with nitric acid and the residue after being dried at 120° is heated in a current of dry hydrogen chloride generated from ammonium chloride and sulphuric acid free from free arsenic. In order to expel the volatile chlorides completely from the combustion tube, very careful heating with a small flame must be employed. The volatile chlorides are collected in water and estimated by the usual process. If it is desired to weigh as such the non-volatile chlorides left in the boat, a current of dry air should be passed whilst the tube is still hot.

Tin, bismuth, arsenic, and antimony are all readily volatilised. In order to prove the accuracy of the process, the authors give the full details of experiments including the separation of tin from cadmium, bismuth from cadmium, bismuth from silver, antimony from lead, antimony from copper, antimony from cadmium, and antimony from silver.

L. DE K.

**Estimation of [small Quantities of] Sugar in Urine.** ARMAND MANASSE (*Chem. Centr.*, 1906, ii, 1692; from *Arbeit. Path. Inst. Berlin*).—Knapp's process proved unsuitable. The Fehling titration process modified by Patein and Dufau (*Abstr.*, 1900, ii, 176) gives, as a rule, satisfactory results. Lavalley's modified Fehling titration (*Abstr.*, 1905, ii, 558) gives good results only when the titration is carried out with addition of ammonia in a closed flask [compare Lavalley, this vol., ii, 137].

L. DE K.

**Volumetric Estimation of Dextrose.** PIO LAMI (*Boll. Chim. Farm.*, 1906, 46, 6—8).—For the volumetric estimation of dextrose, the author makes use of a flask fitted with a double-bored stopper, through one hole of which passes the delivery tube of a burette containing the thoroughly defecated and decolorised dextrose solution (0.15—0.25%), whilst through the other passes a tube which is bent twice at right angles, and widens out into a vertical branch about 70 cm. long, dipping under mercury. In the flask are placed 1 c.c. of Fehling's solution or 0.5 c.c. of a copper sulphate solution of known titre, together with 25 c.c. of 25% ammonium carbonate solution and 25 c.c. of water. The mixture is then boiled, the carbon dioxide evolved expelling the oxygen from the flask. The dextrose solution

is then gradually run in from the burette until the liquid is completely decolorised. Prolonged ebullition may expel all the ammonia from the liquid before the cupric salt is all reduced, so that the cuprous oxide becomes precipitated; in this case a few c.c. more of the ammonium carbonate solution should be added. T. H. P.

**Criterion of Purity of Mannitol.** OTTORINO CARLETTI (*Boll. Chim. Farm.*, 1906, 46, 5—6).—The presence in mannitol of carbohydrates such as sucrose or dextrose, which yield furfuraldehyde under the action of sulphuric acid, may be detected as follows. Two or three c.c. of concentrated sulphuric acid, and 5 drops of a 1% alcoholic solution of a phenol such as  $\alpha$ -naphthol, menthol, or thymol, which gives a coloration with furfuraldehyde, are placed in a test-tube, and on to the mixture a solution of 0.1 of the mannitol in 5 c.c. of water is carefully poured. If sucrose, dextrose, or other carbohydrate is present, even in small quantity, the contact-layer of the two liquids assumes a bluish-violet coloration if  $\alpha$ -naphthol is used, or a red coloration if thymol or menthol is used. T. H. P.

**Detection of Sucrose in Presence of Lactose.** ADOLF BEYTHIEN and A. FRIEDRICH (*Pharm. Centr.-h.*, 1907, 48, 39—44).—A little of the sample is sprinkled over sulphuric acid when any sucrose will rapidly char (Schmidt's method). By way of confirmation some other tests may be applied such as Pinoff's test with alcoholic solution of resorcinol and sulphuric acid which gives a red coloration in presence of sucrose. Cotton's test, the blue coloration produced on warming with molybdic acid in presence of dilute hydrochloric acid, is also trustworthy; also the red coloration obtained by agitating the sample with sesame oil and hydrochloric acid. Lorin's method, based on the fact that sucrose is readily charred on heating in a water-bath with dry oxalic acid, may also be recommended. L. DE K.

**Separation of Carbohydrates by Pure Yeasts.** JOSEF KÖNIG and P. HÖRMANN (*Zeitsch. Nahr.-Genussm.*, 1907, 13, 113—132).—Acid and malt dextrins behave towards yeasts differently from honey dextrin, which is readily assimilated by wine-yeasts and vigorously fermented by beer-yeasts. Honey dextrin also undergoes greater esterification when treated with benzenesulphonic chloride, and has, therefore, a lower molecular weight than acid or malt dextrins. Yeasts are only applicable to the separation of different sugars, in so far as they allow one sugar, not attacked by the yeast used to be estimated; the estimation of the fermented sugar from the weight of carbon dioxide lost does not always give accurate results. The separation of dextrins from sugars by means of yeast has the advantage that it gives more accurate results than precipitation by alcohol and the disadvantage that it requires a much longer time. The quantitative fermentation of pure sugars in nutrient salt solutions requires from six to seven days, whilst, if maltose is to be fermented in presence of dextrin, two or three days longer are necessary. Yeasts are applicable to the separation of dextrose from

maltose, for example, in the analysis of starch-syrups and starch-sugars, as no other accurate method of effecting this separation is known. For estimating dextrose and lævulose in presence of sucrose and maltose, *Torula pulcherrima*, *Saccharomyces Marxianus*, and the bottom fermentation yeast from Danzig Jopenbier are recommended (compare Lindner, Abstr., 1901, ii, 182, 263). T. H. P.

**Estimation of isoButyric and Valeric Acids by Duclaux's Method.** A. LASSERRE (*Ann. Inst. Pasteur*, 1907, 21, 76—79).—The results given show that this method (Abstr., 1886, 322) affords a means of distinguishing butyric from isobutyric acid and valeric from isovaleric acid, but that it is not applicable to mixtures of the acids. The rate of distillation of valeric acid is almost identical with that of isobutyric acid. W. P. S.

**Analysis of Indigo.** JAN Q. ORCHARDSON, S. H. WOOD, and W. POPPLEWELL BLOXAM (*J. Soc. Chem. Ind.*, 1907, 26, 4—9).—The paper deals with the isolation of the impurities of cake indigo, the estimation of indigotin obtainable from the leaf, and a new method which has been worked out for this purpose. The impurities separated were indigo-gluten, indigo-brown, and indigo-yellow (kaempferol), and it is shown that these substances are not precipitated along with the potassium indigotintetrasulphonate in the method described previously by one of the authors (Abstr., 1906, ii, 819). The following method was adopted for estimating indigotin from the leaf: 200 c.c. of the aqueous extract of the leaf were warmed to a temperature of 60°, 100 c.c. of a mixture of equal parts of 2% ammonium persulphate and 4% sulphuric acid were added, and the whole kept at 60° for one hour. The liquid was then boiled and filtered hot through asbestos; the precipitate was washed successively with hot 1% sodium hydroxide, acetic acid, and water. After being dried at 110°, the precipitate and asbestos were ground up with sand and sulphonated by heating for one hour with 10 c.c. of 96% sulphuric acid. The sulphonic acid was next diluted to 500 c.c., and 100 c.c. of this solution were titrated with 0.1% permanganate solution. Some experiments on the isatin method are described, showing that the process, which is based on the condensation of indoxyl and isatin, indirubin being formed, gives a larger yield of indigotin than the persulphate method. The method proposed by Bergtheil and Briggs (Abstr., 1906, ii, 818) was found to give "irregular" results. W. P. S.

**Estimation of Tannin in Tanning Materials.** WILHELM VAUBEL and OTTO SCHEUER (*Zeitsch. angew. Chem.*, 1906, 19, 2130—2133).—*Gasometric Method.*—Twenty c.c. of the solution containing 6—7 grams of tannin in 100 c.c. are introduced into a specially constructed apparatus (essentially a Cloez's washbottle) of known capacity, and containing 600—700 c.c. of oxygen. 100 c.c. of *N* sodium hydroxide are added next, and the whole is well shaken at intervals for some three days. By admitting a measured volume of the alkali into the apparatus, the volume of oxygen absorbed is found. 229.3 c.c. of oxygen at *N.T.P.* represents 1 gram of gallotannic acid. In weight

this gives 0.328 gram of oxygen for every 1 gram of tannin. If alkali of a different concentration is employed, this factor no longer holds good.

*Gravimetric Estimation.*—Fifty c.c. of *N* sodium hydroxide are introduced into a Voit's washbottle with drying arrangement attached, the whole is weighed and 0.5 gram of dry tannin is added. Through the liquid is now passed a current of purified air or oxygen for some twenty-four hours, and the increase in weight is noticed. In these circumstances the factor will be 0.3092. The experiments, which must not as yet be taken as fully decisive, are being continued.

L. DE K.

**Bilberry Juice, and a Colour Reaction of the Same.** WILHELM PLAHL (*Zeitsch. Nahr.-Genussm.*, 1907, 13, 1—5).—The following results were obtained on the analysis of seven samples of bilberry juice pressed from the fruit in the author's laboratory: total solids, 3.94—9.51%; ash, 0.247—0.313%; total acidity, 15.52—19.64 c.c. *N*/1 alkali; alkalinity of ash (total), 3.05—3.41 c.c. *N*/1 acid; alkalinity of soluble ash, 2.24—2.50 c.c. *N*/1 acid. During the examination of a sample of bilberry cider, a blue coloration was obtained on heating the cider with hydrochloric acid for the inversion of the sugars present. This colour did not result from the action of the acid on the natural red colour of the berries, or on artificial colours present, as juice pressed from the berries and decolorised by means of lead acetate still gave a blue coloration on being heated with hydrochloric acid to a temperature of 67°. The reaction appears to be peculiar to the *Vacciniaceæ*, as *V. vitis Idaea* (cranberry) and *V. oxycoccus* give the coloration, whilst cherries, elder-berries, grapes, and currants yield no colour.

W. P. S.

**Method for the Removal of Colloids from Solutions, Especially for Removing Proteids from Blood-Serum.** LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1906, 2, 219—224).—The following method gives good results. One volume of diluted blood-serum is mixed with three volumes of absolute alcohol, and after several hours, or if the precipitate is removed, immediately, one volume of a 50% solution of mastic in alcohol is added, and the whole is diluted with water until the liquid contains 30% of alcohol. After the solution is made slightly acid with acetic acid, a 10% solution of magnesium sulphate is added in the proportion of 10—15 c.c. for each litre of liquid, and the mass filtered after some time. Copper acetate may be used instead of magnesium sulphate; the copper can then be removed in the form of sulphide.

When the original solution contains only some 0.5% of albumins the acetic acid and mastic solution may be used without the previous addition of alcohol.

J. J. S.

## General and Physical Chemistry.

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**Refractive Indices of Water and of Sea-water.** J. W. GIFFORD (*Proc. Roy. Soc.*, 1906, A, 78, 406—409).—The refractive indices of water and sea-water have been measured at 15° for a number of wave-lengths. For three different wave-lengths the temperature coefficients have also been determined.

The refractive index of a sample of water, prepared and kept in platinum vessels, for the iron line *E* (wave-length 5270·11) was found to be  $n_E^{15^\circ} = 1\cdot3356359$ .  
H. M. D.

**Refractive Indices of Gaseous Potassium, Zinc, Cadmium, Mercury, Arsenic, Selenium, and Tellurium.** CLIVE CUTHBERTSON and E. PARR METCALFE (*Phil. Trans.*, 1907, A, 207, 135—148. Compare Abstr., 1905, ii, 129).—The earlier investigation (*loc. cit.*) has been continued with an improved apparatus, one chief alteration being the substitution of fused silica tubes for the glass ones previously employed.

No accurate determination could be made of the index of refraction of potassium, but rough observations indicated that its value was less than unity both for  $\lambda 5460$  and  $\lambda 6562$ . The values obtained for the refractive indices of the other elements are summarised in the following table :

Element.	$\lambda 6562$ .	$(\mu - 1) \times 10^6$ .			
		$\lambda 5893$ .	$\lambda 5460$ .	$\lambda 5183$ .	
Cadmium.....	2675	2675	2725	2780	
Zinc.....	1960	2057	2150	2070	
Arsenic .....	—	1552	1579	—	
Selenium .....	1535	1565	1570	—	
Tellurium .....	2370	2495	2620	—	
Mercury .....	1799	1866	1882	1885	

The dispersion, except for potassium, is normal in direction and of very great magnitude. The indices of zinc, cadmium, and tellurium are higher than that of any gaseous element previously investigated.

The refractivities of selenium and tellurium are to that of sulphur as 3 and 5 respectively to 2, so that in this case the rule of simple integral ratios between the refractivities (see *loc. cit.*) is approximately fulfilled. No such rule, however, applies to phosphorus and arsenic, or to zinc, cadmium, and mercury. To the rule that, in each group of elements, refractivity increases with atomic weight, mercury forms a striking exception.  
J. C. P.

**Volume, Valency, and Refraction.** The Refraction and the Volume Stere. II. ISIDOR TRAUBE (*Ber.*, 1907, 40, 723—733).—The author has shown (this vol., ii, 145) that the real volume of an atom (the expression "real volume" does not include the ether



envelope) as measured by its atomic refraction in organic compounds containing carbon, hydrogen, oxygen, nitrogen, and in some cases boron, phosphorus, or silicon, is proportional to the number representing the valency. In compounds containing C:C, C:O, C:N, or N:N or N:N, the increment,  $(M_a/0.787) - n$  (where  $M_a$  is the molecular refraction, 0.787 is the mean value of the refraction stere, and  $n$  is the total number of valency linkings), increases with the number of multi-linked atoms; multilinked carbon atoms, therefore, have a greater real volume than those singly linked, whereas the reverse would be expected from the theory that such carbon atoms are trivalent or bivalent.

The increment has been determined for a number of typical organic compounds containing one or more halogen atoms. For the four compounds containing fluorine the increment is about 1, but for nine compounds containing chlorine it is about 7 per halogen atom, a number representing the maximum valency of the element. Moreover, the molecular refraction is the same for substances such as ethylene dichloride and succinonitrile, which contain Cl or C:N; the number of linkings in the latter is 7. Chlorine is septavalent, not because the atom is surrounded by 7 valones, but because its volume is 7 steres, the maximum valency of an atom being determined by the stere value of the valone volume (*loc. cit.* for definitions).

The increment in the case of bromine, iodine, sulphur, selenium, zinc, mercury, tin, and lead is 11, 17, 10, 14, 10, 16.4, 17.6, and 22.4 respectively, numbers which do not bear any apparent relation to the maximum valency of the elements. The discrepancies disappear, however, when the other magnitudes comprising the molecular volume are taken into account. The molecular volume is composed of the real volume of the atoms, the atomic covolume,  $b - M_a$  (electron or valone volume), and the molecular covolume,  $v - b$ ; the last in particular is influenced by change of temperature. At the absolute zero the molecular covolume becomes zero, and the atomic covolume becomes  $v_0 - M_a$ . For the evaluation of  $v_0$  compare Guldberg (Abstr., 1900, ii, 264) and Berthelot (*ibid.*, 335). In non-associated organic compounds containing carbon, hydrogen, oxygen, and nitrogen, the value  $(v_0 - M_a)/n$  is approximately constant, and the mean value 1.70 represents the stere of the atomic covolume. This stere is greatest when that of the real volume of the atom is least, and *vice versa*. The cause of this reciprocity is, according to the author, an intra-atomic pressure, which, acting outwards, resists the affinity pressure binding the atoms and contracting the atomic covolume.

The same relation is true for cyclic and for halogen containing compounds. In the case of the latter, the increment,  $(v_0 - M_a/1.70) - n$ , for chlorine, bromine, and iodine is in the ratio 6:7:8.9, numbers very near that of the maximum valency.

At the critical temperature, similar relations hold for non-associated compounds; the stere,  $(b_k - M_a)/n$ , is nearly constant if the values in  $n$  for chlorine, bromine, iodine, sulphur, and selenium are taken respectively as 6, 7, 9, 6, 7, and the value of  $n$  is diminished by 6 units for each benzene, cyclohexane, or pyridine nucleus.

At the normal boiling point, the calculated molecular covolume (Abstr., 1902, ii, 551), even for associated substances, is equal to the number of valency linkings, and the author deduces that a liquid, whether associated or not, boils when the molecular covolume is directly, the internal pressure inversely, proportional to the number of valency linkings. Since for associated liquids at the normal boiling point  $v/v - b = 3.75$ , it follows that the molecular volume  $= 3.75 \times$  number of valency linkings; this deduction is confirmed in the case of forty organic compounds. The equation also holds for cyclic and for halogen compounds if the correction previously stated is applied to  $n$ , the correction for benzene, cyclohexane, and pyridine being 4.5 units.

Since isomeric compounds have nearly equal molecular covolumes at  $0^\circ$  and different boiling points, the more associated substance at  $0^\circ$  must have the smaller molecular covolume.

The author points out that Barlow and Pope (Trans., 1906, 89, 1675), starting from totally different premises, have arrived at conclusions concerning structure and valency which are almost identical with his own. C. S.

**Associated Substances. III. ISIDOR TRAUBE** (*Ber.*, 1907, 40, 734—736. Compare preceding abstract).—For associated liquids and solids, the stere of the atomic covolume (electronvolume),  $b - M_a/n$ , calculated on the assumption that oxygen is bivalent, is not constant and equal to about 1.70, but is greater than this in a degree approximately proportional to the association factor of the compound under examination. The abnormality vanishes if oxygen is regarded as quadrivalent, and hence such liquids and solids might be regarded as atomic compounds were it not for evidence furnished by the real volume of the atoms. Strongly associated substances such as glycerol, ethylene glycol, and lactic acid give quite normal values for the refraction stere, calculated on the assumption that oxygen is bivalent.

Moreover, the more highly associated of two isomeric substances has the smaller molecular covolume (*loc. cit.*), and, since the latter quantity is inversely proportional to the internal pressure, so-called associated substances may be regarded as compounds which exist under an unusually great internal pressure.

By this theory the author accounts for the existence of gaseous associated molecules, for the action of associating and of non-associating solvents on associated solutes, and the dissociating action of solvents on salts, &c. C. S.

**Principle of Optical Superposition. II. M. A. ROSANOFF** (*Zeitsch. physikal. Chem.*, 1907, 57, 739—741. Compare Abstr., 1906, ii, 320).—The author, criticising the work and the conclusions of Guye and Goudet (Abstr., 1896, ii, 458), finds that the principle of algebraic superposition is false. J. C. P.

**Optical Rotation of Iodonium Tartrate. RICHARD PRIEBRAM** (*Annalen*, 1907, 351, 481—485).—Oudemans held that in moderately dilute solutions the molecular rotations of salts are independent of the

nature of the inactive component. Guye (Abstr., 1892, 399, 758), on the contrary, published a number of results which indicated that the molecular rotation of an active substance is influenced by the molecular weight of the inactive group with which it is combined, and concluded that the molecular rotation of tartaric acid is increased by all bases (compare Pribram, Abstr., 1888, 1229).

It has been observed that the molecular rotation of thallium tartrate in dilute solution is greater, but in concentrated solution less, than that of tartaric acid; the point at which the rotation curves for various strengths of thallium tartrate cuts that of similar solutions of tartaric acid represents the concentration at which the inactive thallium is without influence in the rotation of the active tartaric acid.

The optical activity of diphenyliodonium tartrate has now been investigated, the analogy of such salts with those of thallium having been pointed out by Victor Meyer. As the tartrate could not be obtained in the crystalline state, solutions in which diphenyliodonium hydroxide and tartaric acid were mixed in equivalent proportions were examined, and the observed rotations in solutions containing 2.945—7.125% of the iodonium tartrate found to be in each case greater,  $\alpha_D^{25} + 0.39$  to  $+1.30$ , than that of solutions containing the equivalent amounts, 0.623—1.506%, of free tartaric acid,  $\alpha_D^{25} + 0.29$  to  $+0.65$ .  
G. Y.

**Influence of Formaldehyde on the Rotatory Power of Dextrose in Relation to the Theory of Multirotation.** GABRIELE LANDINI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 52—58).—In the hydrolysis of sucrose by hydrochloric acid in presence of formaldehyde, the reaction constant exhibits a gradual increase which must be attributed to some action of the formaldehyde, either on the sucrose itself or on its products of hydrolysis. Also, when a mixture of 40 c.c. of 40% formaldehyde solution with 10 c.c. of 50% sucrose solution is maintained at 40°, the rotation of the solution increases from 26.667°, two minutes after mixing, to 30.033°, 137 minutes after mixing, in spite of the presence of a small quantity of acid (0.0105*N*) in the aldehyde. A similar increase in rotation is observed in a mixture of equal volumes of the 40% formaldehyde solution and 10% dextrose solution kept at a temperature of 40°; the value of *K*, calculated on the hypothesis that a molecule of  $\beta$ -dextrose forms a compound with the formaldehyde, falls from  $9.406 \times 10^{-3}$  to  $2.504 \times 10^{-3}$ . Displacement of the equilibrium between the  $\alpha$ - and  $\beta$ -forms of dextrose is insufficient to explain this observation, since this also would require *K* to remain constant.

The results of experiments on the action of formaldehyde on the rotation of  $\alpha$ -dextrose are not in accord with the assumption that the  $\alpha$ - is merely converted into the  $\beta$ -form. The author is of opinion that either the  $\alpha$ - or the  $\beta$ -form, or both, enters into combination with the formaldehyde (compare Jungius, Abstr., 1905, i, 573; Milroy, Abstr., 1905, i, 174).  
T. H. P.

**Lamps for Spectra. V. New and Simple Spectrum Lamp for Analytical Work.** ERNST BECKMANN (*Zeitsch. physikal. Chem.*, 1907, 57, 641—648. Compare Abstr., 1900, ii, 701; 1901, ii, 53, 81; 1902, ii, 373).—The air supply to an ordinary bunsen burner is led through a wide, short-limbed U-tube, in which is put a little of the solution to be tested along with zinc and acid. The effervescence from the zinc sprays the dissolved salt, and the current of air as it passes over the solution carries the spray with it and colours the flame accordingly. Slight alterations in the apparatus permit its use with the various forms of bunsen burner. J. C. P.

**Spectrum Analysis.** FRANZ EXNER [with E. HASCHECK] (*Annalen*, 1907, 351, 12—23).—With the aid of large Rowland's gratings, the authors have photographed the ultra-violet portion of the arc and spark spectra of 74 elements, and have measured the wave-lengths of the lines by projecting the spectra on to a scale. These results have been published in wave-length tables. Tables are now given showing the number of lines in the ultra-violet in the arc and in the spark spectra of these elements. A few have no lines in the ultra-violet, whilst the greater number have from one to a hundred, and only three have over 2,000 lines in the ultra-violet of both spectra. The application of these new spectrum measurements is discussed. G. Y.

**Employment of Spark Spectra in Proving Homogeneity.** CARL AUER VON WELSBACH (*Annalen*, 1907, 351, 458—466).—It is customary in testing the homogeneity of a supposed element to divide the substance into a series, as long as possible, of fractions which are compared in the majority of cases by examination of their spectra. For this purpose, the author strongly recommends the employment of spark spectra wherever possible. Against the use of spectrum photography in those cases in which differences in the composition of fractions have to be determined by observation of slight differences in the intensity of the lines of two spectra, it is urged that in consequence of the great sensitiveness of dry plates these differences disappear on unsuitable exposure, that the rays and especially the least refracted rays from a substance present in small proportion are suppressed, and hence an impurity represented by lines in the red is less easily recognised than one the lines of which lie in the violet, still more in the ultra-violet, and that closely related elements have always moderately intense lines in common, these being most frequent in the ultra-violet, and appearing in all spectra of a series of fractions tend to lead to wrong conclusions. To simplify the direct observation of a prolonged series of spark spectra, the author uses a modified apparatus, which is described shortly, further details being promised. The method of employing the spark spectra is illustrated by reference to the separation of ytterbium ammonium oxalate into two fractions differing completely in the visual portion of the spectrum, but showing lines in common in the ultra-violet. G. Y.

**Continuous Rays observed in the Spark Spectra of Metalloids and Some Metals.** W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1906, A, 78, 403—405).—The continuous rays in certain spark spectra have been examined by passing sparks between electrodes of cadmium, lead, tin, arsenic, and antimony in closed vessels containing different gases. The nature of the gas surrounding the electrodes appears to have a distinct influence on the continuous ray spectrum, the influence varying from one metal to another. In contradiction to an opinion expressed previously, the continuous spectrum is not caused by oxidation, because in every case it is strongest when the electrodes are immersed in hydrogen or nitrogen. All the spectra are weakest in an atmosphere containing oxygen, whether free or combined, and the conclusion is drawn that oxidation weakens or destroys the continuous spectrum.

Some experiments on flame spectra indicate that the best continuous ray spectrum is obtained from an acetylene oxygen flame. The rays are in this case continuous and of equal intensity from the red to beyond wave-length 2700.

H. M. D.

**Influence of a Strong Magnetic Field on the Spark Spectra of Titanium, Chromium, and Manganese.** JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1907, 14, 41—84. Compare Abstr., 1906, ii, 421; 1907, ii, 2).—The effect on a large number of the spectral lines of titanium, chromium, and manganese is recorded, the following being some of the more important results. On comparing the lines of each separate metal with one another, it is found that several of them may be correlated in that the constituents have the same values of  $d\lambda/\lambda^2$ , the same polarisation and similar appearance. It frequently happens that a simple numerical relationship exists between the constituents of a line which divides into either eight, six, five, or four constituents, and that amongst the lines which divide into three, the values of  $d\lambda/\lambda^2$  for the constituents of some lines are simple multiples of the values of those of other lines.

W. H. G.

**Band Spectra of Nearly Allied Compounds.** CHARLES MORGAN OLMSTED (*Chem. Zentr.*, 1907, i, 146—147; from *Zeitsch. Wiss. Photograph. Photophys. Photochem.*, 4, 255—291).—The band spectra of the halogen salts of barium, strontium, calcium, and magnesium have been photographed, a Rowland concave grating of 1 m. curvature being used. The powdered salts were wrapped in a roll of filter paper and burnt in an oxyhydrogen flame. The spectra were compared with that of iron, which was photographed on the same plate. The results are tabulated in the original paper. The spectra are composed of a series of bands each of which consists of a great number of lines. A relationship between the position of these bands and the atomic weight of the atoms is distinctly apparent. The spectra of the chlorides, bromides, and iodides of calcium, strontium, and barium resemble each other much more than the spectra of the fluorides. The results show that the more nearly equal the atomic weights of the components the greater is the power of emission of the molecule, and that in the case of a given halogen salt, the less the atomic weight of the metal, the

greater is the apparent displacement of the bands towards the violet end. These rules hold for all salts of barium, strontium, calcium, and for magnesium iodide and bromide, but not for magnesium chloride and fluoride. The spectrum of glucinum chloride contained no band, possibly because the temperature was too low.

The equation:  $N = A \pm (B.m + C)^2 = \alpha + \beta m + \gamma m^2$ , in which  $N$  = frequency,  $A$ ,  $B$ ,  $C$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$  = constants, and  $m$  = series of positive whole numbers, holds for the lines of each band. A more precise numerical relationship between the atomic weight and the constants could not be determined, but the absolute values of  $\alpha$  and  $\beta$  in the case of each metal were found to decrease as the atomic weight of the halogen increased and for a given halogen increase of the atomic weight of the metal had the same effect. The value of  $\gamma$  is dependent only on the atomic weight of the metal and not on that of the halogen.

E. W. W.

#### Band Spectra of Mercuric Chloride, Bromide, and Iodide.

JOHANNES LOHMEYER (*Chem. Zentr.*, 1907, i, 396; from *Zeitsch. wiss. Photograph. Photophys. Photochem.*, 4, 367—383).—The spectra of mercuric chloride, bromide, and iodide have been photographed by means of a Rowland grating of 1 m. curvature. The compounds were placed in Geissler tubes which were heated and evacuated; it was found necessary to continue the action of the pump during the exposure in order to reduce the pressure to a few thousandths of a millimetre. The dispersion was not great enough to cause separation of the bands. The spectra are somewhat complicated. As the atomic weight increases the band complex moves towards the shorter wave-lengths, although Wedemann found the reverse effect in the case of the halogen compounds of the alkaline earths (*Boltzmann Festschrift*, 1904, 826). Deslandres's law that the frequency of consecutive bands forms an arithmetical series is not absolutely confirmed by the data, but the distances between the bands of a series appear to increase to a definite limit and then to decrease.

E. W. W.

Structure of the Bands in the Spectrum of Effect Carbons (Effektkohlen) and of Barium Fluoride. JOSEPH RÖSCH (*Chem. Zentr.*, 1907, i, 396—397; from *Zeitsch. wiss. Photograph. Photophys. Photochem.*, 4, 384—393).—The band spectra of the fluorides of calcium, barium, and strontium have been photographed by means of a large Rowland grating of 6.5 m. curvature, and the results are arranged in tables in the original paper. The measurements, unlike the less exact data of Fabry (*Astrophysical J.*, 1905, 21), are not in agreement with Deslandres's law, but conform to Thiele's rule.

E. W. W.

Absorption Spectra of Certain Salts in Aqueous Solution as Affected by the Presence of Certain Other Salts with Large Dehydrating Power. HARRY C. JONES and HORACE S. UHLER (*Amer. Chem. J.*, 1907, 37, 207—244. Compare this vol., ii, 147).—The

detailed account of the spectroscopic investigations, continued from the previous paper, is completed, and a general summary of the results given, supplemented by conductivity and freezing point determination.

The photographic records indicate that the absorption bands of solutions of cobalt and copper chlorides increase in width as the concentration of the solution increases. Addition of a strong dehydrating agent such as calcium or aluminium chloride has the same effect as an increase in concentration, and aluminium chloride is more effective than calcium chloride. In a series of solutions the concentrations of which increase in arithmetical progression, the increments of absorption gradually become less and less.

These observations are explained by the authors on the assumption that the coloured salts form hydrates in solution. The period of vibration of a group of atoms will be greatly affected by its union with water molecules. The more complex the hydrate, the more the vibrations of the original group of atoms will be interfered with and consequently the smaller the number of wave-lengths with which it will be able to respond. In consequence of this, the solution in which the hydrates are the most complex will show the narrowest absorption bands. Earlier work has shown that the hydration of the dissolved molecules increases with dilution. The hydration theory therefore offers an explanation of the spectroscopic observations, since the presence of a dehydrating agent will result in a diminution of the amount of water available for the coloured salt.

The freezing point measurements for solutions of cobalt chloride together with either calcium chloride or bromide indicate that the number of molecules in solution increases with time. This change is supposed to be due to hydrolysis.

H. M. D.

**Absorption Spectra of Certain Salts in Non-aqueous Solvents as Affected by the Addition of Water.** HARRY C. JONES and HORACE S. UHLER (*Amer. Chem. J.*, 1907, **37**, 244—274. Compare preceding abstract).—The change in the absorption spectra on the addition of water to solutions of cobalt chloride in methyl alcohol, of copper chloride in methyl alcohol, ethyl alcohol and acetone, and of copper bromide in methyl and ethyl alcohols has been examined. The photographic plates show that the absorption bands are in all cases widest in the anhydrous solvents and gradually become narrower as the amount of water added increases. It is supposed the coloured salts do not combine to any appreciable extent with the non-aqueous solvents and are therefore capable of responding to vibrations of very different wave-lengths. When water is added, hydrates of the coloured salts are, however, formed, the complexity of these increasing with the amount of water present, and the ability of the atomic groups to respond to incident light waves undergoes a gradually increasing restriction. The evidence thus obtained from the study of non-aqueous solutions is regarded as supporting the hydrate theory of solutions.

H. M. D.

**Photochemical Oxidation of Hydrogen Iodide by Oxygen.** JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1907, **58**, 214—244).—When water charged with oxygen and containing also potassium

iodide and hydrochloric acid is kept in the dark, the oxygen is gradually used up, and the course of the oxidation may be followed by determining at intervals the amount of iodine liberated. When the potassium iodide and hydrochloric acid are in large excess the diminution of the oxygen concentration takes place according to the formula for a unimolecular reaction. When the potassium iodide and hydrochloric acid are present in limited quantity, the rate of decrease of the oxygen concentration is proportional to the  $2/3$  power of the potassium iodide concentration, and to the  $4/3$  power of the hydrochloric acid concentration, so that the course of the change may be represented by the empirical equation:  $-d(O_2)/dt = K_d(O_2)(KI)^3(HCl)^{4/3}$ . The ratio  $K_{\tau+10}/K_{\tau}$  for the reaction in the dark is found to be 2.86. The ions  $Mn^{++}$  and  $Pb^{++}$  exert no catalytic influence, but  $Cu^{++}$  does so to a limited extent, as also does  $Fe^{++}$  and  $Fe^{++} + Cu^{++}$ ; the catalytic effect, however, gradually falls off in the last two cases. Nitrous acid is found to exert a remarkably great catalytic influence on the reaction, but the effect falls off rapidly as the reaction proceeds, because of the decomposition of the acid.

The course of the change is markedly accelerated when the reaction mixture is exposed to the light from a mercury lamp, and it is shown that for this acceleration the blue rays are chiefly responsible. The solution of the reacting substances does not absorb the rays to any appreciable extent, and the velocity coefficient of the reaction is directly proportional to the intensity ( $I$ ) of the light. For blue light ( $\lambda = 436$ ) the course of the reaction may be represented by the empirical equation:  $-d(O_2)/dt = K_{\lambda} \cdot I_{\lambda}(O_2)(KI)^3(HCl)^{4/3}$ . It will be observed that the order of the reaction in relation to the hydrochloric acid is different in the light from what it is in the dark. For the change under the influence of light the ratio  $K_{\tau+10}/K_{\tau}$  is found to have the value 1.4. In presence of uranium nitrate, eosin, starch, or copper sulphate the reaction is retarded; in presence of quinine sulphate, æsculin, or chloroform it is accelerated.

J. C. P.

**Phosphorescence of Uranyl Salts in Liquid Air.** HENRI BECQUEREL (*Compt. rend.*, 1907, 144, 459—462).—As an immediate consequence of the discovery (J. Becquerel) of the resolution, at very low temperatures, of the more or less wide bands in the absorption spectra of certain crystals at ordinary temperature, into fine and multiple bands, and of the intimate connexion long known (compare H. Becquerel, *Abstr.*, 1886, 189) to exist between the phosphorescence emission spectra and the absorption spectra, particularly of uranyl salts, it is to be expected that the variations observed at a very low temperature in the absorption spectra of uranyl compounds will be repeated in their phosphorescence emission spectra under the same conditions. This is confirmed by experiment. The phosphorescence emission spectrum of uranyl nitrate at the ordinary temperature consists of a series of simple diffuse bands, whilst in liquid air the latter become intense narrow double bands between which other much weaker bands appear. The double sulphate and especially the double chloride of uranyl and potassium give groups of bands which in liquid



air are resolved into fine intense bands arranged in the same order in each spectrum.

The phenomenon is also observed with uranium glass. A table is given of the wave-lengths of the principal bands of the phosphorescence emission spectra of the above three salts at the ordinary temperature and in liquid air.

The identity in the modifications undergone by each band in the spectrum of the same salt gives a fresh proof that all the bands either in the absorption or the phosphorescence emission spectrum of uranium compounds have the same origin. In the case of crystals of which the phosphorescence is due to the formation or destruction of compounds of multiple elements existing only in traces in a substance acting as a solid solvent, the phenomenon has a different appearance. Thus in the cathodic phosphorescence spectrum of chlorophane, most of the bands are enfeebled at low temperatures, whilst others, such as the bands  $604\mu$ ,  $564\mu$  attributed by Urbain to samarium, become finer while keeping their original intensity. A sample of leucophane of which the phosphorescence spectrum at the ordinary temperature consists of two parts both continuous, one from  $650\mu$  to  $543\mu$  of great intensity, and the other an intense blue beginning at  $493\mu$ , gives at low temperatures almost exclusively the region 627—600 with a less extensive and feebler blue spectrum. The roseate colour of the light emitted at the ordinary temperature becomes red on cooling.

Thus lowering of the temperature, as with its elevation and the unequal duration of the extinction observed with the phosphoroscope, gives a means of detecting the difference in origin of different bands or regions of the phosphorescence spectra of certain substances of which the phosphorescence appears to accompany the formation or destruction of compounds unequally stable at different temperatures.

E. H.

**Lecture Experiment on the Auxochrome Theory.** The Sulphonic Group as Fluorogen. HUGO KAUFFMANN (*Ber.*, 1907, 40, 838—843. Compare *Abstr.*, 1900, i, 480).—The relation of luminescence to chemical constitution is illustrated by the following experiment. A small amount of each of the three dihydroxybenzenes is heated with concentrated sulphuric acid, not sufficiently strongly to cause decomposition, and the product is poured into an excess of dilute sodium carbonate. Nothing is to be observed with catechol or resorcinol, but with quinol the liquid is yellow and has a strong violet fluorescence which becomes a very intense blue if sodium hydroxide is added. This effect is explained on the basis of the auxochrome theory as being caused by the introduction of fluorogenic sulphonic groups into the luminophoric quinol; catechol and resorcinol having only a very slight tendency to luminescence, are not rendered fluorescent by the sulphonic groups.

Solutions of free quinoldisulphonic acid are only slightly fluorescent, whilst its potassium salt has a strong violet fluorescence in aqueous, and a green to intense blue fluorescence in alkaline, solutions. It would appear that the group  $\text{SO}_3\text{K}$  is the fluorogen, but quinoldisulphonic acid is highly dissociated in its aqueous solution, which must

contain the same anion as is present in the solution of the potassium salt. The difference in the fluorescence is ascribed to a disturbing influence of the hydrogen ions in the solution of the free acid.

The author argues from the foregoing to the conclusion that, contrary to Hantzsch's view, the oxidation product of ethyl succinylsuccinate is ethyl dihydroxyterephthalate and not an isomeric quinonoid substance, and that all the hydrolysis products and salts obtained from ethyl dihydroxyterephthalate, whether coloured or colourless, must be derivatives of quinol if fluorescent. G. Y.

**Relation of Colour to Constitution of Acids, Salts, and Esters.** HUGO KAUFFMANN [and, in part, BURR] (*Ber.*, 1907, 40, 843—846. Compare *Abstr.*, 1906, i, 841; Hantzsch, *ibid.*, 833).—Hantzsch has stated that an appearance, or a change in colour of, ensuing on the formation of salts with colourless metallic atoms must be ascribed to isomeric change. In reply to this and in support of his auxochrome theory, the author shows that a true, aromatic aldehyde, incapable of undergoing isomeric change, may be coloured.

2:5-Dimethoxybenzaldehyde, prepared in a 40% yield by the action of aluminium chloride, hydrogen chloride, and hydrogen cyanide on quinol dimethyl ether in benzene solution, crystallises in needles which appear colourless when observed singly, but greenish-yellow when heaped together; the substance is greenish-yellow when fused and in solution exhibits the same colour phenomena as does nitroquinol dimethyl ether, solutions in associating solvents being colourless whilst those in dissociating solvents are coloured: in water, greenish-yellow with bluish-green fluorescence; in alcohol, yellow with blue fluorescence, and in glacial acetic acid, yellow with bluish-green fluorescence. As the corresponding solutions of benzaldehyde are colourless, the methoxy-groups must be auxochromic.

2:5-Dimethoxybenzaldehyde dissolves also in *isobutyl* alcohol, ethyl benzoate, or chloroform, forming solutions with blue or violet fluorescence. The fluorescence is ascribed to the influence of the fluorogenic aldehyde group on the luminophoric quinol dimethyl ether.

The yellow potassium salt of salicylaldehyde, to which Hantzsch has ascribed a quinonoid structure, is fluorescent in solution or when solid, from which the author argues that it must be, similarly to 2:5-dimethoxybenzaldehyde, a true benzene derivative in which the fluorogen is the aldehyde group whilst the potassium phenoxide nucleus acts as the luminophore. G. Y.

**Chemical Action of Radium.** MARCELLIN BERTHELOT (*Annalen* 1907, 351, 504—509).—An account is given of certain chemical reactions induced by radium rays, reactions of solid substances under the influence of rays which have passed through a gas only, and of rays which have passed through varying thicknesses of glass. The reactions are compared with those resulting from the action of the electric current, of light, and of heat.

Under the direct influence of radium rays, paper absorbs nitrogen

and oxygen, forming carbon dioxide and nitrogen compounds analogous to those formed when paper in contact with nitrogen is subjected to a silent discharge (Abstr., 1899, i, 657); the absorption of oxygen is similar to that which takes place when paper is heated in air. Nitrogen is not absorbed if the radium rays have passed through glass.

Details of experiments on the action of radium rays on glass and on other substances after passing through glass have been published previously (Abstr., 1902, ii, 18, 136).

In consequence of the extreme slowness of the reactions, no conclusions can be drawn as to the individual effect of the  $\alpha$ -,  $\beta$ -, or  $\gamma$ -rays. G. Y.

**Effect of Temperature on the Activity of Radium and its Transformation Products.** HOWARD L. BRONSON (*Proc. Roy. Soc.*, 1906, A, 78, 494—500).—The influence of temperature on the  $\gamma$ -radiation of radium and its transformation products has been examined by placing a sealed quartz tube containing a few tenths of a milligram of pure radium bromide in liquid air or in a platinum resistance furnace placed directly below an electroscope. In order to protect the electroscope from convection currents of air, it was entirely surrounded by another vessel and separated from the quartz tube by two layers of asbestos and one of lead with air spaces between them. Errors due to change in the distribution of radium *C* in the quartz tube were avoided by using a quartz tube short in comparison with the diameter of the electroscope. The ionisation measurements show no evidence whatever of any change in the activity of the transformation products of radium between  $-180^{\circ}$  and  $1600^{\circ}$ . If any change does take place it must be less than 1% in the case of radium *C* between these temperature limits, or less than 1% for the emanation of radium *B* between the limits  $-180^{\circ}$  and  $1500^{\circ}$ .

The conclusion arrived at by Makower that the rate of decay of radium *C* is increased by a rise of temperature is thus shown to be untenable. H. M. D.

**An Attempt to Explain the Radioactivity of Radium.** LORD KELVIN (*Phil. Mag.*, 1907, [vi], 13, 313—316).—Assuming that there is a position of stable equilibrium for an electron near the boundary of an atom and another position at the centre, corresponding respectively with very small and very large potential energy, an explanation of radioactivity is suggested. An atom is termed "loaded" when an electron is contained within the range of stability of the central position, "unloaded" when no electron is present in this region. Starting out with a quantity of radium in which all the atoms are supposed to be unloaded, the equilibrium state corresponding with a permanent average of loadings and unloadings will require a certain interval of time. The energy required for the loading of the atoms is taken from the heat energy of the substance, which is thereby cooled and takes up heat by conduction and radiation from surrounding matter. In the unloading of the atoms, electrons are projected out with enormous velocities. Those discharges which send the electrons towards the interior of the crystals of the radioactive sub-

stance, will, by the recoil, send the unloaded atoms outwards with comparatively small velocity. The unloaded atoms which are positively charged constitute the  $\alpha$ -rays. On account of the much greater velocities the  $\beta$ -particles must be chiefly effective in the heat production observed. An ideal calorimetric arrangement for measuring the steady, permanent, thermal effect of radium is described. H. M. D.

**Criticisms of the Disintegration Theory of Radioactivity and the Theory of Chemico-Physical Molecular Dissociation.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1907, 5, 12—20).—The author considers that the fact that the physical character of the earth's crust has not appreciably changed during the lapse of geological ages is opposed to the disintegration theory according to which substances such as radium and uranium possess only a limited period of existence. The idea is advanced that, intermediate between the atoms of the chemist and the molecule of the physicist, there exist, under conditions of considerable instability, complexes which are called *chemico-physical molecules*; such would appear to be formed by the union of certain of the heavy atoms (uranium and thorium) with the inactive elements, helium and its congeners. The decomposition or rearrangement of such complexes is accompanied by the so-called radioactive phenomena; this view is discussed at some length. W. A. D.

**Radioactivity of the Alkali Metals.** NORMAN R. CAMPBELL and ALEXANDER WOOD (*Proc. Camb. Phil. Soc.*, 1907, 14, 15—21. Compare Abstr., 1906, ii, 411).—A comparison of the activities of various potassium salts confirms the theory that the activity is an atomic property. Potassium salts exhibit a radioactivity greater than that of any other substance yet examined not containing a so-called radioactive element; this is shown to be due, not to any impurity contained in the salts, but to the potassium itself. As measured by its ionising power, the activity of potassium is one-thousandth of that of uranium as measured by the ionisation caused by the  $\beta$ -rays of that substance. The rays from potassium salts are heterogeneous and vary in penetrating power from that of the  $\beta$ -rays of uranium downwards; they seem to be able to produce an effect on a photographic plate.

The activity of rubidium salts is much less than that of potassium salts, and that of caesium, lithium, and sodium salts is too small to measure. W. H. G.

**Production of Radioactivity in Liquids Exposed to the Emanation of Minerals from San Rafael de el Espinar.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1907, 5, 21—22).—The radioactivity of water exposed to the action of the emanation from chalcocite increases with the duration of the exposure. W. A. D.

**Conductivity of De-aerated Water in Presence of Radium Emanations.** UGO GRASSI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 179—183. Compare Abstr., 1905, ii, 793).—The author finds that the emanations of radium produce no sensible increase in the conductivity of de-aerated water. The increase observed (*loc. cit.*) in

liquids in presence of gas is hence due to a specific action of the dissolved gas. In the first few moments, during which the radium emanations are passed through the de-aërated water, the conductivity of the latter exhibits a slight decrease, from  $1.537$  to  $1.530 \times 10^{-7}$  reciprocal ohms, which is probably due to the shaking produced. The experiments are to be continued with solutions of acetylene in acetone.

T. H. P.

**Radioactivity of Certain Fresh-water Springs of the Taunus.** III. AUGUST SCHMIDT (*Physikal. Zeitsch.*, 1907, 8, 107—112. Compare Abstr., 1905, ii, 220).—Reference is made to certain observations contained in the two previous papers, and it is shown that the results can easily be expressed in absolute measure. Monthly measurements of the radioactivity issuing from two fresh-water springs (Wahlsborn and Eiserne Hand) during 1906 indicate that this depends on the rate of outflow and on the temperature; it increases with increase in the quotient—rate of outflow/temperature.

Observations have also been made of the radioactivity of the air in the immediate neighbourhood of various hot springs. The activity is from three to six times as great as that of the air at some distance from the springs. Reference is made to the possibility of this circumstance having some physiological significance.

H. M. D.

**Radioactivity of Mineral Springs and their Sediments.** CARL ENGLER and H. SIEVEKING (*Zeitsch. anorg. Chem.*, 1907, 53, 1—25).—The radioactivity of the water from some hundreds of mineral springs in south-west Germany, Austria, and Italy has been determined under exactly equivalent conditions, and the results are tabulated. The measurements were made with a special apparatus; a known volume of the water was shaken for half a minute with a definite volume of air, and the conductivity of the latter subsequently measured in the same vessel with an electroscope. The apparatus can also be employed in a slightly modified form for determining the radioactivity of solids.

Thermal springs are in general more radioactive than cold springs, but the colder thermal springs are usually more active than the warmer ones. The majority of the highly radioactive springs issue from granite. Water loses its radioactivity to a great extent by being passed through long pipes.

The sediment from the hot springs at Baden-Baden is strongly radioactive; it contains barium and manganese, but no thorium or uranium. It was separated into two parts by boiling with hydrochloric and sulphuric acids, and radium was detected in the insoluble part, whilst the filtrate contained radio-thorium (compare Elster and Geitel, *Physikal. Zeitsch.*, 1905, ii, 720; Hahn, Abstr., 1905, ii, 432, 789).

G. S.

**The Radioactivity of Spanish Medicinal Springs.** VI. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1906, 4, 444—445. Compare this vol., ii, 62—64).—Measurements of the radioactivity of samples of water from eleven different springs are given. The samples

from the Fuente Aceñas, Lerez, have an extraordinarily high activity, exceeding 10,000 volts per hour per litre; such a value is greater than that hitherto observed for any other mineral spring in Europe. The gas and residues from this water are also highly active. The high activity of the water would appear to indicate that in the neighbourhood of Pontevedra a deposit of radioactive material exists similar to that of the Joachimsthal.

W. A. D.

**Decay of Radioactivity of Spanish Mineral Waters.** José MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1907, 5, 22—33).—The rate of decay of the radioactivity of the water from the hot springs of Besaya and Oviedo shows that the principal and almost the sole active constituent is radium. Coefficients are given by which the radioactivity of samples of these mineral waters can be calculated for therapeutic purposes at different periods subsequent to bottling.

W. A. D.

**Scattering of  $\alpha$ -Rays in Metals.** B. KUČERA (*Physikal. Zeitsch.*, 1907, 8, 103—107).—The ionisation produced by  $\alpha$ -rays (from radium *F*) after passing through screens of two different metals, such as aluminium and tin, varies according to the order in which the screens are placed. It is greater when the rays pass through the aluminium screen first. The phenomenon is explained by the author as being due to the scattering of the rays by the metal screens, the scattering power of a metal increasing with its atomic weight. It is shown that the observations of E. Meyer (*Physikal. Zeitsch.*, 1906, 7, 917) on the ionisation produced by  $\alpha$ -rays after passing through successive screens of different metals can be easily accounted for on this view. The data agree better with this view than with that of Meyer, according to which the  $\alpha$ -rays undergo transformation in passing through the metal screens, secondary rays being produced which cause ionisation, this ionisation being proportional to the absorption of the  $\alpha$ -rays which takes place in the metals.

H. M. D.

**Ionisation of Various Gases by the  $\alpha$ -Particles of Radium.** No. 2. WILLIAM H. BRAGG (*Phil. Mag.*, 1907, [vi], 13, 333—357. Compare Abstr., 1906, ii, 322).—Further measurements of the relative amounts of ionisation produced in various gases and vapours by the  $\alpha$ -particle of radium *C* have been made. A method of determining the total ionisation due to the  $\alpha$ -particles without using large chambers and high potentials is described, and the assumptions involved in the deduction of the specific ionisation values are discussed. The results obtained are in agreement with the view that the ionisation  $\delta_i$  produced by a loss of energy  $\delta_e$  of the  $\alpha$ -particle is related to the latter quantity by the equation  $\delta_i = k f(v) \delta_e$ , in which  $f(v)$  is a function of the velocity of the particle and  $k$  the specific ionisation of the gas under consideration referred to air as standard. The values of  $k$  for eighteen gases and vapours are recorded.

The values of the product  $ks$ ,  $s$  being the stopping-power of the gas, are also given, and it is shown that these values are nearly related to additive properties such as molecular volume and molecular refractive

power. Since the values of  $k$  for a number of gases are nearly equal, it follows that the stopping-power is of an additive nature. By putting the stopping-power of  $H_2 = 0.24$ ,  $C_2 = 0.85$ ,  $O_2 = 1.03$ ,  $Cl_2 = 1.78$ , the calculated stopping-powers of a number of gases are in good agreement with the observed values. Apart from its additive character the stopping-power of an atom is found to be nearly proportional to the square root of the atomic weight. H. M. D.

**Secondary Röntgen Radiation.** JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1907, 14, 109—114).—A very intimate relationship is found to exist between the atomic weight of an element and the secondary Röntgen radiation, an increase in the atomic weight being accompanied, except in the case of nickel, by an increase in the stream of radiant energy. The author concludes that the atomic weight of nickel is therefore greater than that of cobalt. W. H. G.

**Properties of Uranium and Actinium.** MAX LEVIN (*Physikal. Zeitsch.*, 1907, 8, 129—133. Compare this vol., ii, 150).—A preparation of uranium nitrate which has been kept over calcium chloride for some time exhibits irregular variations in respect of its  $\beta$ -radiation when placed in an atmosphere saturated with water vapour. The  $\beta$ -activity diminishes rapidly, attains a minimum value, and then increases rapidly to a maximum, after which a slow fall takes place. The explanation suggested is that the original diminution is due to absorption of water and the formation of a thin film of solution on the surface of the crystals. The increase in the observed activity is accounted for by the greater solubility of uranium  $X$  in this superficial liquid film and the slow decrease by the further absorption of water. Similar, but smaller, variations are observed in the case of the  $\alpha$ -radiation.

Uranium  $X$ , prepared by boiling uranium nitrate solution with animal charcoal and combustion of the carbon, is found to emit both  $\alpha$ - and  $\beta$ -rays. Measurements of the ionisation produced by uranium  $X$  with and without interposed screens and magnetic field indicate that about 8% of the total activity is due to  $\alpha$ -rays. The higher value of 34% found by Schlundt and Moore is probably due to the fact that easily absorbed secondary  $\beta$ -rays are produced in considerable quantity.

Experiments on the electrolysis of actinium solutions show that actinium  $X$  can only be separated at the cathode in pure condition if actinium and radioactinium have been removed previously. Zinc, lead, copper, and silver precipitate actinium  $A$  from acid or ammoniacal solutions of actinium  $X$ ; actinium  $B$  is also recognisable in the product obtained by using zinc and strongly acid solutions. Animal charcoal which has been boiled with nitric acid solutions of actinium contains large quantities of radioactinium and small quantities of actinium  $X$ . Similarly, thorium  $B$  is the chief product separated from thorium nitrate solutions. H. M. D.

**Ultimate Disintegration Products of the Radioactive Elements. Part II. The Disintegration Products of Uranium.** BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1907, [iv], 23, 77—88. Compare this vol., ii, 62).—From the analytical data for a large number of

uranium minerals it is found that the amount of lead in unaltered primary minerals from the same locality is proportional to the amount of uranium present. In primary minerals from different localities, the relative proportion of lead is greatest in minerals from the locality which, on the basis of geological data, represents the oldest formation and is least in minerals from the locality of most recent geological formation. The maximum value of the ratio is about six times the minimum. The data are considered to prove that lead is the final disintegration product of uranium. From the value of the rate of decay of radium, regarded as one of the intermediate disintegration products, the author calculates the ages of the various minerals. The data available also indicate that the amounts of helium in various radioactive minerals are of the expected order of magnitude, and in no case exceed the quantities which are calculated on the assumption that helium is produced according to the equation : uranium = lead + helium.

In minerals containing uranium and thorium, the proportions of these may vary very considerably without exercising any noticeable effect on the value of the lead-uranium ratio for the particular locality. From this it appears that lead is not a disintegration product of thorium. The mineral thorite, in which very little uranium is present, contains neither lead nor helium according to published analytical data.

H. M. D.

**Electrification Produced by Heating Salts.** JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1907, 14, 105—108).—An investigation to see if any relation exists between the sign and amount of electricity given off when a salt is heated and the chemical nature of the salt. It is found that the sign of electrification given off on heating depends on the class of the salt and not on the metal, and that it is the same, with the exception of the higher oxides of a metal, as that produced by friction of the cold, dry, powdered salt or oxide. All the phosphates examined gave off positive electricity at a red heat, aluminium phosphate to the greatest extent; nitrates give off positive electricity as do likewise chlorides, but nothing like so much as the phosphates. Oxides when heated give out an excess of negative electricity, the largest quantities being obtained from the oxides of barium and calcium.

W. H. G.

**Chemical Effects of the Electric Discharge in Rarefied Hydrogen and Oxygen.** P. J. KIRKBY (*Phil. Mag.*, 1907, [vi], 13, 289—312. Compare *Abstr.*, 1905, ii, 236).—Experiments have been made to determine the amount of water formed by the passage of a coulomb of electricity through one centimetre of the positive column in the discharge through a mixture of hydrogen and oxygen in equivalent proportions, and also to determine the fall of potential in the positive column. At a given gas pressure this fall of potential is independent of the current, whilst at other points of the discharge it varies with the current as well as with the pressure. When the distance between the electrodes is large, the weight of water formed per coulomb is greater for the lower pressures than for the higher. A



maximum is reached at a pressure of 1.4 mm. of mercury, the water formation being smaller in amount at lower pressures than this. Although at the lower pressures the number of impacts made by an ion in moving through a centimetre is smaller than at the higher pressures, yet this is apparently more than counterbalanced by the higher velocities of impact of the ions with the gaseous molecules in the former case. Some of the molecules dissociated by impact yield ozone, but the proportion of these is relatively small.

An experiment is also described which confirms the previous conclusion that the cathode column is the region of greatest chemical activity.

H. M. D.

**Methods of Determining the Internal Resistance of Galvanic Cells.** WALTER BLOCK (*Zeitsch. physikal. Chem.*, 1907, 58, 442—448).—The method due to Mance and Lodge is found to be much less accurate and trustworthy than the methods which depend on the use of alternating currents. The latter methods are discussed and compared.

J. C. P.

**Electromotive Force of Iron Under Various Conditions, and the Influence of Occluded Hydrogen.** THEODORE W. RICHARDS and GUSTAVUS E. BEHR (*Zeitsch. physikal. Chem.*, 1907, 58, 301—349).—For the purpose of this investigation, iron free from all impurity except hydrogen has been prepared by dissolving piano-wire of good quality in dilute nitric acid, igniting the crystallised nitrate, and reducing the oxide in a current of pure hydrogen (compare Richards and Baxter, *Abstr.*, 1900, ii, 407). On the assumption that the potential of the calomel normal electrode is 0.56 volt, the potential of the porous iron prepared by the foregoing method and immersed in a normal solution of ferrous sulphate is found to be 0.17—0.18 volt. This value is higher by about 0.02 volt than the potential of pure compact iron which has been fused; the difference is probably connected with the size of the iron particles. The potential of iron is inappreciably affected by exposing it to very high pressures, by stretching it to breaking point, or by cooling it rapidly from a high temperature. If porous iron is immersed in ferrous sulphate solution, the *E.M.F.* observed slowly increases, probably because it has become altered by exposure to the air; if the iron is left long enough in the ferrous sulphate solution, a constant *E.M.F.* is attained. Finely-divided iron, obtained by reduction at comparatively low temperatures, has the power of absorbing hydrogen, but the potential of the metal is not appreciably affected thereby, unless the surface is fully charged with hydrogen, when the potential is somewhat lowered. When iron which has been heated in an atmosphere of hydrogen or nitrogen is suddenly cooled by plunging into water, it absorbs hydrogen from the water in a specially active form, in virtue of which the potential is raised by about 0.15 volt. This hydrogen is not readily removed when the iron is kept in water or potassium sulphate solution, but is rapidly expelled when the iron is immersed in ferrous sulphate solution, the potential returning to its normal value. The active hydrogen occluded by iron in this way seems to be of the same nature as that

taken up by iron in presence of nascent hydrogen originating either from chemical or electrolytic processes. It is probable that this active hydrogen is in the atomic condition, although not ionised. J. C. P.

**Relation Between Current and Potential Difference at the Cathode and Anode in the Electrolysis of Solutions of Iodine in Potassium Iodide.** ERICH BRUNNER (*Zeitsch. physikal. Chem.*, 1907, 58, 1—126).—The experiments recorded in the paper were undertaken in the attempt to decide whether the cathodic reduction of iodine to iodine ion and the anodic oxidation of iodine ion to iodine is to be regarded as purely a diffusion process for all potential differences. Solutions of iodine in potassium iodide with excess of potassium chloride and a little hydrochloric acid were used, and the polarisation was measured between the platinum observation electrode, through which a current of known strength passed, and a platinum auxiliary electrode, through which no current passed. The values thus observed ( $\epsilon$ ) for the polarisation were compared with those calculated ( $\epsilon_0$ ) on the supposition that the polarisation is determined only by the concentration of iodine and iodine ion at the electrode; in other words, that for a given polarisation the current strength depends simply on diffusion velocities. For the purpose of this calculation it was necessary to determine the ratio of the diffusion coefficients for the ions  $I'$  and  $I_3$ ; this was found = 1.5. It was shown also that the diffusion coefficients of  $I_2$  and  $I_3$  have practically the same value.

Only for a very dilute solution of iodine was the relation  $\epsilon = \epsilon_0$  found to be verified. In other cases the relation between these two quantities is adequately represented by the equation  $\epsilon = \epsilon_0 + I(\omega_0 + \omega')$ , where  $I$  is the current strength. The factor  $\omega_0 + \omega'$  is the apparent resistance between the observation electrode and the auxiliary electrode;  $\omega_0$  is constant for a given arrangement and a given conductivity of the solution;  $\omega'$  represents the real difference between calculation and experiment, and for a given arrangement and a given conductivity of the solution depends only on  $d\epsilon/dI$ . The difference between calculation and experiment is attributed by the author to unequal distribution of current density and potential over the electrode, but experiments made with varying conditions are not decisively in favour of this explanation.

The paper deals also at considerable length with various theoretical points bearing on the subject of electrolytic oxidation and reduction.

J. C. P.

**Electrolysis Through Precipitation Films.** W. S. MILLAR and WILLIAM W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1906, 26, 447—463).—Measurements have been made of the resistance which precipitated films of aluminium and chromium hydroxides offer to the motion of various ions. For the experiments, a U-shaped vessel with a narrow tube connecting the wider limbs was used chiefly. It was cut into two equal parts, the edges carefully ground, and a brass coupling joint was cemented on in such a way that the diaphragm could be mounted, liquid-tight, between two rubber washers. Porous earthenware was found to give the best results as diaphragm material. In order to avoid

the enclosure of foreign soluble salts by the precipitated film the following procedure was adopted. Fairly concentrated solutions of ammonium chloride were placed in each compartment of the cell and the electrical resistance was measured. Equally concentrated ammonium chloride solutions, the one containing a considerably smaller quantity of ammonia, the other an equivalent quantity of aluminium chloride, were then introduced into the separate compartments and measurements of the resistance made from time to time until constant results were obtained. The conductivity of solutions of ammonium chloride, bromide, and sulphate is reduced by a film of aluminium hydroxide prepared in this manner to the extent of 3, 7, and 20% respectively, and this difference is attributed to the different effects exerted on the anions. A similar but smaller difference is found for the cations when ammonium, potassium, and sodium sulphate solutions are compared. When the results obtained with films of aluminium and chromium hydroxide are compared, the ions arrange themselves in the same order, although the magnitude of the diminution of the conductivity is different in the two series. The values obtained for the diminution in the conductivity of a particular solution are not all identical, but appear to group themselves around two values. This effect is supposed to be due to the existence of more than one modification of the colloidal film.

The temperature coefficient of the conductivity of an ammonium sulphate solution divided into two parts by a chromium hydroxide film is much greater than for ammonium sulphate solution alone. This is supposed to be due to a change in the nature of the precipitation film.

The conductivity of solutions of sodium ammonium *d*-tartrate and racemate is diminished to the same extent, and from this the conclusion is drawn that the racemate solution does not contain any considerable proportion of racemate ions.

H. M. D.

**Electrolytic Applications of Alternating Currents.** ANGELO COPPADORO (*Gazzetta*, 1906, **36**, ii, 693—723. Compare Abstr., 1906, ii, 214, 849).—This paper is divided into three parts, the first dealing with the industrial use of alternating currents in electrolysis, the second with the aluminium valve-cell or rectifier, and the third with the behaviour of nickel electrodes towards alternating currents.

Using ordinary alternating currents with a periodicity of 42 per second, the process of Richards and Roepper (*Eng. Pat.*, 9637 and 9638, 1898) for the preparation of insoluble compounds cannot be applied to the manufacture of the sulphides of zinc, cadmium, &c., the yields being very small. With electrodes of lead and solutions of sulphuric acid, however, these alternating currents give good yields of lead sulphate; the best energy yield is obtained with 50% acid, the difference of potential at the electrodes not exceeding 4 volts. The action on the lead seems to depend on the formation of persulphuric acid during the anodic phase.

The experiments with the aluminium rectifier show that by this means it is impossible to resolve the alternating current completely into two equal and opposite direct currents; two new alternating currents are always obtained in which one phase has an intensity much

greater than that of the other, the ratio between the two intensities being variable.

With sulphuric acid having a concentration between 5 and 40%, nickel is dissolved almost quantitatively under the action of an alternating current when the density of the latter exceeds 50 amperes per sq. cm. With densities lower than this value, the condition of the surface of the electrodes exerts a considerable influence on the amount of metal dissolved. With 50—60% sulphuric acid, the yield of dissolved nickel first increases to a maximum with augmentation of the current density and subsequently diminishes considerably, indicating that the metal becomes passive; at the same time, oxygen appears mixed with the hydrogen evolved. The amount of nickel dissolved is increased by the presence in the acid of oxidising agents such as potassium permanganate or hydrogen peroxide, or even by the passage of air through the electrolyte. The current yield of nickel dissolved in other acids, such as hydrochloric, nitric, and acetic acids, is also high. Using potassium chloride solution as electrolyte, the current yield of dissolved nickel never exceeds about 10%; hydrogen unmixed with chlorine is evolved, nickel hydroxide is precipitated, and the electrodes become coated with a thin, black film of finely-divided nickel. Addition of potassium hydroxide to the chloride lowers the yield considerably, and increase of the current density then causes further diminution in the yield, the nickel exhibiting the passivity it presents in alkaline solutions under the action of a direct current. When sodium nitrate solution is used, the passivity is perfect, no nickel being dissolved or gas evolved; with sodium chlorate, the passivity is almost perfect, but with potassium sulphate, slightly more nickel is dissolved, nickel hydroxide being also formed. T. H. P.

**Mobility of Ions in Water.** KARL DRUCKER (*Zeitsch. Elektrochem.*, 1907, 13, 81—83).—Using the best experimental material available, the mobilities of some ions in aqueous solution at 18° are recalculated. The values obtained are:  $K = 64.4$ ,  $Na = 42.7$ ,  $Ag = 54.0$ ,  $H = 313$ ,  $Cl = 65.2$ ,  $NO_3 = 62.3$ ,  $\frac{1}{2}SO_4 = 66.7$ . In salts of heavy metals, the anions appear to have different mobilities. T. E.

**Specific Heat of Gases at Constant Volume and High Pressure.** W. A. DOUGLAS RUDGE (*Proc. Camb. Phil. Soc.*, 1907, 14, 85—89).—The mean value for the specific heat of carbon dioxide at constant volume and under a pressure of approximately 420 atmospheres is found to be 0.45, the gas employed being that sold in small bulbs or “sparklets” used for aerating water. Incidentally, it is shown that the latent heat of liquid carbon dioxide at the critical temperature is zero. W. H. G.

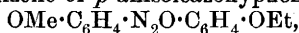
**Specific Heat of Calcium and Lithium.** ARCIERO BERNINI (*Physikal. Zeitsch.*, 1907, 8, 150—154).—The specific heats of calcium and lithium have been measured between 0° and 157° by means of a Bunsen ice calorimeter. The following results were obtained: calcium, 0—20.3°, 0.1453; 0—78°, 0.147; 0—100°, 0.149; 0—157°, 0.1521; lithium, 0—19.3°, 0.8366; 0—78°, 0.9875; 0—100°, 1.0925; 0—157°, 1.1025.

1.3215. The specific heat of lithium thus increases very rapidly with the temperature. Comparing the rate of increase in the case of lithium, sodium, potassium and calcium, it is found that this increases with decreasing atomic weight. Previous determinations of the specific heat of sodium and potassium have been repeated with the same result, and the author draws the conclusion that the much higher values obtained by Joannis are due to impurities in the material used.

H. M. D.

**Molecular Attraction. VI. The Mutual Neutralisation of the Attraction by the Attracted Particles and the Nature of Attractive Forces.** JAMES E. MILLS (*J. Physical Chem.*, 1907, 11, 132—166. Compare Abstr., 1906, ii, 216).—The question as to whether the validity of the equation  $(L - E)/(\frac{2}{3}d - \frac{2}{3}D) = \text{constant}$ , where  $L$  is the latent heat of vaporisation of a liquid,  $E$  the energy spent in overcoming external pressure, and  $d$  and  $D$  are the densities of the liquid and vapour, may be due to the attraction between the molecules operating otherwise than according to the law of inverse squares is discussed. A more rigorous deduction of the equation is given and the experimental evidence in favour of it is summarised. Applying Helmholtz's method of calculating the amount of energy given out by the contraction of the sun to the process of the vaporisation of a liquid, the result is obtained that the work done should vary as the five-thirds power of the mass, and that the equation  $(L - E)/(\frac{2}{3}d - \frac{2}{3}D) = \text{constant}$  should only be valid when a constant mass of liquid is taken. An explanation of the apparent contradiction is suggested, which involves a new conception in regard to the operation of attractive forces in general. According to this, the attractive forces proceeding from a particle, whatever their nature, whether chemical, molecular, magnetic, electrical or gravitational, have a finite value. If this attractive force is exerted on another particle, the amount of the attraction remaining for operation on other particles is diminished by an exactly equivalent amount. As a consequence of this view it follows that all these various attractive forces are measured by the amount of the attraction neutralised, and the idea that the gravitational attraction, for instance, of a particle can remain undiminished regardless of the amount of the attraction which it exerts on other particles, is claimed by the author to be contrary to the law of the conservation of energy. H. M. D.

**Thermal Investigation of an Anisotropic Liquid.** L. ROTIN-  
IANTZ and TH. ROTARSKI (*J. Russ. Phys. Chem. Soc.*, 1906, 38,  
782—789).—The anisotropic or liquid crystalline substance, 4-meth-  
oxy-4'-ethoxyazoxybenzene or *p*-anisoleazoxyphenetole,



is shown to be a mixture of dimethoxy- and diethoxy-azoxybenzenes. Curves are drawn showing the variation in melting points, and the transparency of different mixtures of these substances, from which it is evident that there is no relation between the transparency and melting point curves. The transparency curve is a straight line which satisfies the equation  $T = (ut + u_1t_1)/(u + u_1)$ , where  $t, t_1$  are the temperatures of transparency of the respective substance; and  $u, u_1$

the respective number of molecules present in the mixture. Riesing's compound, having an anisotropic phase,  $94-149.6^{\circ}$ , was probably a 50% mixture, but those obtained by others were probably not free from azo-compounds. It is considered that, in general, methoxyethoxy-azoxybenzene cannot exist, for, whenever an attempt is made to produce such a compound from the corresponding nitro- and hydroxylamine derivatives, the two respective azoxy-compounds are obtained, but never a mixed derivative such as the one in question. Z. K.

**Behaviour of Certain Substances at their Critical Temperatures.** ISIDOR TRAUBE (*Zeitsch. physikal. Chem.*, 1907, 58, 475-478. Compare Abstr., 1904, ii, 110, 237; also Teichner, *Ann. Physik*, 1904, [iv], 13, 595).—A criticism of Travers and Usher's recent work (this vol., ii, 8). Relying chiefly on Teichner's experiments (*loc. cit.*), the author maintains that the temperature at which the meniscus disappears is not the true critical temperature. If it is permissible to speak of a critical temperature at all, it must be considerably higher than the temperature of Cagniard de la Tour. The author suggests that the conception of a "critical temperature" should be replaced by that of a "critical temperature period" extending over a definite range of temperature.

J. C. P.

**Variation of Vapour Tension as a Function of the Temperature and the Determination of Ebullioscopic Constants.** GEORGES BAUME and D. E. TSAKALOTOS (*Compt. rend.*, 1907, 144, 373-376).—The latent heat of vaporisation  $L$  of a liquid can be calculated (neglecting the volume of the liquid compared with that of the vapour) from the equation  $L = RT^2/JMp.dp/dT$ , where  $J$  is the mechanical equivalent of heat,  $p$  the vapour pressure,  $M$  the molecular weight of the vapour at the absolute temperature  $T$ , and  $R$  the gas constant; and also from van't Hoff and Le Chatelier's expression,  $L = 0.02T^2/E$ . By equating these two values of  $L$  the relation  $dp/dT = 0.01Mp/E$  is obtained,  $E$  being the molecular elevation of the boiling point of the liquids as solvents, and the ratio  $R/J$  being taken as equal to 2. This relation can be used to study the variation  $dp/dT$  of the vapour tension with the temperature, at temperatures near the boiling point, under the pressure  $p$ , provided the value of  $E$  (which varies with  $p$ ) is known, and has been employed by the authors to calculate the elevation  $\Delta T$  of temperature corresponding with a variation of pressure  $\Delta p$  of 1 mm. (initial pressure 760 mm.) for the liquids water, alcohol, ether, acetic acid, acetone, chloroform, ethylene dibromide, benzene, aniline, phenol, carbon disulphide, and sulphur dioxide. The values of  $E$  experimentally obtained by Beckmann were used in the calculation, and the numbers obtained agree very well with those obtained by experiment, in the case of all the liquids except acetic acid. In the latter case the deviation is due to polymerisation of the vapour, and applying the necessary correction to the molecular weight  $M$  gives a result agreeing with experiment.

Conversely the same equation can be used to calculate the molecular elevation  $E$  of the boiling points of liquids of which the molecular weight and variation of vapour tension with temperature are known.

The values of  $E$  for the above liquids so obtained (taking  $p = 760$  mm.) agree well with the experimental numbers, and fairly well with those obtained by van't Hoff's expression (compare Beckmann, Fuchs, and Gernhardt, *Abstr.*, 1896, ii, 236). This equation also shows that  $E$  is not constant, but increases proportionately to the pressure,  $dp/dT$  being practically constant for small variations in  $p$  (compare Beckmann, *Abstr.*, 1890, 323; 1891, 389). The values of  $E$  for water at  $70^\circ$ ,  $100^\circ$ , and  $130^\circ$  calculated both by this and by van't Hoff's equation are given.

Finally, the authors' equation shows that two substances having the same value for the ratio  $E/M$  have the same variation in their vapour tension. This agrees with the kinetic theory. E. H.

**Is it Permissible to Draw Conclusions as to the Molecular Condition of a Solvent from an Abnormal Boiling Point Elevation Observed for a Dilute Solution?** JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1907, 57, 742—744).—The answer is in the negative, but it is remarked that some information as to the molecular condition of the solvent might be obtained from abnormal elevations of the boiling point for concentrated solutions. Incidentally, it is pointed out that in the vapour pressure and boiling point formulæ for dilute solutions the ratio  $n/N$ , and not  $n/(N+n)$ , should appear. J. C. P.

**Molecular Weight Determinations of Oils and Fats.** WILHELM NORMANN (*Chem. Zeit.*, 1907, 31, 211—214).—The molecular weights of various vegetable and mineral oils have been determined by the cryoscopic and ebullioscopic methods in order to see how far these methods are applicable in these cases. It is found that the mol. weights of glycerides cannot be so determined. The values obtained by the cryoscopic method for castor, olive, rape, and train oils, using phenol or nitrobenzene as solvent, are in dilute solutions smaller than those calculated from the saponification values, but increase considerably as the concentration increases; on the contrary, when benzene is the solvent the reverse is the case, high values for the mol. weight being obtained in dilute solutions, which become smaller as the concentration increases. Similar results are also obtained by the ebullioscopic method, using benzene, chloroform, carbon disulphide and ether as solvents, very high values for the vegetable oils being obtained in dilute solutions, which diminish as the concentration increases.

The values obtained for mineral oils by either method, using benzene as solvent, are not affected to any great degree by the concentration, the oils having the greatest viscosity giving the greatest values for the molecular weight. W. H. G.

**Cryoscopic Behaviour of Iodoxy-derivatives in Formic Acid.** LUIGI MASCARELLI and MEDARDO MARTINELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 183—186).—The authors have determined the molecular weights of various iodoxy-derivatives in freezing formic acid, the results being as follow. Iodoxybenzene, 207.3 and 217.3 instead of 236; *o*-iodoxytoluene, 183.1, 188.1, and 182.9 instead of 250; *m*-iodoxytoluene,

178.4—217.4 instead of 250; and *p*-iodoxytoluene, 219.9—220.8 instead of 250. These low values are probably to be explained in the same way as the abnormal numbers obtained for nitro-derivatives in formic acid by Bruni and Berti (Abstr., 1900, ii, 591, 592). T. H. P.

**Critical Solution Temperature of Ternary Mixtures.** J. TIMMERMANS (*Zeitsch. physikal. Chem.*, 1907, 58, 129—213).—Naphthalene, anthraquinone, camphor, benzophenone, and benzil are all found to raise the critical solution temperature of mixtures of phenol and water, apparently because these substances are soluble in only one of the components of the binary mixture. Similarly, the critical solution temperature of the system phenol + water is raised by the addition of salts, such as potassium chloride, potassium bromide, and sodium chloride, and the molecular elevation of the critical solution temperature is abnormally great in these cases. If the third added substance, for example, azobenzene or boric acid, is soluble in both liquids, but in very different degrees, the critical solution temperature is still raised, but the molecular elevation is abnormally small. Lastly, if a third substance be added, the solubilities of which in the two liquids are of the same order of magnitude, for example, salicylic acid, mercury cyanide, or sodium oleate, the critical solution temperature is lowered. Besides the system phenol + water, the systems succinonitrile + water and hexane + nitrobenzene have been examined, and similar results have been obtained. The phenomena here observed are apparently governed by laws analogous to those deduced by Centnerszwer (Abstr., 1904, ii, 158; see also van Laar, Abstr., 1905, ii, 434; Büchner, Abstr., 1906, ii, 71) and van't Hoff (Abstr., 1904, ii, 237) for the critical temperature of vaporisation.

A liquid mixture containing two completely miscible components may frequently be made to separate into two phases by the addition of a third substance. Salts are especially effective in this direction, and the author has studied the effect of potassium bromide in salting out propyl alcohol from water. Consideration of the critical solution temperatures for the higher alcohols and water indicates that for propyl alcohol and water the centre of a hypothetical saturation curve should be about 50°, that the upper critical solution temperature should be about 30°, and the lower critical solution temperature about 70°. Addition of potassium bromide, it is supposed, raises the upper critical solution temperature (30°) and depresses the lower critical solution temperature (70°) until a condition of saturation is reached. The conception of the existence of a negative saturation curve for systems of two completely miscible liquids is used to interpret various properties of solutions.

In the case of two liquids that are very slightly soluble in each other, it may be supposed that the upper critical solution temperature lies above the higher boiling point, and that the lower critical solution temperature lies below the cryohydric point. The addition of a little quinol to the system water + *sec*-butyl alcohol raises the lower critical solution temperature above the freezing point of the mixture, and the addition of much quinol makes the alcohol and the water miscible in all proportions at all temperatures.



Ternary systems of three liquid components are discussed at length from the point of view of the phase rule, and several cases have been found where three liquid phases occur; an example, specially suitable for demonstration, is furnished by the system water + nitrobenzene + hexane.

When the salts are arranged in the order of their ability to cause the system water + propyl alcohol (or water + pyridine) to separate into two layers, or in the order of their power to raise the upper critical solution temperature of the system water + phenol, the order is roughly the same as when they are arranged according to the magnitude of their influence on the solubility of phenylthiocarbamide (see Rothmund, *Abstr.*, 1900, ii, 467; Biltz, *Abstr.*, 1903, ii, 358).

Experiments are described showing that the analogy between the critical temperature of vaporisation and the critical temperature of solution extends also to the phenomena of retrograde separation into two phases, and retrograde solidification. By reference to the behaviour of the system water + ether + cadmium iodide, it is shown that the parallelism between the critical temperature of vaporisation and the critical temperature of solution may be explained by the continuity of the liquid and gaseous states.

J. C. P.

**Use of Oxygen, Prepared Electrolytically, in Experiments with Berthelot's Calorimetric Bomb.** PAWEŁ W. ZUBOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1123—1128. Compare *Abstr.*, 1904, ii, 382).—Further experiments, in which oxygen containing varying proportions of hydrogen was employed, show that only that part of the hydrogen mixed with the oxygen actually used up in the calorimetric bomb undergoes combustion. The correction regarded by Berthelot (*Abstr.*, 1903, ii, 70) as necessary when electrolytic oxygen containing small quantities of hydrogen is employed in the calorimetric bomb must hence be reduced to about 20% of the value given.

T. H. P.

**Heats of Combustion and of Formation of Certain Nitrogenous Substances of Physiological Importance.** MARCELLIN BERTHELOT and PHILIPPE LANDRIEU (*Compt. rend.*, 1907, 144, 457—459).—A sample of hæmatin consisting of brilliant dark violet crystals gave on analysis: C, 64.0%; H, 5.1%; N, 9.9%; Fe, 9.9%, and O, 11.1%. The heat of combustion of 1 gram is 5231 cal. at constant volume or 5236 cal. at constant pressure. The heat of formation of 1 gram is +1691 cal.

A sample of bilirubin, a non-crystalline brown powder, gave on analysis: C, 66.01%; H, 6.01%; N, 9.03%; and O, 18.95%; the formula suggested being  $C_{16}H_{18}O_4N_2$ . The heat of combustion of 1 gram is 6787 cal. at constant volume and 6793 cal. at constant pressure. Molecular heat of combustion, 2051.5 Cal. The molecular heat of formation, 454.5 Cal.

A sample of hæmoglobin (from the horse) formed brilliant, dark red needles. The heat of combustion of 1 gram of the substance dried over sulphuric acid is 5822 cal. at constant volume or 5826 cal. at constant pressure; or for the substance dried at 115° becomes

5889 cal. at constant pressure. Berthelot and Andre obtained 5914.8 cal., and Stohmann (Abstr., 1892, 141) obtained 5885 cal. Berthelot and Andre's analysis leads to the value 1091 cal. for the heat of formation. E. H.

**Heat of Dilution of Concentrated Solutions.** G. RÜMELIN (*Zeitsch. physikal. Chem.*, 1907, 58, 449—466).—The double calorimeter described by Steinwehr (Abstr., 1901, ii, 641) has been employed, but in addition to the electrical method of standardisation used by that worker, the device has been adopted of adding a known quantity of heat by introducing a slightly warmed Beckmann thermometer bulb (a so-called calorifer). The accuracy of the apparatus has been improved, and it is possible to measure heat effects of the order of 1 gram calorie to within 1%. By way of testing the apparatus, the heat effect of the reaction  $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$  was found from the explosion of 6—7 cub. cm. of electrolytic gas to be 68150 cal. at constant pressure.

The author's object was the determination of the differential heat of dilution ( $Q$ ), that is, the heat effect (referred to 1 gram mol. of solvent) produced when a very small quantity of solvent is added to a large quantity of solution. The value of  $Q$  has been determined for solutions of numerous substances, the most interesting of which perhaps was sulphuric acid. According to Thomsen,  $\delta Q_{(x)}/\delta x = 32150/(x + 1.798)^2$  cal., where  $x$  is the number of molecules of water per molecule of sulphuric acid, but it is shown that this formula is not valid for values of  $x$  greater than 10. It is shown further that for values of  $x$  between 10 and 32, the experimental values for the differential heat of dilution are in good agreement with those given by the empirical formula  $\delta Q_{(x)}/\delta x = -558/x + 28120/x^2$ . J. C. P.

**Organic Solvent and Ionising Media. VI. Heats of Solution.** PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1907, 58, 479—511. Compare Abstr., 1904, ii, 227; Abstr., 1906, ii, 149, 335, 336, 527).—The variation with temperature in the solubility of sparingly soluble electrolytes in water has been shown to be in harmony with the equation  $d \log_e(iC)/dT = q/2i T^2$  (see van't Hoff, *Zeitsch. physikal. Chem.*, 1895, 17, 147, 546; Goldschmidt and Maarseveen, Abstr., 1898, ii, 152; Noyes and Sammet, Abstr., 1903, ii, 468). The author's work shows that this formula is valid also for non-aqueous solutions of binary electrolytes. The suppositions which are at the foundation of the osmotic theory of electrolytes, and which are involved in the foregoing formula, may be expressed by the three equations: (1)  $PV = iRT$ ; (2)  $i = 1 + (n-1)\alpha$ ; (3)  $\alpha = \Lambda/\Lambda_\infty$ ; the author's work justifies the use of these relationships in dealing with solutions of electrolytes in organic solvents. The results obtained furnish also a confirmation of Le Chatelier's theorem regarding the relation between the variation of solubility with temperature and the sign of the heat of solution. The equation deduced by van Laar (see Abstr., 1895, ii, 434) may also be used to calculate the heats of solution in good agreement with experiment; the values calculated by van Laar's equation are somewhat smaller than those calculated by van't Hoff's equation, already referred to.

For the purpose of this investigation, the specific heats of a number of organic solvents were determined, with the results recorded in the following table. The calorimeter employed was a four-walled Dewar vacuum vessel :

Liquid.	Temperature.	Mean specific heat.
Methyl alcohol.....	18—20°	0·603
Ethyl alcohol .....	16—21	0·577
Acetone .....	17—20	0·515
Salicylaldehyde .....	18	0·382
Formamide .....	19	0·551
Acetonitrile .....	17—19	0·518
Propionitrile.....	14—17	0·510
Nitromethane .....	15—19	0·412
Nitrobenzene .....	20	0·386

The author has further determined (1) the heats of solution of potassium iodide, tetraethylammonium iodide, and tetrapropylammonium iodide in the foregoing solvents; (2) the solubility of tetraethylammonium iodide and tetrapropylammonium iodide in the same at 0° and 25°; and (3) the conductivity of these two salts when dissolved to saturation in the foregoing solvents at 0° and 25°.

J. C. P.

**Determination of Viscosity.** KARL BECK and K. EBBINGHAUS (*Zeitsch. physikal. Chem.*, 1907, 58, 409—419).—The viscosity of water in which castor oil has been suspended by shaking is not appreciably altered, even when the oil amounts to as much as 10% of the water. If, however, the oil and the water are made into an emulsion with the help of gum arabic the viscosity constant of the water is markedly increased.

In the case of a liquid of high specific gravity and low viscosity, the usual method of allowing the liquid to flow through a long, narrow capillary under pressure gives too high values for the viscosity. The difficulty is got over to a large extent by allowing the liquid to flow slowly against an opposing pressure (see Beck, *Abstr.*, 1904, ii, 646), and chloroform has been examined in detail from this point of view. At 25° the viscosity constant for chloroform is 0·60, that for water being taken as = 1.

J. C. P.

**Relative Viscosity.** KARL BECK, WILHELM TREITSCHKE, and K. EBBINGHAUS (*Zeitsch. physikal. Chem.*, 1907, 58, 425—441).—Experiments on the viscosity of fused mixtures of *p*-dichloro-, *p*-chlorobromo-, and *p*-dibromo-benzene, and of mercuric bromide and iodide show that the viscosity of isomorphous mixtures is approximately a linear function of the composition. It is shown that the presence of amorphous sulphur in fused, crystalline sulphur reveals itself in an increased viscosity constant. From viscosity measurements it appears that the compounds phenol + *p*-toluidine,  $\alpha$ -naphthol + *p*-toluidine, and phenol +  $\alpha$ -naphthylamine (see Philip, *Trans.*, 1903, 83, 814) exist to a certain extent as such even when fused, but that they are largely

dissociated into their components. As the temperature rises the extent of the dissociation increases.

J. C. P.

**Calculation of the Vapour Density of Dissociating Substances.** OTTO BRILL (*Zeitsch. physikal. Chem.*, 1907, 57, 721—738).—Working out the theory recently brought forward by Nernst (Abstr., 1906, ii, 727), and making one or two approximations, the author arrives at the formula  $\log(1-x^2)/x^2P = -Q/4.571T - 1.75\log T - 3$  for a dissociating system of the type  $AB \rightleftharpoons A + B$ . In this formula,  $Q$  is the heat of dissociation per molecule of  $AB$ , and  $x$  is the degree of dissociation at the pressure  $P$  and the temperature  $T$ . The formula makes possible the calculation of the temperature at which a dissociating substance is dissociated to any given extent  $x$ , provided the heat of dissociation is known. Tested by available data for nitrogen peroxide, acetic acid, formic acid, amyl bromide, bromine, phosphorus pentachloride, and methyl ether hydrochloride, the formula is satisfactory.

The Nernst equation for non-homogeneous equilibria,  $\log p = -Q/4.571T + 1.75\log T + C$ , has been tested, and it is shown that the formula permits the calculation with satisfactory accuracy of the dissociation temperatures for carbonates and nitrates.

J. C. P.

**Relation Between Osmotic Pressure and Surface Tension.** ANGELO BATTELLI and ANNIBALE STEFANINI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 11—22. Compare Abstr., 1905, ii, 629).—The law previously enunciated by the authors (*loc. cit.*) stating that dilute solutions having equal surface tensions, although not equimolecular, are in osmotic equilibrium, is shown to be deducible from simple theoretical considerations independently of any hypothesis as to the nature of osmotic pressure. Further experimental results are given which confirm this law. It is also shown that if two dilute solutions are isosmotic, they have the same surface tensions and the same vapour pressures.

When two solutions having either equal vapour pressures or equal surface tensions are sufficiently concentrated to cause their specific gravities to differ appreciably, the one with the lower specific gravity will have the higher osmotic pressure. This is illustrated by solutions of sodium chloride (D 1.03) and sucrose (D 1.14) having equal vapour pressures and by solutions of barium chloride (D 1.168) and potassium nitrate (D 1.062) having equal surface tensions.

From the above properties of solutions the authors conclude that a semi-permeable membrane consists of a network of small bubbles of vapour communicating, on the one hand, with the pure solvent and, on the other, with the solutions, by means of capillary tubes. The passage of the solvent from one side to the other then proceeds by the evaporation of the liquid and the subsequent condensation of the vapour. The only substances which, when dissolved in a liquid, do not traverse freely a semi-permeable membrane separating the solution from the pure solvent are those which do not pass from the dissolved to the vaporous state.

T. H. P.

**Ionic Migration in the Natural Diffusion of Acids and Salts. Phenomena in the Diffusion of Electrolytes.** REGINALD GRAHAM DURRANT (*Proc. Roy. Soc.*, 1906, A, 78, 342—379).—Observations on the diffusion of acids into jellies, of acids into ferric solutions without the use of jellies, and of concentrated solutions of sodium chloride, calcium chloride, and silver nitrate into distilled water are recorded. Using litmus as indicator, the formation of definite zones with sharply-defined boundaries is observed. When, for example, water is placed over a concentrated calcium chloride solution, both being coloured purple by the addition of litmus, a blue and a bleached zone are formed. The ratio of the distances of the upper boundaries of these zones is very nearly the same as the ratio of the mobilities of the calcium and the chlorine ions. In a similar experiment with silver nitrate, four distinct zones are produced. Starting from the bottom, the lowest zone contains precipitated silver, the next is colourless, the third blue, and the uppermost red. The distances of the upper boundaries of the several zones from the original surface of separation are approximately in the same ratio as the mobilities of the silver, nitrate, hydroxyl, and hydrogen ions. The observations are regarded as evidence that ionic separation takes place to an appreciable extent in natural diffusion processes. The hydrogen ions appear to move in advance of the diffusion front, whereas the other ions produce their characteristic effects in the rear of this. For the details of the experiments the original must be consulted. The data, generally, are in agreement with the theory of Nernst and Planck. H. M. D.

**Separation of Colouring Matters by Diffusion.** ERICH LEHMANN (*Zeitsch. physikal. Chem.*, 1907, 57, 718—720).—Some preliminary experiments show that when a glass tube filled with 5—10% gelatin or 2% agar-agar is kept for some time dipping in a solution of two dyes, one of the latter in general diffuses more rapidly into the jelly, and produces a characteristically coloured zone. This zone is found to be quite free from the other dye, which diffuses more slowly. J. C. P.

**Osmotic Pressures of Some Concentrated Aqueous Solutions.** EARL OF BERKELEY and ERNALD G. J. HARTLEY (*Phil. Trans.*, 1906, A, 206, 481—507. Compare *Proc. Roy. Soc.*, 73, 436; *Abstr.*, 1906, ii, 599).—In these direct measurements of osmotic pressure for solutions of sucrose, dextrose, galactose, and mannitol the authors have used a copper ferrocyanide membrane deposited close to the outer surface of a porous porcelain tube. To get the membrane deposited in this position the tube was immersed in a solution of copper sulphate in a desiccator which was then kept evacuated for several days. When by this procedure all air had been removed from the pores of the porcelain, the tube was taken out, dried superficially, plugged at the ends, and rotated in a solution of potassium ferrocyanide. In this way an even deposit of copper ferrocyanide, very close to the outer surface of the porcelain, is obtained, and after being subjected to electrolysis under pressure (compare Morse and Horn, *Abstr.*, 1901, ii, 543) the tube is ready for use. It was found desirable that the membrane

should be "remade" electrolytically at  $0^{\circ}$  at frequent intervals during the progress of the work.

The porcelain tube carrying the semi-permeable membrane passed horizontally through the centre of a gun-metal chamber, which had a capacity of about 250 c.c., and contained the solution. This chamber consisted of various parts which were screwed tightly together, so as to avoid leakage even under high pressure, and was connected with an apparatus by means of which a known hydrostatic pressure could be applied to the solution. With each end of the porcelain tube there was connected a vertical capillary glass tube; water was filled into the porcelain and attached tubes up to a convenient height; one of the glass tubes was then closed by a tap, whilst the other was used as a gauge. Observation of the level of the water in the latter showed whether water was entering the solution through the membrane, or whether the applied hydrostatic pressure was squeezing water out of the solution. In the latter case the applied hydrostatic pressure must be greater than the osmotic pressure, in the former case less. By adjusting the apparatus, therefore, so that water was neither entering nor leaving the solution, an equilibrium pressure was found which was equal to the osmotic pressure. In actual practice the method adopted was to take the rates of movement of the level in the gauge, corresponding with slightly differing pressures, both above and below the turning point; this allowed the application of a small but necessary correction for the "guard-ring leak," a leak due to the fact that the semi-permeable membrane is never quite on the surface of the porcelain tube.

Even with the very best membranes there is generally an indication that a very small quantity of sugar has come through the membrane during an experiment, and an attempt has been made to estimate this in each case. In the final computation of the equilibrium pressure, only those experiments were accepted in which it had been shown that no more than 0.0003 gram of sugar had come through.

The experiments were carried out at  $0^{\circ}$ , and the results obtained are summarised in the following tables, which give the values for the equilibrium pressures of the various solutions when there is a pressure of 1 atmosphere on the solvent:

Grams per litre.	Pressure in atmospheres.	Grams per litre.	Pressure in atmospheres.
<i>Sucrose.</i>		<i>Dextrose.</i>	
180.1	13.95	99.8	13.21
300.2	26.77	199.5	29.17
420.3	43.97	319.2	53.19
540.4	67.51	448.6	87.87
660.5	100.78	548.6	121.18
750.6	133.74		
<i>Galactose.</i>		<i>Mannitol.</i>	
250	35.5	100	13.1
380	62.8	110	14.6
500	95.8	125	16.7

When the pressures are plotted against concentrations, the curves obtained for all four substances deviate considerably from the straight lines drawn on the assumption that  $PV = RT$ , where  $P$  is the osmotic pressure and  $V$  is the volume of solution containing 1 gram mol. of solute. The deviation is very marked at high concentrations, but on extrapolating the various curves towards the origin they appear to merge in the straight lines before the origin is reached, indicating that dilute solutions will give pressures corresponding to the Boyle-Avogadro law.

The values obtained by the authors for the osmotic pressures of sucrose solutions are, as far as the ranges of concentration overlap, somewhat higher than those recorded by Morse and Frazer (Abstr., 1905, ii, 575; 1906, ii, 601).

The osmotic pressures of the more concentrated sucrose solutions have been deduced from their vapour pressures, determined by the method previously described (Abstr., 1906, ii, 599), and the values reached in this indirect way are in good agreement with the directly observed equilibrium pressures, as is shown in the following table:

Grams sucrose per litre.	Osmotic pressure in atmospheres at 0° deduced from vap. press.	Equilibrium pressure in atmospheres at 0° directly observed.
540	69.4	67.51
660	101.9	100.78
750	136.0	133.74

J. C. P.

**Relation Between the Velocity and the Volume of Organic Ions in Aqueous Solution.** GEORGE A. CARSE and T. H. LABY (*Proc. Camb. Phil. Soc.*, 1907, 14, 1—12).—The value for the product, velocity  $\times \sqrt[3]{\text{volume}}$ , has been calculated for the cations of several organic bases in aqueous solution, the results obtained supporting the authors' suggestion (Abstr., 1906, ii, 420) that the motion of an ion through an electrolyte is similar to that of a small body through a viscous medium.

W. H. G.

[Hydrate Theory.] WILHELM BILTZ (*Zeitsch. physikal. Chem.*, 1907, 58, 250—252).—A reply to Jones (this vol., ii, 78). J. C. P.

**Ultramicroscopic Determination of Solubility.** WILHELM BILTZ (*Zeitsch. physikal. Chem.*, 1907, 58, 288—292. Compare Abstr., 1906, ii, 824).—In the case of solutions of two salts which interact giving an insoluble compound by double decomposition, it is possible by the use of the ultramicroscope to determine when the solutions have been so far diluted that no precipitate is produced. Hence the solubility of the precipitate in question may be calculated. The following solubilities have been determined in this way, the numbers meaning gram molecules per litre of saturated solution. The temperature for which the numbers are valid is 16—18°. Thallium bromide,  $1.3 \times 10^{-3}$ ; silver chloride,  $1.6 \times 10^{-5}$ ; silver bromide,  $1.4 \times 10^{-6}$ ; manganese sulphide,  $1.1 \times 10^{-4}$ ; cadmium sulphide,  $6.6 \times 10^{-6}$ ; lead

sulphide,  $5.5 \times 10^{-6}$ ; cupric sulphide,  $4.1 \times 10^{-6}$ ; arsenious sulphide,  $2.1 \times 10^{-6}$ ; silver sulphide,  $8.0 \times 10^{-7}$ . These values are in most cases somewhat higher than the values deduced from conductivity measurements (see Böttger, *Abstr.*, 1904, ii, 241; Weigel, next page).  
J. C. P.

**Investigations with Inorganic Solvents at Low Temperatures.** **Apparatus.** GIUSEPPE MAGRI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 171—178).—The author proposes to measure, at various temperatures and for solutions of various concentrations of substances in liquid sulphur dioxide and hydrogen sulphide, the following magnitudes: surface tension, dielectric constant, internal friction, electrical conductivity, density and molecular weight, and also to investigate the products obtained on electrolysis of the solutions. For these purposes he has had constructed a complicated piece of apparatus arranged to avoid access of moisture to the solutions, or exchange of heat with the surrounding air, to allow of successive measurements without unmounting, and to permit of the solution or solvent being heated or cooled, or maintained at a constant temperature. The present paper contains a description and sketch of the apparatus.  
T. H. P.

**Solubility of Stereoisomerides in Optically Active Solvents.** HUMPHREY O. JONES (*Proc. Camb. Phil. Soc.*, 1907, 14, 27—29).—The statement is sometimes made that the solubilities of stereoisomerides are different in an optically active solvent; if this is true, then it should be possible to separate a *d* + *l* mixture by crystallisation from an active solvent. It is shown, however, that the solubility and rotatory powers of *d* and *l* isomerides are identical in an optically active as well as in an inactive solvent.  
W. H. G.

**Solubility of the Sulphides of the Heavy Metals in Pure Water.** OSKAR WEIGEL (*Zeitsch. physikal. Chem.*, 1907, 58, 293—300).—The solubility of a number of metallic sulphides has been determined by the conductivity method (compare Böttger, *Abstr.*, 1904, ii, 241). In calculating the solubility from the conductivity, it has been assumed that the dissolved sulphide is completely hydrolysed, that the hydroxide thus produced is completely dissociated, and that the conductivity of the hydrogen sulphide produced by the hydrolysis is negligible compared with that of the hydroxide. A number of the sulphides have been examined both in the crystallised and in the amorphous state; the crystallised sulphides were either the naturally occurring products or had been prepared by heating the precipitated sulphides in an electric furnace to about 1800° in an atmosphere of nitrogen. The solubilities found (in gram molecules per litre) are recorded in the following table:



Crystallised Sulphides.		Precipitated Sulphides.	
Manganese sulphide	$54.5 \times 10^{-6}$	Manganese sulphide	$71.6 \times 10^{-6}$
Pyrrhotine .....	53.6	Zinc sulphide .....	70.6
Pyrites (Freiberg) ..	48.9	Ferrous sulphide ...	70.1
Pyrites (artificial) ...	40.8	Cobalt sulphide .....	41.6
Wurtzite .....	28.8	Nickel sulphide .....	39.9
Millerite .....	16.3	Cadmium sulphide ...	9.0
Greenockite .....	8.99	Antimony sulphide	5.2
Zinc blende		Lead sulphide .....	3.6
(Santander)	6.65	Cupric sulphide .....	3.51
Zinc blende		Silver sulphide ...	0.55
(artificial)	6.63	Bismuth sulphide ...	0.35
Cuprous sulphide ...	3.1	Mercuric sulphide ...	0.054
Lead glance			
(Freiberg)	1.21		
Lead glance			
(artificial)	1.21		
Stannic sulphide .....	1.13		
Silver sulphide .....	0.55		
Stannous sulphide ...	0.14		

The foregoing values show that the labile modification is more soluble than the stable modification of the same substance. In some cases, for example, zinc and lead sulphides, the amorphous form in contact with water rapidly changes into the crystallised form, as is shown directly by the alteration of the conductivity.

The results obtained in this investigation do not appear to be in harmony with Bodländer's formula (Abstr., 1898, ii, 554).

J. C. P.

**Neutral Salt Action.** BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1907, 58, 420—424).—The yellow colour of dilute methyl-orange solutions is changed to an orange-yellow by carbon dioxide, to an orange-pink by acetic acid, and to a bright pink by strong acids. The tint of the methyl-orange solution is therefore a measure of the concentration of the hydrogen ion (compare Friedenthal, Abstr., 1904, ii, 288; Salessky, *ibid.*, 319; Fels, *ibid.*, 320; Salm, *ibid.*, 536; Veley, Trans., 1907, 91, 153; this vol., ii, 76). If methyl-orange is dissolved in saturated sodium chloride solution, and carbon dioxide, even in small quantity, is passed into the solution, the original yellow colour is changed to pink. The same effect is observed when barium chloride takes the place of sodium chloride, but the influence of sodium nitrate, potassium chloride, and potassium nitrate is less marked.

It appears, therefore, that the dissociation constant of carbonic acid in saturated sodium chloride solution is greater than that of acetic acid in water. In other words, saturated salt solution, regarded as a solvent, possesses a dissociative power much greater than that of water, and it is to such increase of the dissociative power of water that the author refers neutral salt action. The dissociation of acetic acid and that of ammonia (shown by phenolphthalein) appear to be similarly increased in saturated sodium chloride solution. J. C. P.

### Solidification of Inorganic Salts and Salt Mixtures. II. Solidification of Salt Mixtures and Their Thermal Properties.

WILHELM PLATO (*Zeitsch. physikal. Chem.*, 1907, 58, 350—372. Compare Abstr., 1906, ii, 521).—The method previously described has been used in the study of the freezing points of inorganic salt mixtures, and the various forms of cooling curve have been determined for the cases (1) where a pure salt separates out, (2) where mixed crystals are formed. The systems examined were  $\text{SrCl}_2 + \text{SrF}_2$ ,  $\text{BaCl}_2 + \text{BaF}_2$ ,  $\text{CaCl}_2 + \text{CaF}_2$ ,  $\text{NaCl} + \text{NaF}$ ,  $\text{KCl} + \text{KF}$ . The freezing phenomena were not followed above  $1200^\circ$ , so that the freezing-point curves in the first three cases are not complete at the fluoride end. In the first three systems double salts occur, which form series of mixed crystals (interrupted by eutectics) with the chlorides. The double salts form mixed crystals also with the fluorides as far as a second eutectic point, but from liquid mixtures containing more fluoride than corresponds with this second eutectic point pure fluoride separates in all three cases. It is noteworthy that barium chloride exists in an  $\alpha$ - and a  $\beta$ -form, the  $\alpha$ -form being stable between the freezing point and a transition temperature  $34.4^\circ$  lower. The double salt,  $\text{BaCl}_2, \text{BaF}_2$ , forms mixed crystals with  $\beta$ -barium chloride only. In the systems  $\text{NaCl} + \text{NaF}$  and  $\text{KCl} + \text{KF}$  no mixed crystals are formed and no double salts are indicated by the freezing-point curves.

The regularities previously observed (Ruff and Plato, Abstr., 1903, ii, 588) in connexion with the composition of eutectic mixtures appear also in the cases studied in this investigation. Thus, for example, the eutectic mixture in the system  $\text{NaCl} + \text{NaF}$  has the composition  $100\text{NaCl} + 37.93\text{NaF}$ , whilst the eutectic mixture in the system  $\text{KCl} + \text{KF}$  has the composition  $100\text{KCl} + 63.95\text{KF}$ ; it will be found that the numbers 37.93 and 63.95 are in the same ratio as the atomic weights of sodium and potassium. Formulæ are recorded by which it is possible to calculate how much of the one salt must be added to the other in order to reach the eutectic point.

The latent heat of fusion of most of the salts has been determined with the following results:  $\text{KCl}$  (m. p.  $772.3^\circ$ ), 86.0;  $\text{NaCl}$  (m. p.  $804.1^\circ$ ), 123.5;  $\text{CaCl}_2$  (m. p.  $773.9^\circ$ ), 54.6;  $\text{SrCl}_2$  (m. p.  $871^\circ$ ), 25.6;  $\text{BaCl}_2$  (m. p.  $958.9^\circ$ ), 27.8;  $\text{NaF}$  (m. p.  $992.2^\circ$ ), 186.1;  $\text{KF}$  (m. p.  $859.9^\circ$ ), 108.0. The molecular depression calculated by van't Hoff's formula agrees fairly well with the observed depression in the case of the alkali salts. In the case of the salts of the alkaline earth metals, it is necessary to assume complete dissociation of the added component.

J. C. P.

**Periodic Phenomena in Crystallisation.** D. W. ALEXÉEFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1120—1123).—The author describes periodic phenomena observed during the crystallisation of ethyl ethanetetra-carboxylate from the molten condition.

When the molten ester is spread out in a thin layer, solidification begins at a centre and then proceeds in concentric zones which widen periodically. If a thin layer of the supercooled ester is seeded with a crystal of the same substance, crystallisation takes place radially from

the nucleus for some time, after which the separation of crystals ceases for a period, then proceeds rapidly and so on.

Examination of the concentric zones by means of polarised light shows that each zone is limited by sharp edges, of which only certain points act as centres of crystallisation for the succeeding zone. The formation of these zones and the subsequent stoppage of the crystallisation are regarded as due to changes in the surface tension of the liquid. The heat set free during the solidification heats part of the remaining liquid and so considerably diminishes its surface tension. Owing to the greater surface tension of the supercooled layers, the whole of the liquid is separated from the part which is crystallising, in the same way as water is driven away from a drop of alcohol.

Phenomena similar to those described above are observable with supercooled benzophenone and coumarin, but in these cases the zones formed are very indetinite.

T. H. P.

**The Regular Growth of Soluble Salts on Each Other.** THOMAS V. BARKER (*Min. Mag.*, 1907, 14, 235—257. Compare *Trans.*, 1906, 89, 1120).—The isomorphous group of the cubic haloids and cyanides of the alkalis was chosen for examination. Considerations of molecular volume, crystalline form and cleavage, miscibility, and the capability of forming parallel growths suggest that this series may be divided into two isostructural groups, as indicated below (the numbers are the molecular volumes).

Group A.—					
NaCl, 29·92	(NaCN, ? )	NaBr, 32·21	NaI, 41·06		
KCl, 37·49	KCN, 41·31	KBr, 43·30	KI, 53·06		
RbCl, 43·10	RbCN, 48·60	RbBr, 49·30	RbI, 59·62		
Group B.—					
AmCl, 34·96	(AmCN, ? )	AmBr, 43·45	AmI, 58·14		
CsCl, 42·15	(CsCN, ? )	CsBr, 47·81	CsI, 57·25		

In the same isostructural group of substances non-parallel growths are only obtained when the molecular volumes are widely different.

L. J. S.

**Deduction from van der Waals's Equation.** R. H. MCCREA (*Chem. News*, 1907, 95, 101—102).—If van der Waals's equation is written in the form  $v - b = K/p(1 + a/pv^2)$  and  $p = \infty$ , then  $v - b = 0$ , which result, the author considers, corresponds with the elimination of the intermolecular spaces and in consequence to the attainment of the solid state. In consequence of the small value of the expression  $K/(a/b^2)$ , the solid state will persist, provided the temperature is kept low even when the pressure has been greatly reduced.

H. M. D.

**Distribution of Stannic Chloride between Water and Xylene.** WLADIMIR SMIRNOFF (*Zeitsch. physikal. Chem.*, 1907, 58, 373—380).—The three hydrates of stannic chloride,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ , have been shaken up with xylene at various temperatures between 66° and 111°, and the amount of chloride in each phase has then been determined. In the system,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O} + \text{xylene}$ , the value of  $c_1/c_2$ , where  $c_1$  and  $c_2$  are the percentages of chlorine in the water and xylene phases respectively, falls from 504·4 at 66° to 59·3 at 111°.

In the system  $\text{SnCl}_4 \cdot 4\text{H}_2\text{O} + \text{xylene}$ , the value of  $c_1/c_2$  falls from 45.3 at  $66^\circ$  to 12.9 at  $111^\circ$ . In the system  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O} + \text{xylene}$ , the value of  $c_1/c_2$  is independent of temperature. It may be supposed that the hydrates are readily dissociated into their components, that only the free stannic chloride is soluble in xylene, and that the degree of dissociation of the hydrates increases with rising temperature and diminishing content of water. Thus it is concluded that even at  $66^\circ$  the hydrate,  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ , is completely dissociated. J. C. P.

#### Equilibrium Between Ammonia and Hydrogen Sulphide.

J. P. MAGNUSSEN (*J. Physical Chem.*, 1907, 11, 21—46).—Although the decomposition pressure of ammonium hydrosulphide was determined by Isambert (1881) both alone and in the presence of excess of either of its dissociation products, yet the results are not in accord with the theoretical result  $p_1 p_2 = \text{const.}$ , and the equilibrium has been reinvestigated by the author over a considerable range of pressures at  $20^\circ$ . He finds that considerable adsorption of ammonia by the solid hydrosulphide occurs and that, when this is allowed for, the results are in satisfactory accord with the mass action law.

In the paper an ingenious, efficient, and simple electric thermostat is described in which rise of temperatures causes a mercury contact to interrupt, by an ordinary magnetic interrupter, the heating circuit.

L. M. J.

**Peculiar Action of Hydrogen Ions in the Formation of Alkyl Hydrogen Sulphates by Means of Water in Heterogeneous Systems.** ROBERT KREMANN (*Monatsh.*, 1907, 28, 13—32).—As is well known, ethyl and methyl hydrogen sulphates are prepared most simply by shaking the alkyl sulphates with hot water. The study of the kinetics of this method of preparation offered a particular interest, as the reaction constitutes a prominent example of the partial hydrolysis of the ester of a polybasic acid.

At  $30$ — $50^\circ$  the decomposition of ethyl sulphate is negligible in comparison to the rate of hydrolysis by means of water, which may be measured conveniently between these temperatures by determining the increase in the acid titre. As the alkyl sulphates are only sparingly soluble in water, the reaction takes place in a heterogeneous system, and the reacting substances must be mixed thoroughly. The velocity constant, calculated by the equation for unimolecular reactions, remains constant until near the end of the reaction, hence under the conditions of the reaction the hydrogen ions cannot act as catalytic accelerators. In agreement with this, it is found that the rate of hydrolysis is not accelerated by the substitution of sulphuric acid for the water (compare Praetorius, *Abstr.*, 1905, i, 186). On the other hand, the rate of hydrolysis is accelerated by the addition of alkalis in proportion to the alkali concentration, although in this case also the system is heterogeneous.

If hydrogen chloride is added, the formation of ethyl chloride takes place as a side reaction, its velocity in 2*N*-hydrochloric acid being markedly greater than that of the hydrolysis by water which is not accelerated. A similar side reaction takes place on addition of nitric acid. The rate of formation of the ethyl chloride or nitrate is propor-

tional to the concentration of the acid. The following velocity of hydrolysis constants have been determined.

Methyl sulphate + water at  $33.5^{\circ}$ ,  $k=0.0080$ , or at  $24^{\circ}$ ,  $k=0.0024$ ; + *N*-sulphuric acid at  $24^{\circ}$ ,  $k=0.0020$ . Ethyl sulphate + water at  $34^{\circ}$ ,  $k=0.00155$ , or at  $44^{\circ}$ ,  $k=0.0066$ ; + 2*N*-sulphuric acid at  $44^{\circ}$ ,  $k=0.00445$ ; + *N*-sulphuric acid at  $44^{\circ}$ ,  $k=0.0046$ , or at  $36^{\circ}$ ,  $k=0.0015$ ; + 0.4*N*-sulphuric acid at  $44^{\circ}$ ,  $k=0.0067$ ; + 0.4*N*-sodium hydroxide at  $34^{\circ}$ ,  $k=0.0045$ ; + *N*-sodium hydroxide at  $34^{\circ}$ ,  $k=0.0095$ ; + 2*N*-hydrochloric acid at  $44^{\circ}$ ,  $k=0.0067$ ; + *N*-hydrochloric acid at  $44^{\circ}$ ,  $k=0.0068$ ; or at  $36^{\circ}$ ,  $k=0.00235$ , or at  $34^{\circ}$ ,  $k=0.0014$ ; + 0.4*N*-hydrochloric acid at  $35^{\circ}$ ,  $k=0.00185$ ; + *N*-nitric acid at  $35^{\circ}$ ,  $k=0.0021$ ; + 2*N*-nitric acid at  $35^{\circ}$ ,  $k=0.0026$ .

In a series of experiments with ethyl sulphate at  $34^{\circ}$  with 0.2*N*- to 2*N*-hydrochloric acid, the velocity constant for the formation of ethyl chloride was found  $k=0.00010$ — $0.00181$ , whilst that for the hydrolysis by the water was  $k=0.0015$ . Similarly, with *N*- and 2*N*-nitric acids the velocity constants for the formation of ethyl nitrate were found to be  $k=0.00033$  and  $0.00127$ , whilst that of the hydrolysis was  $k=0.0024$ .

The temperature coefficient for the action of water on methyl sulphate for a temperature interval of  $10^{\circ}$  is 3.5, and for the action of water on ethyl sulphate, 4.2, or approximately double the normal. This high temperature coefficient is considered to be a peculiarity of heterogeneous systems (compare Goldschmidt and Bräuer, *Abstr.*, 1906, i, 159). The generally accepted view that the temperature coefficients of physical processes are abnormally small in comparison with those of chemical reactions cannot be always correct, as the velocities of reactions in heterogeneous systems are determined mainly by physical changes. G. Y.

**Esterification of *o*-, *m*-, and *p*-Nitrobenzoic Acids by Means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Annalen*, 1907, 351, 186—217. Compare *Abstr.*, 1906, ii, 659; this vol., ii, 158).—The rates of esterification of the three nitrobenzoic acids by means of alcoholic hydrogen chloride in presence of varying amounts of water have been determined in the same manner as those of benzoic and the three aminobenzoic acids (*loc. cit.*). Goldschmidt, who determined the rates of esterification of the nitrobenzoic acids by means of "absolute" alcoholic hydrogen chloride (*Abstr.*, 1896, i, 229), gave no particulars as to the amounts of water present, which must be assumed, therefore, to have been extremely small. The constants now observed agree with those of Goldschmidt in the case of *m*-nitrobenzoic acid, but for *p*-nitrobenzoic acid are greater in all strengths of alcohol. In consequence of the low rate of esterification of *o*-nitrobenzoic acid, the constant was determined only for solutions in alcohol containing merely traces of water, and was found to agree with Goldschmidt's. In this case the influence of the formation of ethyl chloride, which in absolute alcohol has the velocity constant  $k \times 10^5 = 2.7 \times 10^{-5}$  at  $25^{\circ}$  (compare Cain, *Abstr.*, 1894, ii, 133), cannot be neglected. When corrected for this, the esterification constant of *o*-nitrobenzoic acid for concentrations of hydrogen chloride between  $c=0.166$  and  $c=0.665$ , and concentrations of water between  $w_m=0.047$  and  $w_m=0.059$ , is  $k/c=0.00270$ — $0.00308$ ,

The esterification constants for *m*- and *p*-nitrobenzoic acids are proportional to the concentration of the hydrogen chloride only in alcohol containing 0.15% or less of water; in the presence of higher proportions of water, the velocity constants increase more quickly than the concentration of the hydrogen chloride. The rate of hydrolysis of ethyl *m*- and *p*-nitrobenzoates by water or hydrochloric acid is so small as to be negligible in calculating the esterification velocity constants.

The relation of the esterification constant of *m*-nitrobenzoic acid at 25° to the concentration of the hydrogen chloride and of the water is represented by the expression:  $1/k = 18.46 + 21.20/c + (-35.25 + 9.874/c + 26.89/c^2)w + (-136.2 + 161.5/c + 6.452/c^2)w^2$ , which applies to solutions in which the molecular concentration of the water lies between  $w = 0.04$  and  $w = 1.66$ , and that of the hydrogen chloride between  $c = 0.16$  and  $c = 0.66$ .

In the case of *p*-nitrobenzoic acid, the relation of the esterification constant to the molecular concentrations of the water and the hydrogen chloride is represented by the expression:  $1/k = 24.27/c + (6.57 + 14.87/c + 5.153/c^2)w + (-145.2 + 140.2/c + 11.112/c^2)w^2$ , which applies to solutions with  $w = 0.085$ — $1.333$ , and  $c = 0.1631$ — $0.6783$ .

It is shown that the esterification of *m*- and *p*-nitrobenzoic acids is closely analogous to that of benzoic acid. G. Y.

**Esterification of Hydroxybenzoic Acids by Means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Monatsh.*, 1907, 28, 115—152. Compare Abstr., 1906, ii, 659; this vol., ii, 158; Goldschmidt, Abstr., 1896, i, 229).—It is found that in the titration of the three hydroxybenzoic acids in alcoholic solution, the most accurate results are obtained by using rosolic acid as the indicator (compare Walker and Wood, Trans., 1898, 73, 621).

The constants for the velocity of esterification of the three hydroxybenzoic acids have been determined in the same manner as those for the esterification of the nitro- and amino-benzoic acids (*loc. cit.*), and found, when not more than traces of water are present, to be proportional to the concentration of the hydrogen chloride. A correction for the formation of ethyl chloride,  $6 \times 10^{-5}$  *Ct* c.c.  $c_m = c_0 - d/2$ , must be introduced into the calculation of the esterification constant of salicylic acid.

The relations of the velocity constants, for esterification in aqueous alcoholic solution, are represented by the expressions, for *m*-hydroxybenzoic acid:  $1/k = 4.81 + 14.01/c - 0.5371/c^2 + (7.61 - 5.263/c + 15.06/c^2)w + (-103.6 + 112.1/c - 7.642/c^2)w^2$ , which applies to solutions with the molecular concentration of the water between  $w = 0.02$  and  $w = 1.3$ , and that of the hydrogen chloride between  $c = 0.16$  and  $c = 0.66$ ; and for *p*-hydroxybenzoic acid:  $1/k = 15.83 + 33.45/c - 0.4722/c^2 + (-94.05 + 90.04/c + 20.27/c^2)w + (-119.6 + 158.9/c - 4.066/c^2)w^2$ , which applies to solutions with  $w = 0.02$ — $1.3$ , and  $c = 0.16$ . The results obtained give no indication of hydrolysis of ethyl *m*- or *p*-hydroxybenzoate by alcoholic hydrogen chloride.

The behaviour of the hydroxybenzoic acids on esterification is shown

to be analogous with that of benzoic acid and the nitro- and amino-benzoic acids. G. Y.

**Velocity of Hydrolysis of Keto- and Hydroxy-Esters.** HEINRICH GOLDSCHMIDT and VICTOR SCHOLZ (*Ber.*, 1907, 40, 624—641. Compare Goldschmidt and Oslan, *Abstr.*, 1900, i, 132, 373).—H. Meyer's statement (this vol., i, 179) that the substance previously worked with as ethyl dimethylacetoacetate is in reality the methyl ester is confirmed; the velocity constant for the methyl ester has been found to be 2.43, whilst, on the other hand, the velocity constant for ethyl diethylacetoacetate is only 0.0058.

The abnormal velocity of methyl acetoacetate is explained if (1) only the free ester and the hydroxyl ions interact; (2) the concentration of the free ester compared with that of the salt is small; (3) one molecule only of the base combines with one of acid. The equation representing the change is  $dx/dt = k\chi(a - x - \xi)$ , where  $k$  is the true velocity constant of the free ester,  $\chi$  the hydrolytic constant of methyl sodioacetoacetate,  $a - x$  the change in concentration of the salt, and  $\xi$  the part of the salt hydrolysed. For strong bases,  $\xi$  is small compared with  $a - x$ , and consequently the reaction proceeds as one of the first order.  $\xi$  was found to be 0.0375, and from the mean of experiments with the weak bases, ammonia, triethylamine, and diethylamine,  $\chi$  was found to be 0.00065. The velocity constant at 25° of methyl acetoacetate is  $2 \times 10^{-11}$  from the above results, and is identical with that of the ethyl ester. The ethyl ethylacetoacetate reaction does not proceed as one of the first order as the formation of salt is here incomplete. The values of  $\xi$  and  $\chi$  have therefore to be found in a slightly different way, 0.015 is found as the hydrolytic constant of ethyl sodioethylacetoacetate, and the velocity constant is  $0.9 \times 10^{-12}$  at 25°.

Experiments with methyl salicylate are complicated by the fact that a disodium salt is formed in small quantity, and this is estimated by hydrolysing ethyl acetate in the presence of monosodium salicylate. The hydrolytic constant of methyl sodiosalicylate is 0.001 compared with Shield's value of 0.000094 for sodium phenoxide (*Abstr.*, 1893, ii, 448). The velocity constant is between 6 and 7 and is higher than those of other aromatic esters.

Experiments with the weak bases piperidine and diethylamine bear out these conclusions. W. R.

**Aminolysis. II.** HEINRICH GOLDSCHMIDT and A. BAKSCHT (*Annalen*, 1907, 351, 108—133).—Goldschmidt and Salcher's determinations of the aminolytic constants of bases (*Abstr.*, 1899, ii, 551) were carried out at 45°. The aminolytic constants of pyridine, quinaldine,  $\alpha$ -picoline, and 5-collidine have been redetermined in the same manner, but at 25°, with the object of obtaining aminolytic temperature coefficients.

In the first place, the velocity constant for the change of diazoaminobenzene into aminoazobenzene at 25° was determined for aniline nitrate,  $k = 0.00924$ — $0.00927$ , and aniline hydrobromide,  $k = 0.0113$ , these, together with the velocity constants for this change, in a number of other salts of aniline at 25°, determined previously

(Goldschmidt and Reinders, Abstr., 1896, ii, 515; Bandke, *Inaug. Diss.*, Heidelberg, 1898), show that the difference between strong and weak acids is maintained in aniline solution, and that nitric, hydrobromic, and hydrochloric acids, which are equally dissociated in aqueous solution, have in this case different effects and in the same order as in aniline solution at 45°.

At 25° in aniline solution, the aminolytic constants for the bases examined are: pyridine,  $\chi = 3.41$ ;  $\alpha$ -picoline,  $\chi = 12.4$ ; *s*-collidine,  $\chi = 489$ ; quinaldine,  $\chi = 6.62$ .

The salts of the tertiary bases are decomposed to the greater extent at the higher temperature; the aminolytic temperature coefficients,  $\chi_{25}/\chi_{45}$ , are: pyridine, 1.50;  $\alpha$ -picoline, 1.16; *s*-collidine, 1.70; quinaldine, 1.25. There does not appear to be any simple relation between the strength of the base and the temperature coefficient; Hantzsch and Sebaldt (Abstr., 1900, ii, 69) found that similarly the variation of the affinity with change of temperature is different for different bases.

The heat of neutralisation of tertiary bases by acids in aniline solution is calculated by means of the expression:

$$q = 2T_1T_2/T_2 - T_1 \cdot \log \chi_{25}/\chi_{45};$$

that for pyridine, 3.600, does not differ greatly from the heat of neutralisation of pyridine in aqueous solution, 4800 cal. (Constam and White, Abstr., 1903, i, 276). As the aminolytic constants for aniline nitrate and aniline hydrobromide are identical, the heat of neutralisation of tertiary bases by strong acids in aniline solution is independent of the nature of the acid.

The aminolytic constants and the affinity constants in aqueous solution for the four bases in question vary in the same order, and do not differ greatly for the individual bases.

The velocity constant for the change of *p*-diazaminotoluene into aminoazotoluene, in *p*-toluidine hydrochloride, was measured by Goldschmidt and Reinders (*loc. cit.*) and has been determined now in 0.1*N* solution at 45° for *p*-toluidine nitrate,  $k = 0.0119$ ; hydrobromide,  $k = 0.0147$ ; *o*-nitrobenzoate,  $k = 0.00176$ , or in 0.2*N* solution,  $k = 0.00375$ . These constants are compared with those for the aniline salts:  $k(\text{aniline})/k(\text{p-toluidine})$ , for nitric acid, 9.75; hydrobromic acid, 9.53; hydrochloric acid, 8.42; *o*-nitrobenzoic acid, 5.0. It follows that the difference of the velocity of the conversion in the aniline and *p*-toluidine series results not only from the differences of the reaction, and of the medium, but must be caused also by a difference in the state of the catalyst, especially in the use of weak acids. The following aminolytic constants in *p*-toluidine at 45° were obtained:  $\alpha$ -picoline, 2.11; *s*-collidine, 30.5; benzyldimethylamine, 813; benzyldiethylamine, 1674. These constants are smaller than the constants in aniline at the same temperature, but increase in the same order. *p*-Toluidine acts as a stronger base than aniline, which is the case also in aqueous solution. The factor  $\chi(\text{aniline})/\chi(\text{toluidine})$  is similar for benzyldimethylamine, 12.9, and benzyldiethylamine, 13.0, but is much smaller, 5.1 and 9.4, for  $\alpha$ -picoline and *s*-collidine respectively.

G. Y.



**Autoracemisation of Optically Active Ammonium Salts.**

HANS VON HALBAN (*Zeitsch. Elektrochem.*, 1907, 13, 57—58).—Wedekind (Abstr., 1906, i, 419) explained the loss of optical activity of a solution of *d*-phenylbenzylmethylpropylammonium iodide in chloroform by supposing that the salt is dissociated to a small extent into its constituents and that these re-combine to form the inactive compound. The author shows that a solution of phenylbenzylmethylallylammonium iodide in chloroform decomposes moderately fast into its constituents. The quantity of undecomposed iodide in the solution is estimated by shaking the solution with an aqueous solution of silver nitrate. The change is shown to be unimolecular, and it leads to an equilibrium in which the greater part of the salt is decomposed.

The loss of optical activity in this case is therefore due to decomposition of the salt. T. E.

**Autoracemisation of Optically Active Ammonium Salts.**

EDGAR WEDEKIND (*Zeitsch. Elektrochem.*, 1907, 13, 58—59).—The author agrees with Halban (preceding abstract) that the loss of optical activity of phenylbenzylmethylallylammonium iodide is due to decomposition, but points out that the corresponding propylammonium salt is very much more stable, and that the pure salt may be precipitated from the chloroform solution by adding ether, long after it has become entirely inactive, which is not the case with the allyl salt. T. E.

**Dynamics of Tautomerism. I. Brilliant-Green.** NEVIL Y. SIDGWICK and TOM S. MOORE (*Zeitsch. physikal. Chem.*, 1907, 58, 385—408).—Brilliant-green undergoes a gradual transformation in the presence of an alkali. The rate at which the change takes place in very dilute solution can be conveniently measured with the aid of a colorimeter, and is found to be proportional to the product of the concentrations of the coloured salt and of the hydroxyl ion. The value of the velocity coefficient is approximately the same as that deduced by Hantzsch and Osswald from the change in conductivity (see Abstr., 1900, i, 256; compare also Gerlinger, Abstr., 1904, i, 1040).

In presence of hydrochloric acid, brilliant-green is slowly transformed into a colourless acid salt. The reaction is reversible, and with the aid of the colorimeter it is shown that at the point of equilibrium  $k_1c_1c_2 = k_2c$ , where  $c_1c_2$  and  $c$  are the concentrations of coloured salt, acid, and acid salt respectively. The ratio  $k_2/k_1$  is independent of the acid, but  $k_1$  and  $k_2$  are inversely proportional to the cube root of the acid concentration, provided the latter is not too small.

If a solution of the carbinol is treated with hydrochloric acid, three reactions take place, namely, (1) formation of coloured salt, (2) formation of the acid salt, (3) decomposition of the latter into coloured salt and acid. If the velocities of the processes (2) and (3) are known, it is possible by a complicated formula to calculate the velocity of (1). It is shown that the rate of formation of coloured salt from the carbinol is  $=MC$ , where  $C$  is the concentration of the carbinol, and  $M$  is a function of the acid concentration  $s$ , such that  $Ms^3$  remains constant.

J. C. P.

**Mechanism of Induced Reactions.** W. LASH MILLER (*J. Physical Chem.*, 1907, 11, 9—20).—Many cases are known in which reducing and oxidising agents,  $R_1$  and  $O_1$ , which do not react with one another ordinarily, readily react in the presence of other compounds,  $R_2$  and  $O_2$ , which themselves react readily;  $R_1$  and  $R_2$  or  $O_1$  and  $O_2$  may be, and usually are, identical. Such reactions are called induced reactions, and the author classifies them on a kinetic basis in three classes: (1) cases of catalysis, combined with destruction of the catalyst; (2) cases in which the inducing reaction is unaffected by the induced reaction; (3) cases in which (2) does not obtain. The reaction between chromic acid, ferrous sulphate, and potassium iodide is an example of the third class; that between chromic acid, arsenious acid, and potassium iodide is an example of the second class; and this case can be explained by the formation of a peroxide, although other explanations are possible.  
L. M. J.

**Rate of Oxidation of Arsenious Acid by Chromic Acid.** RALPH E. DE LURY (*J. Physical Chem.*, 1907, 11, 47—53).—The oxidation of arsenious acid by a mixture of potassium dichromate and sulphuric acid was investigated at  $0^\circ$  and  $10^\circ$ . The rate of oxidation was found to be nearly proportional to the first power of the concentration of the dichromate, the inexactness being probably ascribable to incomplete dissociation. It was proportional to the first power of the concentration of the arsenious acid, and to the 1.4th power of that of the sulphuric acid. The deviation from the second power is considered to be probably due to the influence of the hydrogen ion on the dissociation of the arsenious acid. The temperature coefficient is low; the rise from  $0^\circ$  to  $10^\circ$  only increased the rate of oxidation by 26% (compare Abstr., 1903, ii, 471).  
L. M. J.

**The Induction by Arsenious Acid of the Reaction Between Chromic Acid and Hydriodic Acid.** RALPH E. DE LURY (*J. Physical Chem.*, 1907, 11, 54—90; see also Abstr., 1903, ii, 471, and preceding abstracts).—The oxidation of arsenious acid and of potassium iodide by acid solutions of dichromate having been investigated, the reaction in solutions of the four compounds was studied. In this case the arsenious acid acts as the inductor and the potassium iodide as the acceptor of the oxidation. It was found that the rate of reduction of the chromic acid in solutions of arsenious acid and iodide is equal to the sum of the rates of reduction of the arsenious acid and iodide separately, the retardation of the former being equal to the acceleration of the latter. The temperature coefficients of the single actions and the joint action are equal. The ratio also of the rate of oxidation of the iodide alone and in presence of arsenious acid is independent of the concentrations of dichromate and sulphuric acid. The results may be accounted for by the assumption of the formation of a higher oxide (most probably a complex oxide of chromium and arsenic), which is reduced instantaneously by arsenious acid or iodide, the quantity reduced by each in mixtures being dependent on their relative concentrations.  
L. M. J.

**Some Catalytic Reactions Effected under the Influence of Wood Charcoal.** GEORGES LEMOINE (*Compt. rend.*, 1907, 144, 357—358).—When ethyl alcohol is led into a tube containing wood charcoal in pieces 1—2 mm. in diameter heated by electricity to 350°, a gas, containing no appreciable quantity of carbon monoxide, but about 20% of hydrogen, is obtained, whilst the alcoholic liquid product strongly reduces ammoniacal silver nitrate solution, and colours a solution of magenta decolorised by sulphur dioxide. It would seem, therefore, that as in Sabatier and Senderens's experiments with copper, charcoal reduces alcohol vapour, giving acetaldehyde and hydrogen, whilst with animal charcoal the reaction is different (compare Senderens, next abstract). Similarly, the decomposition of hydrogen peroxide at low temperatures is greatly accelerated by the catalytic action of charcoal charged with hydrogen, carbon monoxide or dioxide, oxygen, or nitrogen. The reaction of iodic and oxalic acids slowly producing iodine and carbon dioxide is greatly accelerated by the presence of charcoal, much less by sugar charcoal, whilst with platinum black the evolution of gas is extremely rapid. E. H.

**Reducing and Catalytic Power of Amorphous Carbon Towards Alcohols.** JEAN B. SENDERENS (*Compt. rend.*, 1907, 144, 381—383).—Nearly pure carbon prepared from animal charcoal absorbs oxygen from the air at 200°, and reduces nitrous and nitric oxide at 300°, giving nitrogen, carbon dioxide, and a small quantity of carbon monoxide, without becoming incandescent. When the vapour of ethyl alcohol is passed over this carbon heated at 400°, it is, in part, transformed into a gaseous mixture of the composition: CO<sub>2</sub>, 0.5%; C<sub>2</sub>H<sub>4</sub>, 35.5%; CO, 4.5%; CH<sub>2</sub>, 54.7%, and H<sub>2</sub>, 4.8%. Formaldehyde is simultaneously produced, and probably by its partial destruction gives the small quantities of carbon monoxide and hydrogen shown. From this it seems that the action of the carbon is not one of reduction, but one of catalysis according to the two equations: C<sub>2</sub>H<sub>5</sub>·OH = C<sub>2</sub>H<sub>4</sub> + H<sub>2</sub>O; C<sub>2</sub>H<sub>5</sub>·OH = CH<sub>4</sub> + CH<sub>2</sub>O. With propyl alcohol, the second reaction scarcely occurs. This alcohol readily decomposes when passed over the carbon at 340°, giving a mixture of C<sub>3</sub>H<sub>6</sub>, 87.8%; CO, 1.3%; C<sub>2</sub>H<sub>6</sub>, 9.5%; H<sub>2</sub>, 1.4%. Formaldehyde is here also produced, explaining the presence of carbon monoxide and hydrogen. In this case the decomposition is almost entirely expressed by the equation C<sub>3</sub>H<sub>7</sub>·OH = CH<sub>3</sub>·CH:CH<sub>2</sub> + H<sub>2</sub>O.

The results are not attributable to the sole action of heat which does not decompose the alcohols below 500°. Moreover, it is found that very fine siliceous sand, pumice stone, dicalcium phosphate, magnesia, and other inert substances have a similar and more powerful catalytic action on the two alcohols. The peculiar action of the carbon used is probably due to the small amount of siliceous matter remaining in it, as sugar charcoal decomposes ethyl alcohol giving 29% carbon monoxide and only 4.7% ethylene, and propyl alcohol giving 8% carbon monoxide and 32% propylene.

Red phosphorus acts as a very powerful catalyst towards alcohols,

causing the elimination of a molecule of water at 200—240°, and furnishing a general method of preparing pure olefine hydrocarbons.

E. H.

**Constitution of the Atom.** HENRI PELLAT (*Compt. rend.*, 1907, 144, 480—482).—According to the theory of the constitution of the atom advocated by J. J. Thomson, Lorentz, Larmor, and others, it consists of a centre charged with positive electricity around which a very great number of negatively charged corpuscles of infinitesimal size gravitate very rapidly, the centripetal force is electrical, and the period of the luminous vibration emitted by an atom of a gaseous substance is also the period of rotation of a corpuscle of which the velocity has been slightly altered by any cause whatever.

From this theory, Langevin has calculated the wave-length of light emitted by a corpuscle situated at the periphery of a sodium atom and found it to be in the ultra-violet. The author has repeated the calculation in a slightly different manner, accepting the hypothesis (1) that the trajectories are circular, (2) that the atom is spherical, that is, that the orbits of the corpuscles are orientated in all senses, (3) that Coulomb's law is applicable to intra-atomic distances.

The author thereby deduces that the vapours of sodium, zinc, iron, and copper could emit only radiations situated in the extreme ultra-violet. This result being altogether contrary to the facts, it is necessary in order to retain this theory of the constitution of the atom to abandon one of the three hypotheses given above. Of these, the first is rather an approximation than a hypothesis, but the author shows that a modification in the shape of the atom will account for the difference between theory and observation. It, however, remains to be determined whether a flattened form for the atom is reconcilable with its stability and with other phenomena.

E. H.

**Atomic Energy of Gases.** GUTH. ENSRUD (*Zeitsch. physikal. Chem.*, 1907, 58, 257—287).—Atoms are conceived as consisting of a nucleus and a surrounding, less dense, elastic envelope. Between the nucleus and its envelope, also between the nuclei of different atoms, forces of attraction are supposed to be active, whilst between the envelopes of different atoms, forces of repulsion are supposed to be at work. Consideration of these forces shows that the nucleus of an atom must occupy an excentric position. This involves the consequence that two neighbouring atoms are relatively placed so that their nuclei are as near as possible to each other, and this line of least distance will also be the line of maximum force and the direction of the valency. If there are several nuclei in the atom, there will be an equal number of lines of valency.

On the foregoing hypothesis a mathematical treatment of atomic energy is based, and it is found that the distance of the atoms in the molecule of a diatomic gas can be calculated from the specific heat. In the case of elements which do not undergo dissociation (hydrogen, oxygen, nitrogen), this distance is found to be two and a half times as great as the radius of the atom. On the basis of this value and of

the relative volume and weight of the atoms, it is then possible to calculate the position of the atoms, and the centre of gravity of the molecule for numerous chemical compounds. The molecular specific heat for various polyatomic vapours can also be calculated in fair agreement with experiment.

All available data bearing on the ratio of the specific heats and on the values of the specific heat at constant pressure have been collected and are recorded in the paper.

J. C. P.

**Atomic Weights a Function of the Order which they Occupy in the Series of their Increasing Magnitude.** ADOLPHE MINET (*Compt. rend.*, 1907, 144, 428—430).—By assigning to the elements the numbers 1—79 according to the position which they occupy when arranged in order of increasing atomic weight, and plotting the atomic weights of the elements, as ordinates, against the numbers so assigned to them, as abscissæ, two curves are obtained, (1) a straight line  $\alpha$ , represented by the expression  $\gamma = 1.985x$ , comprising the elements numbered 2—20 (helium to calcium), and (2) a parabola  $\beta$ , represented by  $\gamma = x^{1.23}$ , comprising the elements hydrogen, and those numbered 20—79 (calcium to uranium). In both expressions  $\gamma$  represents the atomic weight,  $x$  the position in the series. The atomic weights calculated by means of these formula do not differ by more than 3% from the true values (taking  $H = 1$ ) and the deviations are both positive and negative. By addition of two hypothetical elements to the series, one between hydrogen and helium, and the other between helium and lithium, the relation between the entire 81 elements and their order can be expressed by the single curve  $\gamma = x^{1.215}$ . Here again the discrepancies between the true and calculated values of the atomic weights do not exceed 3% except in the case of radium, thorium, and uranium, with which they amount to 10%.

In order to bring the latter three elements into agreement with the law, it is necessary to introduce four new elements between bismuth and radium, one between radium and thorium, and one between thorium and uranium, making 87 elements altogether. The curve supports Berthelot's views on the unity of matter.

E. H.

**Apparatus for the Demonstration of the Products of Combustion of a Candle.** GEORG LOCKEMANN (*Chem. Centr.*, 1906, ii, 1801—1802; from *Zeitsch. chem. Appar.*, 1, 721—723. Compare this Journ., 1877, i, 437).—In the apparatus described, the candle burns in a wide glass tube, and the products of combustion pass through a narrow connecting tube, bent at right angles to a glass spiral, to which is fitted a small flask connected with a washing flask and a U-tube. The whole apparatus is tared on a balance, and dry air free from carbon dioxide is aspirated through it. The water which condenses in the spiral is collected in the flask, which contains 0.1—0.2 gram of dehydrated copper sulphate, and the carbon dioxide is absorbed by a solution of barium hydroxide and potassium hydroxide contained in the washing flask, whilst the last traces of the products of combustion

are retained by soda lime and calcium chloride in the U-tube. The change of colour of the copper sulphate and the precipitation of barium carbonate serve to demonstrate the formation of water and carbon dioxide respectively. The mixture of the hydroxides which should be freshly prepared, since it has a tendency to deposit crystals of the hydrate  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , is obtained by shaking a warm solution of 100 grams potassium hydroxide in 200 of water with 25 of crystalline barium hydroxide until all the carbon dioxide has been precipitated and the excess of hydroxide dissolved; it is filtered directly into the flask.

E. W. W.

**Calcium as an Absorbent of Gases for the Production of High Vacua and Spectroscopic Research.** FREDERICK SODDY (*Proc. Roy. Soc.*, 1906, A, 78, 429–458. Compare Arndt, *Abstr.*, 1905, ii, 87).—An electrical resistance furnace is described, designed to heat substances in soft glass tubes up to temperatures far above the softening point of glass, and it is shown that metallic calcium when heated to a sufficiently high temperature is a universal absorbent of all gases except those of the argon group. Another form of furnace in which the calcium is heated inductively by an alternating current is for certain purposes more convenient. In this case the temperature of the metal can be fairly accurately judged by the eye, a moderate red heat being suitable for the absorption of gases. When the calcium is at its proper temperature, the chemically valent gases are very quickly absorbed, and if the apparatus is furnished with a Plücker tube for testing purposes, the vacuum tube becomes non-conducting within a minute after the introduction of several cubic centimetres of gas into the apparatus. In the case of hydrogen and its compounds which yield calcium hydride on absorption, the real absorption temperature is apt to be overstepped. This is due to the dissociation tension of the calcium hydride; on lowering the temperature, however, this becomes sufficiently small to permit of a non-conducting vacuum being readily obtained. In the production of high vacua by means of calcium, it is necessary to replace the air in the apparatus before the absorption takes place or the residual argon will prevent the vacuum from being really good. The particular value of calcium as an absorbing agent depends upon its power of absorbing almost instantly the gases condensed on the glass walls as soon as these are expelled by heating. A low initial pressure, not exceeding a few mm. of mercury, is essential for the absorption process, and under proper working conditions the calcium should never be melted, although it may be completely volatilised and redeposited on the cooler parts of the apparatus.

Using metallic calcium as absorbent for foreign gases, experiments have been made on the quantities of argon and helium which can be detected by the spectroscope. The results indicate that a discharge will not pass through a tube containing argon at a pressure less than 1/50 mm. The limiting pressure in the case of helium is 1/20 mm. In the presence of other (chemically valent) gases, very much smaller quantities of argon and helium can be detected by the discharge method. This non-conducting power at pressures within the range of

direct manometric measurement appears to be characteristic of monatomic gases, and the observed facts indicate that the electric discharge method may prove a very faulty guide in regard to the degree of a vacuum. Since the vapour pressure of mercury at room temperature is between  $1/500$  and  $1/1000$  mm., the production of high vacua (as measured by the discharge method) by the aid of mercury pumps is probably due to the fact that mercury is monatomic.

Some experiments, in which quantities of helium far smaller than those necessary to allow the discharge to pass when in the pure state were examined in presence of hydrogen and oxygen, indicate that helium at a partial pressure of  $0.0005$  mm. can be detected spectroscopically. This is only  $1/100$  of the partial pressure requisite in the case of pure helium.

In an appendix (by ARTHUR JOHN BERRY), the results of experiments on the rate of evaporation of liquid air in a Dewar vessel exhausted in different ways are given. Simple exhaustion by a mercury pump gives a better vacuum than the use of cooled charcoal, starting from atmospheric pressure. The best results are obtained by a combination of the two processes.

H. M. D.

**Manostats.** RESTON STEVENSON (*J. Physical Chem.*, 1907, 11, 107—118).—The various forms of apparatus which have been devised for the regulation of pressure are reviewed. The difficulties and disadvantages connected with the use of the special forms are discussed, and certain modified and improved forms are described.

H. M. D.

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## Inorganic Chemistry.

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**Oxidation of Hydrogen by Sulphuric Acid.** JAROSLAV MILBAUER (*Zeitsch. physikal. Chem.*, 1907, 57, 649—684).—At the ordinary temperature impure hydrogen which has been bubbled through sulphuric acid contains appreciable quantities of sulphur dioxide; no such action, however, is observed when pure hydrogen is employed.

The rate of oxidation of pure hydrogen by sulphuric acid was studied in detail at 174° and at constant pressure. For a given rate of passage of the hydrogen, the amount of sulphur dioxide produced per minute is constant for acid containing between 91% and 97% of  $\text{H}_2\text{SO}_4$ . The amount of sulphur dioxide produced per minute is increased by the presence of various catalytic agents, notably by the metals of the platinum group, but also by selenium and gold, by certain soluble sulphates, such as those of mercury, copper, cerium, and lanthanum, and by antimony, tantalum, and arsenic oxides. The amount of sulphur dioxide produced is diminished by the oxides of vanadium, molybdenum, and tungsten, by insoluble sulphates, such as those of thorium, zinc, and magnesium, and by other suspended substances such as silica. The sulphates also of the alkali metals and of the alkaline earth metals



diminish the amount of sulphur dioxide produced, but to a very slight extent. The influence of mixed catalytic agents has also been studied.

The influence of a catalytic agent increases with its concentration up to a certain limit, which appears to correspond with the limit of solubility of the sulphate. As regards the influence of temperature, it was found that in presence of mercuric sulphate there was an appreciable action even at 26°, and the extent of the action increased rapidly with rising temperature.

Some substances (ferrous and mercurous sulphates, and tellurium) when added to the sulphuric acid are oxidised, in spite of the hydrogen and sulphur dioxide. Other substances are first reduced, namely, osmium tetroxide, palladium and cerium sulphates, selenium dioxide, and the oxides of vanadium, molybdenum, and titanium. Selenium is shown to pass through a series of changes involving alternate reduction and oxidation. Light is without effect on the reaction. J. C. P.

**Density and Concentration of Aqueous Solutions of Perchloric Acid.** KONRAD VAN EMSTER (*Zeitsch. anorg. Chem.*, 1907, 52, 270—280. Compare Van Wijk, *Abstr.*, 1906, ii, 79).—The curve representing the percentage composition of solutions of perchloric acid, plotted against the corresponding density at 15° ( $D_4^{15}$ ), consists of two branches; from 0—53% it is slightly convex to the axis of composition, whilst from 53—70% (the strongest solution examined) it is a straight line. The former part of the curve, from the density 1.00 to 1.50, is represented by the equation  $p = 773.96d - 432.74d^2 + 88.838d^3 - 429.92$ ,  $p$  representing the percentage composition; the second part corresponds with the equation  $p = 74.693d - 54.98$ , varying from 1.50 to 1.70.

A series of density measurements have also been carried out at 30° and 50°, and from these and the above results the expansion coefficient from 15°—30° and from 15—50° is calculated; it shows a maximum for a solution containing about 55% of acid. G. S.

**Vapour Pressure of Iodine.** GREGORY P. BAXTER, CHARLES HENDEE HICKEY, and WALTER CHAPIN HOLMES (*J. Amer. Chem. Soc.*, 1907, 29, 127—136).—The vapour pressure of solid iodine between 58° and 86° has been determined by Ramsay and Young (*Trans.*, 1886, 49, 453), whilst for temperatures below 58° measurements have been made by Arctowski (*Abstr.*, 1896, ii, 636) and by Wiedermann, Stelzner, and Niedershulte (*Abstr.*, 1906, ii, 9). In the present investigation the vapour pressure was determined at temperatures between 0° and 53° by passing a measured volume of dry air over pure iodine contained in a U-tube and thence into a solution of sodium sulphite. The amount of iodine absorbed by the sulphite was determined by precipitating it as silver iodide and from this weight the vapour pressure was calculated. The results of the experiments are tabulated and plotted as a curve. The following are the average values obtained: at 0°, 0.030 mm.; at 15°, 0.131; at 25°, 0.305; at 30°, 0.469; at 35°, 0.699; at 40°, 1.025; at 45°, 1.498; at 50°, 2.154; at 55°, 3.084 mm. These results are not altogether in accord with those recorded by other

workers, although the vapour pressure curve, when extended, coincides fairly well with that of Ramsay and Young (*loc. cit.*).

From these values, the molecular heat of sublimation of iodine at these temperatures was calculated and found to be 15.1 Cal. or 63 kilojoules.  
E. G.

**Preparation of Ozone by Electrolysis. II.** FRANZ FISCHER and KARL MASSENEZ (*Zeitsch. anorg. Chem.*, 1907, ii, 229—255. Compare this vol., ii, 162).—In the former paper (*loc. cit.*) an apparatus for obtaining, by electrolysis, oxygen containing a high percentage of ozone has been described; in the present paper slight modifications of the method, which have led to the production of a gas still richer in ozone, are discussed.

The most favourable strength of acid depends somewhat on the current density, but is always less than that of the acid of highest conductivity. It is considered that the best results are obtained when the strength of the acid, added to that formed at the anode when the current passes, is equal to that of the best conducting acid, as then the heating effect, and consequent destruction of the ozone, is least.

In its final form the anode consists of a rhomboidal platinum tube, sealed over completely with glass, a metallic strip 11.5 mm. long and 0.1 mm. broad being then exposed by filing down to one of the acute angles.

The effect of cooling was fully investigated; the best results were obtained by immersing the cell in a current of water at 0° and cooling the anode internally to -14° with calcium chloride solution.

With these improvements, a mixture containing 28% of ozone by weight was obtained, much the highest proportion so far obtained by electrolysis.

Experiments were made with many other electrolytes, including acids and alkalis, and with lead peroxide as anode, but in all cases the yield of ozone was much less.

It is considered probable that ozone is the substance which is first liberated at the anode, and that it subsequently undergoes more or less complete decomposition, depending on the conditions.  
G. S.

**Action of Light on Sulphur.** G. A. RANKIN (*J. Physical Chem.*, 1907, 11, 1—8).—When a beam of light is passed into a solution of sulphur in carbon disulphide, amorphous sulphur is precipitated, but redissolves in the dark, so that in the dark the rhombic form is the more stable. The action is hence a reverse action, and the influence of certain compounds, such as hydrogen sulphide, in preventing the precipitation may be ascribed to their accelerative effect on the reverse action. The effect of temperature was investigated, and it was found that with rise of temperature the intensity of light required to produce precipitation increases. At constant temperature, the intensity is an inverse function of the concentration. Curves for intensity against concentration were obtained for temperatures 22.5° and 40°, the points at which these cut the solubility curve for rhombic sulphur give the equilibrium light intensity, that is, the intensity at which amorphous

sulphur, rhombic sulphur, and solution are in equilibrium; the values found are 5-candle power at 22.5° and 45-candle power at 40°.

L. M. J.

**Action of Thionyl and Sulphuryl Chlorides on Selenium and Selenium Dioxide.** VICTOR LENHER and H. B. NORTH (*J. Amer. Chem. Soc.*, 1907, **29**, 33—35).—When selenium dioxide is treated with thionyl chloride, selenium tetrachloride and sulphur dioxide are produced. Thionyl chloride has but little action on selenium at the ordinary temperature, but when the element is heated in the vapour of the chloride, the following reaction takes place:  $2\text{SOCl}_2 + \text{Se} = \text{SeCl}_4 + \text{SO}_2 + \text{S}$ .

Selenium is attacked rapidly by sulphuryl chloride with development of heat and formation of selenium tetrachloride and sulphur dioxide. Sulphuryl chloride does not react with selenium dioxide, even at high temperatures or under great pressure. E. G.

**Selenium Nitride.** VICTOR LENHER and E. WOLESENSKY (*J. Amer. Chem. Soc.*, 1907, **29**, 215—216).—Michaelis (*Jeanische Zeitsch.*, **6**, 91) has shown that when dry ammonia is brought into contact with selenyl chloride the following reaction takes place:  $6\text{SeOCl}_2 + 16\text{NH}_3 = 3\text{SeO}_2 + 3\text{Se} + 4\text{N} + 12\text{NH}_4\text{Cl}$ .

When dry ammonia is passed into a strong solution of selenyl chloride in benzene or toluene, heat is developed, and a large quantity of selenium is precipitated. If, however, the gas is led into a dilute solution of the chloride (2—4%) in benzene, a buff-coloured precipitate is produced, which becomes orange-red when dry. After washing this product with water and extracting the free selenium with potassium cyanide, selenium nitride,  $\text{SeN}$ , is obtained as a brick-red, highly explosive powder, which, when heated, begins to darken at a comparatively low temperature and explodes at 130°. This substance has also been obtained by Espenscheid (*Annalen*, 1860, **114**, 101), who states that it darkens at 150° and explodes at 200°. E. G.

**Position of Tellurium in the Periodic System of the Elements.** ALEXANDER GUTBIER and FERDINAND FLURY (*J. pr. Chem.*, 1907, [ii], **75**, 99—103).—The authors argue in favour of placing tellurium in the same group as sulphur and selenium, and against the suggestion that it should be placed in the eighth group. W. H. G.

**Hydronitric Acid [Azoimide].** V. LOUIS M. DENNIS and HELEN ISHAM (*J. Amer. Chem. Soc.*, 1907, **29**, 18—35. Compare Abstr., 1904, ii, 558; this vol., ii, 165).—When freshly precipitated copper hydroxide is treated with a solution of azoimide, a dark green, flocculent substance is produced which dissolves in strong solution of ammonia; from this solution the salt,  $\text{CuN}_6, 2\text{NH}_3$ , separates in transparent, dark green crystals. If pyridine is used instead of ammonia, the salt,  $\text{CuN}_6, 2\text{C}_5\text{H}_5\text{N}$ , is obtained. The zinc salts,  $\text{ZnN}_6, 2\text{NH}_3$  and  $\text{ZnN}_6, 2\text{C}_5\text{H}_5\text{N}$ , are also described. By the action of pyridine on solutions of nickel and cobalt azoimides (or trinitrides), the salts,  $\text{NiN}_6, 4\text{C}_5\text{H}_5\text{N}$ ,  $\text{NiN}_6, 6\text{C}_5\text{H}_5\text{N}$ , and  $\text{CoN}_6, 6\text{C}_5\text{H}_5\text{N}$ , are formed.

Silver azoimide is soluble in solution of ammonia, and separates in crystals which do not contain ammonia of crystallisation. *Dihydroxylamine azoimide*,  $2\text{NH}_2\cdot\text{OH}, \text{N}_3\text{H}$ , m. p.  $66^\circ$ , forms colourless, leaf-like crystals.

A comparative study of the different methods which have been recommended for the estimation of azoimide led to the following conclusions. Silver azoimide is soluble in nitric acid even when the acid is present in very small quantity, but can be precipitated quantitatively from neutral solutions or from a solution containing acetic acid. The presence of phenolphthalein does not interfere with the formation of the precipitate.

A solution of azoimide in methyl alcohol can be prepared in the following manner. Potassium azoimide is placed in a flask and treated with a mixture of sulphuric acid (2 parts) and water (1 part). A current of carbon dioxide is passed through the apparatus, the temperature being raised gradually to  $60^\circ$ , and led into a vessel containing methyl alcohol. The residue in the flask contains some azoimide together with other nitrogen hydrides which have a reducing action.

When azoimide is reduced with sugar and sulphuric acid by the Kjeldahl method, one-third of the nitrogen appears as ammonia. Reduction experiments were also made with aluminium and sodium hydroxide, but irregular results were obtained.

If anhydrous azoimide is treated with concentrated sulphuric acid, a violent effervescence takes place, and monoclinic crystals of a volatile alkali are formed which have a double refraction, 0.017; when this substance is recrystallised from water, the resulting crystals show the orthorhombic form of hydrazine sulphate with a double refraction, 0.008.

Experiments on the reaction between azoimide and hydrochloric acid show that it takes place in accordance with the equation  $3\text{N}_3\text{H} + \text{HCl} = \text{NH}_4\text{Cl} + 4\text{N}_2$ , thus confirming the result obtained by Curtius.

E. G.

**Combination of Elementary Carbon and Nitrogen.** MARCELLIN BERTHELOT (*Compt. rend.*, 1907, 144, 354—357).—Pure carbon, free from hydrogen and containing no trace of alkali or alkaline-earth metals, does not combine directly with nitrogen, under the influence of heat alone, even in the electric arc. The formation of cyanogen compounds, by passage of the electric arc through nitrogen under ordinary conditions, is due to the impurities in the arc carbons. These impurities include (1) hydrogen compounds and water-vapour, substances capable of giving acetylene, which, under the influence of electricity, combines directly with free nitrogen, forming hydrogen cyanide, and (2) various metallic compounds which, with the help of carbon, are capable, under the sole influence of heat, of absorbing nitrogen with the production of alkali cyanides. As it is very difficult to purify charcoal completely, it is best to work with diamond or specially purified graphite. It is necessary to use absolutely dry nitrogen and to prevent the access of the slightest trace of hydrogen.

On the other hand, pure cyanogen, when submitted to a series of

electric sparks, decomposes completely and no indication of an equilibrium between carbon, nitrogen, and cyanogen, analogous to that found with hydrogen carbon and acetylene, is observed. To ensure the cyanogen used being dry, it was prepared from mercuric cyanide previously dried by prolonged heating, and collected over dried mercury. Seventy-seven c.c. of the gas were submitted to a series of powerful electric sparks. At first there was produced a large deposit of carbon accompanied by the liberation of nitrogen, after some hours the volume was reduced to 56 c.c., and it contained only a very small quantity of gas absorbed by alkali. The volume of the gas did not become constant, as would result from simple decomposition into carbon and nitrogen, because polymerised compounds (compare Gaudechon, *Abstr.*, 1906, i, 73) were deposited with the carbon. Continued sparking for several hours in another vessel produced a fresh but very slight deposit of carbon. The residual gas consisted of pure nitrogen, not even smelling of cyanogen. It follows that as no stable equilibrium between carbon and nitrogen can be effected, the ordinary thermodynamic calculations and equations cannot be applied in this case. Generally, the study of real equilibria in gaseous systems, according to ordinary theories, appears to require that these systems be maintained *in their totality at a uniform temperature*, and that having reached a state of equilibrium they should continue in it indefinitely, with a fixed composition. Accordingly such theories and equations cannot be applied to instantaneous phenomena (such as are produced by explosions or by the electric spark) or to media in which the distribution of temperature is very irregular. Moreover, these theories and equations rest on the hypothesis that the chemical changes studied are due solely to heat energy, whilst electric energy acting according to very different laws does not enter into the same calculations. E. H.

**Allotropic Forms of Silica.** COSMO JOHNS (*Geol. Mag.*, 1906, 3, 118—120).—Quartz-sand when rapidly heated (in a steel furnace) up to 130J° becomes changed to a milk-white powder of increased volume (the D changing from 2.645 to 2.309), owing to its conversion to tridymite. At a temperature of above 1800° the material is fused. Neglecting the effect of vapour pressure, the presence of quartz or of tridymite in an igneous rock would indicate that crystallisation had taken place either below or above a temperature of 1300°.

L. J. S.

**Lighter Constituents of Air.** JOSEPH EDWARD COATES (*Proc. Roy. Soc.*, 1906, 78, A, 479—482).—The author has made experiments to ascertain whether a large volume of air would yield on systematic fractionation any constituent lighter than helium. The volume of air operated upon amounted to about 73,500 litres. In order to avoid contamination with hydrogen, the gas-holder was well painted inside, and the compressor cylinders lubricated with very dilute alkali. The conclusions arrived at are that there are no unknown lines in the spectrum of the lightest portions of the air, all those observed being traceable to helium, neon, and hydrogen, and that the amount of

hydrogen contained in air is very much less than the values assigned by previous investigators. The exact estimation of the hydrogen is a very difficult matter, but the fractionation experiments indicate that the order of the amount is one volume of hydrogen in one and a half million volumes of air.

H. M. D.

**Densities of Lithium, Sodium, Potassium, Rubidium, and Cæsium.** THEODORE W. RICHARDS and FRANCIS N. BRINK (*J. Amer. Chem. Soc.*, 1907, 29, 117—127).—Whilst studying the significance of atomic volume and atomic compressibility, it was observed that the densities recorded for the alkali metals show considerable diversity, and in order to obtain trustworthy data the present investigation was undertaken.

The methods employed and the precautions taken are described in detail, and the results of all the determinations are tabulated. Several different preparations were used and great care was exercised in every case, but in the case of cæsium the figures are only approximate. From the atomic weights, the atomic volumes were calculated. The following results were obtained :

	D <sup>20</sup>	Atomic weight.	Atomic volume. (Ag=107·93.)
Lithium.....	0·534	7·0	13·1
Sodium .....	0·9712	23·008	23·70
Potassium .....	0·8621	39·114	45·38
Rubidium .....	1·532	85·48	55·8
Cæsium .....	1·87	133·8	71·0

An alloy of potassium (39·9%) and sodium (60·1%) had D<sup>20</sup> 0·919.

E. G.

**Alloys of Potassium Chloride with Potassium Chromate, Potassium Dichromate, and Silver Chloride.** S. F. SCHEMTC-HUSCHNY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1135—1145).—The author has investigated the melting point curves of the systems, KCl + K<sub>2</sub>CrO<sub>4</sub>, KCl + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and KCl + AgCl, and has also examined the micro-structure of the different alloys (mixed crystals) obtained.

The melting point diagram of KCl + K<sub>2</sub>CrO<sub>4</sub> consists of two branches, intersecting at the eutectic point, 658°, which corresponds with a content of 31·5 mols. % of the chromate. Examination of the cooling curve shows that on the potassium chloride part of the curve no solid solutions are formed, whilst on the chromate side solid solutions occur containing the chloride in the definite concentration of about 4 mols. %. The cooling curve of pure potassium chromate exhibits two transition points : (1) at 984°, corresponding with crystallisation of the chromate, and (2) at 679°, the salt being then converted into another modification ; this change corresponds with the change of the yellow salt into the red form on heating. These observations are in accord with the micro-structure, which reveals a basis of eutectic character containing crystals of either chloride or chromate according to the branch of the curve with which the particular section examined corresponds.

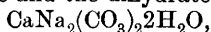
With KCl + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, the melting point diagram also consists of two

branches meeting at the eutectic point,  $366^{\circ}$ , corresponding with the presence of 27.5 mols. % of the chloride. Only on the dichromate portion of the curve are solid solutions found, these containing about 25 mols. % of the chloride. The melting point curve of the pure dichromate shows two transition points: (1) at  $395^{\circ}$ , the salt then crystallising from the molten state, and (2) at  $236^{\circ}$ , corresponding with a change into the second modification; this change is accompanied by considerable alteration of volume. Crystal sections corresponding with the dichromate branch of the curve exhibit the uniform structure of solid solutions, whilst in those from the chloride branch are evident crystals of the chloride on a groundwork of dark eutectic mixture.

The melting point diagram of  $KCl + AgCl$  possesses two branches intersecting at the eutectic point,  $306^{\circ}$ , which corresponds with a content of 30 mols. % of potassium chloride. Solid solutions having a concentration of about 1 mol. % correspond with each of the two branches. The micro-structure reveals the eutectic mixture as groundwork with crystals of either potassium chloride or silver chloride, according to the part of the curve with which the crystal section corresponds.

T. H. P.

**Causticising of Soda.** RUDOLF WEGSCHEIDER and HEINRICH WALTER (*Annalen*, 1907, 351, 87—99. Compare Wright, this Journ., 1867, 20, 407; Scheurer-Kestner, *ibid.*, 1873, 196; Smith and Liddle, *Abstr.*, 1881, 508; Rammelsberg, *Chem. Ind.*, 1881, 50; Reidemeister, *ibid.*, 74; Bodländer and Lucas, *Abstr.*, 1905, ii, 634).—The cause of the loss of sodium carbonate in causticising soda by means of lime has been discussed by various authors and ascribed to the formation of an insoluble sodium calcium carbonate, which in hydrated crystals,  $CaNa_2(CO_3)_2 \cdot 5H_2O$ , forms the mineral gaylussite. The conditions under which this substance and the dihydrate, pirssonite,



are capable of existence have been investigated and the whole problem is discussed from the point of view of chemical equilibrium.

At  $11^{\circ}$ , calcium carbonate, gaylussite, and sodium carbonate solution are in equilibrium when the last has the concentration  $0.86N$ . At higher temperatures, equilibrium is established between calcium carbonate, pirssonite, and sodium carbonate solution when the concentration of the last is, at  $40^{\circ}$ ,  $2.14N$ , at  $60^{\circ}$ ,  $3.77N$ , or at  $80^{\circ}$ ,  $4.34N$ . If the concentration of the sodium carbonate is less than the "equilibrium-concentration," the double salt should be decomposed until the equilibrium is established; this action remains incomplete in consequence of the protection of the double salt by a layer of calcium carbonate.

If sodium or calcium hydroxide is added to the reacting masses, equilibrium is possible with more than one concentration, thus at  $60^{\circ}$ , pirssonite is in equilibrium with a mixture of  $1.8N$ -sodium carbonate and  $2.6N$ -sodium hydroxide, or of  $3.7N$ -sodium carbonate and  $1.3N$ -sodium hydroxide. As was to be expected from the application of the law of mass action, the total normality of the equilibrium mixture increases with the proportion of carbonate present in the whole solution. These results are discussed also from the point of view of the theory of electrolytic dissociation.

As the action,  $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaOH}$ , is reversible, and calcium hydroxide and carbonate are added in the solid state, the conditions necessary for equilibrium are expressed by the equation:  $(\text{NaOH})^2/(\text{Na}_2\text{CO}_3) = \text{const.}$ , in which  $(\text{NaOH})$  and  $(\text{Na}_2\text{CO}_3)$  are the concentrations of the undissociated molecules. If the total concentrations are regarded, the proportion  $a^2/b$  is, with considerable limits of temperature, a linear function of the total titre,  $T'(=a+b)$ . The observed values for  $a^2/b$  agree with the calculated at temperatures between  $80^\circ$  and  $108^\circ$ , and with  $T' = 2.0-4.625$ , but show considerable variations from the calculated with  $T' = 4.9$  or greater. With  $T' = 2.2-5.0$ , the causticising is more complete at  $80^\circ$  than at  $108^\circ$ , but the velocity of the reaction decreases with the temperature.

In agreement with the statements of previous authors, it is found that the formation of the insoluble double salt is favoured by the presence of an excess of calcium hydroxide. G. Y.

**Crystalline Calcium Borates.** WILHELM MEYERHOFER and JACOBUS H. VAN'T HOFF (*Annalen*, 1907, 351, 100-107).—This work was undertaken with the object, only partially achieved, of preparing the naturally occurring compounds: pandermite,  $\text{Ca}_8\text{B}_{20}\text{O}_{33} \cdot 15\text{H}_2\text{O}$ ; borocalcite,  $\text{CaB}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , and colemanite,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ .

*Monoborates.*—The hexahydrate,  $\text{CaB}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$ , described by Ditte (Abstr., 1884, 711) as a heptahydrate, forms the best starting point for the preparation of calcium borates. It is prepared by the action of boric acid on calcium chloride in aqueous potassium hydroxide, and when heated at  $45.5^\circ$  forms an unstable *dihydrate*, the reaction being reversible. If heated at  $24^\circ$  with water, the hexahydrate is converted by a reversible reaction into an unstable  $\alpha$ -*tetrahydrate*,  $\text{CaB}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ , which on further heating changes into a stable  $\beta$ -form; this change is accelerated by the presence of sodium chloride, taking place at  $40^\circ$  in 10% sodium chloride solution.

*Triborates.*—The *dodecahydrate*,  $\text{CaB}_6\text{O}_{10} \cdot 12\text{H}_2\text{O}$ , is formed by shaking the above hexahydrate with boric acid in cold aqueous solution; the conversion is complete in about twenty-four hours. This hydrate is unstable and changes at the ordinary temperature into the *octahydrate*,  $\text{CaB}_6\text{O}_{10} \cdot 8\text{H}_2\text{O}$ , which forms doubly refracting leaflets, and slowly undergoes degradation to Ditte's tetrahydrate,  $\text{CaB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$  (*loc. cit.*).

*Colemanite series.*—In their composition, the naturally occurring borates lie between the mono- and tri-borates. Borates containing calcium and boron in the proportion present in colemanite, are obtained by addition of boric acid to the monoborates or by partial removal of the boric acid from the triborates.

The *nonahydrate*,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 9\text{H}_2\text{O}$ , prepared by heating calcium monoborate hexahydrate with the requisite amount of boric acid in aqueous solution at  $100^\circ$ , or by the action of water on calcium triborate octahydrate at the ordinary temperature, forms crystals resembling augite; when heated with 3% aqueous boric acid at  $100^\circ$  it is converted into the *heptahydrate*,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$ , which forms long, rectangular crystals and may be identical with Kraut's hexahydrate (*Arch. Pharm.*, 1862, 112, 33).



It is noted that the difference between one member and the next of each of these series of borates is 2 mols. of water of crystallisation. G. Y.

**Decomposition of Dicalcium Phosphate by Water.** K. BUCH (*Zeitsch. anorg. Chem.*, 1907, 52, 325—341. Compare Rindell, Abstr., 1902, ii, 208; Cameron and Seidell, 1905, ii, 33).—The gradual transformation of dicalcium phosphate,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  into  $\text{Ca}_3(\text{PO}_4)_2$ , by the action of water at  $25^\circ$  has been investigated. Quantities of the acid salt varying from 0.6—10 grams were treated successively with 500 c.c. of water for twenty hours, the supernatant liquid being removed and analysed after each experiment, and the composition of the insoluble residue also calculated. The results are given in tabular form. After about fifty digestions, the solubility of the residues became constant.

The solubility usually decreases a little at first, then rises to a maximum, beyond which it falls rapidly to a constant value. The  $\text{PO}_4$  concentration in the solution is at first considerably greater than that of the Ca, but at a later stage becomes smaller. The constant solubility is reached at different points depending on the initial amounts of salt present, which points to the formation of intermediate compounds. The less the initial quantity of salt the more highly basic are the end products; only in two series was the transformation to  $\text{Ca}_3(\text{PO}_4)_2$  complete.

The data are not sufficient to establish the formulæ of any of the intermediate compounds, the existence of which is indicated. G. S.

**Valency and Atomic Weight of Glucinum.** SEBASTIAN M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 850—854. Compare Abstr., 1904, ii, 335).—The existence of compounds of the type  $\text{Gl}_4\text{OR}_8$  (where R stands for an acid radicle) can only be explained by assuming glucinum to be either ter- or quadri-valent; the former is considered very unlikely, since the equivalent of glucinum has been well established, and all attempts to obtain compounds of the type  $\text{GlR}_3$  were unsuccessful. On the other hand, the sp. heat of glucinum oxide, determined with all possible care by Berthelot's method for the determination of the sp. heat of liquids, was found to be 0.2898. If then, glucinum oxide is  $\text{GlO}$ , the atomic heat of glucinum will be 3.273, whilst if it is  $\text{GlO}_2$ , the atomic heat will be 6.546, which is almost normal; it is therefore most probable that glucinum is quadri-valent and its atomic weight is 18.2. Z. K.

**Alloys of Thallium and Lead.** KURT LEWKONJA (*Zeitsch. anorg. Chem.*, 1907, 52, 452—456. Compare Kurnakoff and Pushin, Abstr., 1902, ii, 139).—The freezing point curve shows a break at 5% by weight of lead and a maximum at  $374^\circ$  and 34% of the same metal, the latter corresponding with a compound of the formula  $\text{PbTl}_2$ . From 0—5% and 24—100% of lead, mixed crystals separate.

The alloys are very soft and easily oxidised, the compound  $\text{PbTl}_2$  being softer and more easily oxidised than its components.

An unsuccessful attempt was made to determine the effect of lead on

the transition temperature of thallium ; even with 0.5% of the former metal the thermal effect in the neighbourhood of the transition point was no longer appreciable. G. S.

**Alloys of Lead with Thallium and Indium.** NICOLAI S. KURNAKOFF and NICOLAI A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1146—1167).—The melting point curve of the system lead-thallium exhibits a transition point at  $309^{\circ}$  corresponding with 5.5 atoms % of lead. The first part of the curve, rising from the m. p. of thallium to  $309^{\circ}$ , corresponds with the separation of solid solutions which contain from 0 to 5.5 atoms % of lead and crystallise in the same form as thallium. The second branch of the curve rises from  $309^{\circ}$  to a maximum at  $380^{\circ}$ , and then falls to  $327.7^{\circ}$ , the m. p. of lead ; the solid phases here deposited consist of solid solutions which contain from 25 to 100 atoms % of lead and crystallise in octahedra of the regular system. The atomic ratio of lead to thallium corresponding with the maximum temperature varies from 1:1.67 to 1:1.83 for different preparations of lead and thallium ; the inconstancy of this ratio indicates the existence of a solid indefinite compound.

In the case of lead and indium, which both crystallise in the regular system, a continuous series of isomorphous mixtures is obtained, which have a marked capacity for crystallising. The addition of 10 atoms % of lead to indium alters the m. p. of the latter very little, but, with further additions, an approximately straight line curve in the direction of the m. p. of lead is obtained. T. H. P.

**Solution of Copper or its Oxide in Potassium Hydroxide.** S. N. ANTONOFF and B. V. MALYSHEFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 884—890).—When copper or copper oxide is dissolved in melted potassium hydroxide above  $360^{\circ}$ , the resulting substance, when diluted with water and neutralised, decolorises permanganate solution. The solution, however, gives no reaction for peroxides, and continues to decolorise permanganate when a current of hydrogen is passed through it. This decolorising action is found to be due to the presence of cuprous oxide,  $\text{Cu}_2\text{O}$ , formed by the dissociation of cupric oxide above  $360^{\circ}$ . When potassium or hydrogen peroxide is added to the solution of copper oxide in potash, a red colour is first produced which vanishes quickly ; then a yellow precipitate separates, which also redissolves, quickly reproducing the original blue solution, which now contains no trace of either peroxide or cuprous oxide. The yellow precipitate was found to be  $\text{CuO}_2 \cdot \text{H}_2\text{O}$  or  $\text{CuO} \cdot \text{H}_2\text{O}_2$ , its production being a first stage in the decomposition of the peroxide by copper oxide. This reaction is vigorous only in alkaline solution. It is also shown that commercial potash contains peroxide, and whilst, when acting on iron, the latter is converted into ferrous oxide, at the expense probably of the water present in the potash, the action on copper and also on silver is due to the presence of these peroxides. Z. K.

**Salts of Hydrogen Copper Tetrasulphide.** HEINRICH BILTZ and PAUL HERMS (*Ber.*, 1907, **40**, 974—985. Compare Bloxam, this Journ., 1865, **3**, 94 ; Hofmann and Höchtlén, *Abstr.*, 1903, ii, 728).—The alkali salts of the acid,  $\text{HCuS}_4$ , are readily obtained when am-

monium copper tetrasulphide is dissolved in sodium hydroxide and the solution precipitated with the requisite metallic hydroxide dissolved in alcohol. *Potassium copper tetrasulphide* forms a dark red, crystalline powder, sparingly soluble in cold water, and readily decomposed when warmed with water. When an excess of potassium hydroxide is used in the preparation, the product contains an oxy-derivative. Corresponding *cæsium* and *rubidium* salts have been prepared. They are all decomposed when warmed with dilute mineral acids, yielding hydrogen sulphide, copper sulphide, and free sulphur. When dry, they may be kept for some time, but in moist air they decompose slowly, but rapidly when warmed. The same potassium compound is formed when cupric oxide is dissolved in impure potassium pentasulphide. It is precipitated, dried in a desiccator, and freed from a yellow impurity by treatment with a small amount of cold water.

When cuprous oxide or sulphide is dissolved in the pentasulphide solution at  $0^{\circ}$ , deep brown coloured liquids are obtained, from which alcohol throws down yellowish-red prisms of a complex compound,  $K_3Cu_2O_2S_9$ . When freshly precipitated, the crystals dissolve readily in water, and with *cæsium* hydroxide solution give a quantitative yield of *cæsium* copper tetrasulphide. Cuprous oxide dissolves in a solution of purified potassium pentasulphide, yielding potassium copper tetrasulphide. When solutions of the alkali hydroxides are added to a solution of cuprous oxide in sodium pentasulphide, precipitates of the alkali copper tetrasulphides are formed.

Black crystalline compounds of the type  $K_2Cu_3S_{10}$  ( $= 2KCuS_4 \cdot CuS_2$ ) are formed when the freshly precipitated tetrasulphide is dissolved in its mother liquor by shaking, and alcohol is added gradually to this solution, care being taken that the red crystals do not separate. This compound dissolves readily in water, and on the addition of potassium sulphide to its aqueous solution yields a dirty brown precipitate; the addition of potassium polysulphide yields potassium copper tetrasulphide.

J. J. S.

**Theory of the Formation of Aventurine Glass Containing Copper.** VICTOR AUGER (*Compt. rend.*, 1907, 144, 422—424).—It is held generally that the small crystals disseminated throughout aventurine glass consist of metallic copper, but owing to the facts that these crystals are not bleached by mercuric salts, that aventurine glass melted at a high temperature does not give a regulus of copper, and that ammonia at  $100^{\circ}$  dissolves a considerable quantity of cuprous salt giving a colourless solution, Hautefeuille (*Compt. rend.*, 1846, 22, 339) and Pettenkofer (*Jahresber.*, 1861, p. 905) held that the crystals consist of cuprous oxide or silicate. The former theory was supported by Ebell, who showed (*Dingl. polyt. Journ.*, 213, 324) that alcoholic silver nitrate solution dissolves out the crystals, and by Sulkowski, who showed (*Chem. Ind.*, 20, 134) that ammoniacal copper sulphate solution, when heated to  $100^{\circ}$  with the powdered glass, is decolorised, which is possible with metallic copper, but impossible with a cuprous salt. Both Ebell and Sulkowski admit the difficulty of explaining the fact that the incandescent glass will scarcely dissolve metallic copper. The author finds that under a microscope the crystals

in aventurine glass and those in slowly cooled cuprous phosphate have an exactly similar appearance, and points out that all the preceding properties would be explained by the presence in the glass of a cuprous silicate stable at a red heat, but depositing metallic copper on cooling. Moreover, like cuprous phosphate, aventurine glass when very rapidly cooled remains transparent, and becomes cloudy and red on reheating. If the suggested explanation is correct, the glass should contain at least as much copper in the form of cupric silicate as in the metallic state. The amounts actually found were 1.3% in the metallic state, and 2% as cupric silicate in the transparent residue. The conclusions drawn are that fused aventurine glass contains cuprous silicate, which, on cooling, decomposes into metallic copper and cupric silicate, the latter of which, together with the yellow ferric silicate, imparts a green colour to the mass, and that the transparent, rapidly cooled aventurine contains copper as cuprous silicate which decomposes on reheating.

E. H.

**Copper Silicide.** PAUL LEBEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 108—111. Compare Abstr., 1906, ii, 29; Vigouroux, Abstr., 1906, ii, 168, this vol., ii, 82—89).—A reply to Vigouroux (this vol., ii, 89), giving a historical *résumé* of work done on copper silicide, and showing, *inter alia*, that the conditions under which the compound,  $\text{Cu}_4\text{Si}$ , is formed were first definitely ascertained by the author.

T. A. H.

**Chemical Compounds of Potassium and Mercury.** ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1907, 58, 245—249. Compare Kurnakoff, Abstr., 1900, ii, 277).—The author has studied the complete freezing point curve for mixtures of potassium and mercury, and thus obtains evidence of the following compounds:  $\text{KHg}$ ,  $\text{KHg}_2$  (m. p.  $279^\circ$ ),  $\text{K}_3\text{Hg}_9$ ,  $\text{K}_2\text{Hg}_9$ , and  $\text{KHg}_9$ .

J. C. P.

**Mercury Nitrogen Compounds (the Mercuriammonium Salts and Bases).** EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1907, 29, 35—66).—In an earlier paper (Abstr., 1905, ii, 582) the author suggested the abandonment of the substituted ammonium theory as applied to the mercuriammonium compounds, and the substitution of a modified and extended form of the old amide theory. In accordance with this idea, the mercury nitrogen compounds are now classified as (1) ammono-bases and mixed hydro-ammono-bases; (2) mercuric salts with ammonia of crystallisation and with ammonia and water of crystallisation; (3) ammonobasic mercuric salts, and (4) mixed ammono-basic-hydrobasic mercuric salts. All the mercury nitrogen compounds which have been described are arranged under these headings together with such data regarding their preparation and properties as are necessary to show that they all readily find a place in this scheme of classification.

E. G.

**Nitrates of Yttrium Earths and Ceric Nitrate.** VIKTOR VON LANG and LUDWIG HAITINGER (*Annalen*, 1907, 351, 450—457).—The nitrates of the yttrium earths described in this paper were obtained in

the course of an unsuccessful attempt to separate these by fractional crystallisation. If crystallised as basic nitrates, the holmium elements are obtained before yttrium, but on crystallisation of the normal nitrates almost all the yttrium is found in the erbium fractions which are more soluble than the gadolinium-holmium mixture.

Gadolinium nitrate,  $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , containing holmium elements forms triclinic crystals [ $a:b:c = 1:1.795:1.367$ ;  $\alpha = 90^\circ 6'$ ;  $\beta = 109^\circ 55'$ ;  $\gamma = 109^\circ 48'$ ], and is isomorphic with didymium nitrate.

Crystallographical measurements are given for yttrium nitrate,  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and for crystals of this containing erbium nitrate.

Basic ceric nitrate (Meyer and Jacoby, *Abstr.*, 1900, ii, 597; 1901, ii, 510) forms monoclinic crystals [ $a:b:c = 1.7834:1:1.0465$ ;  $\beta = 90^\circ 48'$ ]. G. Y.

**The so-called Passivity of Aluminium towards Nitric Acid.**  
CHARLES M. VAN DEVENTER (*Chem. Weekblad.*, 1907, 4, 69—72. Compare Stillmann, *Abstr.*, 1898, ii, 588; Ditte, *Abstr.*, 1890, 702; 1899, ii, 225, 292, 425, and 426).—The action of nitric acid of varying concentrations on aluminium at  $25$ — $30^\circ$  and different pressures has been investigated. Two experiments were carried out in sealed tubes, and three in open tubes. From the results obtained the author draws the following conclusions: (1) At  $25$ — $30^\circ$  aluminium is slowly attacked by nitric acid of concentration between 20% and 5%, chiefly in accordance with the equation  $\text{Al} + 4\text{HNO}_3 = \text{Al}(\text{NO}_3)_3 + \text{NO} + 2\text{H}_2\text{O}$ . (2) A small proportion of the metal reduces nitric oxide to free nitrogen. (3) At the ordinary pressure, a small amount of ammonia is formed, but at higher pressure almost none. (4) For nitric acid of the same concentration the velocity of reaction is proportional to the surface area of the metal. (5) For nitric acid of different concentrations the velocity of reaction is proportional to the concentration of the acid. (6) The behaviour of aluminium is very different from that of zinc, which dissolves freely in dilute nitric acid with evolution of ammonia. A. J. W.

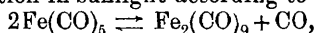
**Solubility of Potassium Permanganate. A Correction.**  
GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1907, 29, 240—241).—In a paper by Baxter, Royston, and Hubbard (*Abstr.*, 1906, ii, 856), reference was not made to the work of Patterson (*J. Amer. Chem. Soc.*, 1906, 28, 1734), Herz and Knoch (*Abstr.*, 1904, ii, 709), and Voerman (*Chem. Weekblad.*, 1905, 2, 766). It is now shown that the results obtained by Patterson and by Herz and Knoch are not comparable with those of the present author, and that Voerman's values are probably slightly too low. E. G.

**New Method of Estimating Fluorine and the Composition of Iron Fluoride.** ERNST DEUSSEN [and HEINRICH KESSLER] (*Monatsh.*, 1907, 28, 163—172).—Fluorine is estimated by heating the substance with calcium oxide in a double crucible, and, after treatment of the product with water, acetic acid, and alcohol, weighing the calcium fluoride so formed. Test analyses of pure sodium fluoride show the error of the method to be  $-0.8\%$ ; commercial ammonium

fluoride, sometimes termed "acid ammonium fluoride," has the composition  $\text{NH}_4\text{F}$ .

Scheurer-Kestner's supposed ferric fluoride, formed together with hydrogen peroxide by the action of hydrogen fluoride on iron in presence of nitric acid, has the composition  $\text{Fe}_3\text{F}_8 \cdot 10\text{H}_2\text{O}$ , and is probably a ferrous ferrifluoride. Werner has suggested for it the formula  $\left[\text{Fe}''(\text{H}_2\text{O})_2\right]_2\left[\text{Fe}(\text{H}_2\text{O})_6\right]\text{F}_4$ . It forms colourless octahedra, which in thick layers appear flesh-coloured, yields with ammonia a reddish-brown precipitate containing iron and fluorine, and gives the ordinary ferrous and ferric reactions only after addition of an acid; the ferrous ions cannot be estimated by means of potassium permanganate. This ferrous ferrifluoride is compared with Weinland and Köppen's ferric ferrous fluoride (Abstr., 1900, ii, 143), which with ammonia yields ferroso-ferric hydroxide, gives the ferrous and ferric reactions directly, and yields quantitative results with potassium permanganate. G. Y.

**New Iron Carbonyl and the Action of Light and of Heat on the Iron Carbonyls.** Sir JAMES DEWAR and HUMPHREY O. JONES (*Proc. Roy. Soc.*, 1907, 79A, 66—80).—In a former paper (Abstr., 1906, ii, 89) it was shown that iron pentacarbonyl, alone or in solution, undergoes decomposition in sunlight according to the equation



diferro-nonacarbonyl separating in orange-red crystals; the velocity of the direct and reverse actions under varying conditions have now been measured. Further, a new iron carbonyl,  $\text{Fe}(\text{CO})_4$ , has been obtained by the action of heat on diferro-nonacarbonyl.

The rate of decomposition of the pentacarbonyl in pyridine and in light petroleum solution at the ordinary temperature in sunlight has been measured by observing the change of pressure; the reaction is approximately unimolecular. The rate of reaction is compared under equivalent conditions with that of certain other reactions which also take place only under the influence of light. The velocity of the reverse reaction, which proceeds in the dark, is very small at the ordinary temperature, but is much greater at  $35^\circ$ ; measurements could not be carried out at higher temperatures owing to decomposition of the diferro-nonacarbonyl as described below. The previous observation, that dissolved iron pentacarbonyl does not undergo decomposition in sunlight from  $56$ — $100^\circ$ , is accounted for on the view that in the reaction,  $2\text{Fe}(\text{CO})_5 \rightleftharpoons \text{Fe}_2(\text{CO})_9 + \text{CO}$ , the equilibrium is displaced towards the left with rise of temperature.

Alumina absorbs about 2.5% of its weight of iron pentacarbonyl; on exposure to light the powder becomes deeply coloured, and carbon monoxide is evolved.

When crystals of diferro-nonacarbonyl are heated with certain solvents at  $50$ — $90^\circ$  in an atmosphere of carbon dioxide, intensely green solutions are obtained, which, on exposure to light, gradually lose their colour, with deposition of iron. From the green toluene solution, *iron tetracarbonyl* was obtained in short, dark green, lustrous, prismatic crystals of  $D$  1.996 at  $18^\circ$ . It is considered that when

diferro-nonacarbonyl is heated alone at  $100^{\circ}$ , or in the presence of solvents, it decomposes primarily according to the equation  $\text{Fe}_2(\text{CO})_9 = \text{Fe}(\text{CO})_5 + \text{FeCO}_4$ .

Iron tetracarbonyl is very stable under ordinary conditions; on heating to  $140$ – $150^{\circ}$ , it decomposes into iron and carbon monoxide. It is soluble in toluene, light petroleum, ethyl ether, and many other organic solvents; the dark green solutions lose their colour slowly on heating at  $100^{\circ}$  but rapidly at  $140^{\circ}$ , iron being deposited. The solutions in pyridine and alcohol, which are also green at first, turn red on standing. Cyroscopic measurements in benzene solution show that the molecular weight of iron tetracarbonyl is very high. G. S.

**Ferronitroso-compounds.** VOLKMAR KOHLSCHÜTTER and M. KUTSCHEROFF (*Ber.*, 1907, 40, 873–878).—In consequence of Manchot and Zechtenmayer's statement to the contrary (compare this vol., ii, 93), the authors publish the data on which is based their conclusion that the absorption of nitric oxide by a solution of ferrous chloride is increased in the presence of hydrochloric acid (compare *Abstr.*, 1904, ii, 734). In 30% hydrochloric acid the absorption is approximately doubled, but the solubility of nitric oxide in ferrous chloride in 10% hydrochloric acid is rather less than in an aqueous solution of the same concentration, as Manchot and Zechtenmayer have observed. C. S.

**Distillation of Nickel and Cobalt.** HENRI MOISSAN (*Annalen*, 1907, 351, 510–513. Compare *Abstr.*, 1906, ii, 232; Copaux, *Abstr.*, 1905, ii, 254).—In view of the closeness of the melting points of nickel and cobalt, it was of interest to determine the relative ease with which these two metals volatilise.

The metals were heated in an electric furnace by means of an alternating current; to maintain a constant resistance during the course of each experiment, the distance between the cylindrical electrodes was increased as the conductivity of the air in the oven became greater in consequence of the presence of metallic vapours. The experiments described show that cobalt is much less volatile than nickel, 56 grams of this, but only 19 grams of cobalt, being distilled in five minutes when heated with a current of 500 amperes and 110 volts. Both metals condense on a cooled copper tube in microscopic crystals. When rapidly distilled, nickel is found to contain calcium oxide. G. Y.

**A Singular State of Matter observed with a Dissolved Chromic Salt.** ALBERT COLSON (*Compt. rend.*, 1907, 144, 325–326. Compare this vol., ii, 177).—All experiments appear to show that the polymerisation of solid violet chromium sulphate to the green sulphate is more complete at  $90^{\circ}$  than at  $110^{\circ}$ . This anomaly would be explained if the salts when dissolved were rapidly altered by the solvent. Observations of the freezing points of one-tenth molecular solutions of the green sulphates prepared at  $90^{\circ}$  and  $110^{\circ}$  made at regular intervals after dissolution confirm this explanation. The depression

of the freezing point of the solution of the sulphate prepared at  $110^{\circ}$  increases from  $0.29^{\circ}$  immediately after dissolution to  $0.415^{\circ}$  after 24 hours, whilst the depression of the sulphate prepared at  $90^{\circ}$  increases from  $0.21^{\circ}$  to  $0.415^{\circ}$  in the same time. The higher initial depression of the first salt results from its slow dissolution necessitating a long contact with water. The conclusion is drawn that *the green chromic sulphate obtained by heating the violet sulphate above  $90^{\circ}$  exists in solution at the same temperature in two states: an initial condensed state of the form  $[\text{Cr}_2(\text{SO}_4)_3]_2$ , and a normal state,  $\text{Cr}_2(\text{SO}_4)_3$ , proceeding from the slow dissociation of the first.* The dissociation of the condensed green sulphate is reversible. This is shown by observation of the freezing point of a one-fifth molecular solution of the gummy mass obtained by evaporation in a vacuum at  $12^{\circ}$ , of a solution of the normal green sulphate. The depression of the freezing point was found to be  $0.61$  instead of the  $0.83^{\circ}$  given by a solution of the normal salt of the same strength. Polymerisation is still more strongly marked when the concentration is continued as far as fusion of the salt in its water of crystallisation.

E. H.

**Fluorides of Sexavalent Molybdenum.** OTTO RUFF [with FRITZ EISNER and WILHELM HELLER] (*Zeitsch. anorg. Chem.*, 1907, 52, 256—269. Compare Abstr., 1905, ii, 255).—Tungsten hexafluoride was previously obtained by interaction of the hexachloride and anhydrous hydrofluoric acid (*loc. cit.*); by the substitution of a platinum apparatus for glass, it has now been obtained in much larger yield. It also results by interaction of the hexachloride and arsenic trifluoride, but even repeated fractionation does not quite free it from the latter compound. The most convenient method for preparing the hexafluoride in a pure condition is by gradually adding antimony pentachloride to tungsten hexachloride cooled by a freezing mixture, and subsequent distillation; in this instance, glass vessels may be used. The compound melts at  $2.5^{\circ}$ , and boils at  $19.5^{\circ}$  under atmospheric pressure.

*Tungsten oxytetrafluoride*,  $\text{WOF}_4$ , is prepared by interaction of equal amounts of the tetrachloride and anhydrous hydrogen fluoride in a platinum vessel at  $20^{\circ}$ , the temperature being subsequently allowed to rise gradually. After 24 hours the retort is heated to  $280^{\circ}$ , while the upper part is kept cool, and the oxyfluoride condenses in the neck as a snow-white mass. It has also been obtained by the action of lead or bismuth fluoride on bismuth trioxide, moisture being carefully excluded.

Tungsten oxytetrafluoride occurs in small, colourless, extremely hygroscopic plates, m. p.  $110^{\circ}$ , b. p.  $185$ — $190^{\circ}$ . It is decomposed by water with precipitation of tungstic acid, has no action on the ordinary metals in the cold, but attacks them slightly on heating; it absorbs a large quantity of ammonia in the cold.

Attempts to obtain pure tungsten dioxyfluoride,  $\text{WO}_2\text{Cl}_2$ , have so far proved unsuccessful. This substance, mixed with the oxytetrafluoride, results when tungsten trioxide and lead fluoride react in presence of a trace of aqueous vapour.

G. S.



**Complex Formation in Molybdic Acid Solutions.** EBERHARD RIMBACH and C. NEIZERT (*Zeitsch. anorg. Chem.*, 1907, 52, 397—405 Compare Rosenheim and Bernheim, *Abstr.*, 1903, ii, 374).—The rotatory power of optically active hydroxy-acids is greatly increased by the addition of molybdic acid, and this is usually regarded as being connected with the formation of complexes in solution. This suggestion has now been confirmed by the observation that the electrical conductivity of mixtures of isohydric solutions of molybdic acid and certain hydroxy-acids is much greater than the calculated values; in some cases the increase amounts to 300%. Mixtures of molybdic acid with phosphoric and arsenic acids show the same phenomenon, but to a much smaller extent. The fatty acids corresponding with the hydroxy-acids above referred to show slightly diminished conductivity on mixing with isohydric solutions of molybdic acid, a result which is ascribed to change in the viscosity of the medium.

As the hydroxy-acids, but not the corresponding fatty acids, form complexes with molybdic acid, it is considered that the latter must be bound in some way by the alcoholic hydroxyl group. G. S.

**Instability of certain Tungstates in Water.** ROGER C. WELLS (*J. Amer. Chem. Soc.*, 1907, 29, 112—117).—In carrying out some electrical conductivity determinations, it was observed that the conductivity of certain tungstate solutions slowly increased at the ordinary temperature, and the present investigation was made with a view to elucidate the nature of this change.

The salts examined were ammonium paratungstate and *sodium octatungstate*,  $\text{Na}_8\text{W}_8\text{O}_{27} \cdot 17\text{H}_2\text{O}$ , which forms efflorescent crystals, and is very soluble in water. The conductivity of solutions of these salts was found gradually to increase; thus, at 25°, a *N*/128 solution of ammonium paratungstate increased from 95.1 to 109.0 in six days, whilst at 50° the rate of increase was still greater. A similar change was observed with solutions of sodium octatungstate. Both transformations became complete in about three hours at 80°. The change is probably the same as that which occurs on boiling solutions of the paratungstates (Knorre, *Abstr.*, 1885, 1184).

The initial and maximum equivalent conductivities of solutions varying in concentration from *N*/32 to *N*/1024 were determined, and the results are tabulated. The data obtained are insufficient to decide whether the transformation consists in the addition or re-arrangement of water, a hydrolytic dissociation, or a decomposition of one salt into a mixture of two others as suggested by Knorre (*loc. cit.*).

The conductivity of a solution of sodium paratungstate was found to increase at 25° even more rapidly than that of the ammonium salt, but the conductivity of a solution of sodium tungstate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , undergoes no change.

The effects of such transformations have probably been overlooked in solubility determinations, and it is therefore likely that the recorded solubilities of the paratungstates are too high.

Determinations of the conductivity of solutions of hydrated tungstic oxide gave  $K \approx 10.3 \times 10^{-6}$ . Very little change took place when the solutions were left for a considerable time, and it was therefore

evident that no large quantity of a soluble acid, such as metatungstic acid, is formed under these conditions. E. G.

**New Methods of Formation and Preparation of Titanium Tetrachloride.** ÉMILE VIGOUROUX and G. ARRIVAUT (*Compt. rend.*, 1907, 144, 485—487. Compare this vol., ii, 97).—Three methods of preparing titanium tetrachloride from industrial ferro-titanium are described. (1) Ferro-titanium, after being roughly crushed, is introduced into a porcelain tube heated in a Mermet furnace. A current of pure dry chlorine is led into the tube, and when the latter has become dull red the ferro-titanium is rendered incandescent by the action of the chlorine. The ferric chloride solidifies in the cooler part of the tube, which must be wide enough to avoid choking. The more volatile titanium tetrachloride is liquefied first by a glass air-condenser, and then by a worm cooled in water. The process is simple and expeditious, its disadvantages being due to the ferric chloride, which partially obstructs the tube and retains some of the titanium chloride. (2) The greater part of the iron is removed previously by treatment with hydrochloric acid. The residue is a very heavy substance, with a reddish-brown reflection, containing a little titanic anhydride and very little iron. The former can be removed by levigation. After washing and drying it is submitted to the action of chlorine, as above. This method is the best. The third process is merely Dumas's method of treating a mixture of charcoal and titanic anhydride with chlorine applied to the residues from the first two methods, containing titanic anhydride.

The liquid so obtained is always coloured red by ferric chloride, of which the greater part, owing to its small solubility, can be removed by filtration. Fractional distillation of the filtrate, with or without previous agitation with mercury, gives a pure substance, b. p.  $136^{\circ}$  (approx.), quite colourless, and not fuming in air (contrary to the statements of certain authors). E. H.

**Preparation of Titanium Tetrachloride from Rutile.** HENRY RUSSEL ELLIS (*Chem. News*, 1907, 95, 122—123).—The process consists in igniting the rutile with powdered aluminium and afterwards heating the mixture in a current of chlorine, the titanium tetrachloride obtained being purified by redistillation. The mineral is first heated to a temperature of about  $1000^{\circ}$  and then plunged into cold water, a process which makes the substance so brittle that it can be powdered in a mortar. The dry powder is next heated in a crucible to  $500^{\circ}$ , and while still hot is mixed with less than half its own weight of powdered aluminium. The mixture is ignited by means of a little burning magnesium. As soon as the contents of the crucible have cooled somewhat, they are transferred to a combustion tube and heated to redness, a current of dry chlorine being passed through the tube. The volatile products are collected in a Wurtz flask, the side tube of which is closed by a calcium chloride drying-tube. The crude product obtained in the flask is then distilled; at first, chlorine and silicon tetrachloride come over, and may amount in quantity to about one-fifth of the whole. The second portion of the distillate ( $120$ — $137^{\circ}$ )

is again distilled from a small quantity of mercury, which retains the last traces of chlorine, when the titanium tetrachloride is obtained, b. p.  $136^{\circ}$ . It is shown that, at the temperature at which the above reaction takes place, silicon is formed by the action of aluminium on silica or silicates.

W. P. S.

**Zirconium Salts. II.** ARTHUR ROSENHEIM and PAUL FRANK (*Ber.*, 1907, 40, 803—810. Compare Abstr., 1905, ii, 256).—The authors have studied the composition of the products obtained, when simple zirconium salts are crystallised from their solutions in acids. In accordance with former data, the compounds,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{ZrOBr}_2 \cdot 8\text{H}_2\text{O}$ , separate from solutions containing hydrochloric and hydrobromic acids respectively. The behaviour of nitric acid solutions is different. From nitric acid solutions, which have been concentrated by heating, the zirconyl salt,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , separates. When, however, a solution of freshly precipitated zirconium hydroxide in nitric acid remains at the ordinary temperature in a vacuum over a mixture of phosphoric oxide and sodium hydroxide, hygroscopic prisms of the salt,  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , previously described by Paykull, separate. The salt,

$\text{ZrO}(\text{SO}_4\text{H})_2 \cdot 3\text{H}_2\text{O}$ ,  
previously described by Ruer, was also made.

The salt,  $\text{Zr}_2\text{O}_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ , is obtained by the addition of ether to an alcoholic solution of zirconium oxychloride; when zirconyl nitrate is treated similarly, the salt,  $\text{Zr}_2\text{O}_3(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ , is obtained. When a solution of zirconium hydroxide in thiocyanic acid is similarly treated, the salt,  $\text{Zr}_2\text{O}_3(\text{SCN})_2 \cdot 5\text{H}_2\text{O}$ , is precipitated. The salt,

$\text{Zr}(\text{SO}_4\text{Na})_4 \cdot 4\text{H}_2\text{O}$ ,  
obtained from zirconium hydroxide and sodium hydrogen sulphate, crystallises in needles.

The oxalate,  $\text{ZrO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , obtained from oxalic acid and zirconyl chloride or nitrate, is a white powder, which readily undergoes hydrolysis. Venable and Baskerville described this compound as containing  $1\text{H}_2\text{O}$ . By allowing the separation to take place more slowly, the compound,  $\text{Zr}(\text{OH})(\text{C}_2\text{O}_4\text{H})_3 \cdot 7\text{H}_2\text{O}$ , separates in needles, as described by Venable and Baskerville.

The tartrate,  $\text{Zr}_3(\text{OH})_8\text{C}_4\text{H}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ , is an amorphous powder, sparingly soluble in water.

The salt,  $\text{ZrO}(\text{C}_4\text{H}_4\text{O}_6\text{K})_2 \cdot 3\text{H}_2\text{O}$ , obtained by dissolving the preceding tartrate in the requisite amount of potassium hydroxide, separates in needles.

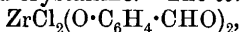
Many of the older data respecting basic zirconium salts are incorrect.

A. McK.

**Zirconium Tetrachloride and Colloidal Zirconium Hydroxide.**  
III. ARTHUR ROSENHEIM and JULIAN HERTZMANN (*Ber.*, 1907, 40, 810—814. Compare preceding abstract).—When zirconium salts are formed either in aqueous or alcoholic solution, compounds, containing the groups  $\text{ZrO}\cdot$  and  $\text{Zr}_2\text{O}_3\cdot$  are formed; it is only rarely that compounds are formed where more than two zirconium valencies are attached to acid groups. Owing to the weak electro-

positive character of the element, it is necessary accordingly, during the formation of compounds with weak organic acids, to work under conditions where hydrolysis is avoided, and from this standpoint the authors have studied compounds of anhydrous zirconium tetrachloride.

Zirconium tetrachloride has a marked tendency to form molecular compounds with organic substances, containing oxygen. Thus, when heated with a dry ethereal solution of ethyl benzoate, it forms the compound,  $\text{ZrCl}_4(\text{Ph}\cdot\text{CO}_2\text{Et})_2$ , which forms glistening, white crystals and decomposes with evolution of hydrogen chloride, on exposure to the air. With methyl salicylate, the compound,  $\text{ZrCl}_2(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me})_2$ , and with ethyl salicylate, the compound,  $\text{ZrCl}_2(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et})_2$ , are obtained, hydrogen chloride being evolved in each case; these compounds are white and crystalline. The compound,



obtained from zirconium tetrachloride and salicylaldehyde, forms yellow crystals. The compound,  $\text{ZrCl}_2(\text{OBz})_2$ , obtained by the action of zirconium tetrachloride on an ethereal solution of benzoic acid, form a crystalline, white powder.

When zirconium chloride is acted on by stronger acids, like formic, acetic, and propionic, all the four chlorine atoms are expelled from the chloride. *Zirconium acetate*,  $\text{Zr}(\text{OAc})_4$ , obtained by heating a mixture of anhydrous zirconium chloride and anhydrous acetic acid until the evolution of hydrogen chloride ceases, forms microscopic prisms, from which, on exposure to the air, acetic acid is rapidly evolved. In contact with air, dried by sulphuric acid, this acetate is converted, after several days, into *zirconyl acetate*,  $\text{ZrO}(\text{OAc})_2$ , which is stable in dry air; in moist air, however, it undergoes hydrolysis with formation of acetic acid. When dissolved in water, zirconyl acetate undergoes hydrolytic dissociation with formation of acetic acid and colloidal zirconium hydroxide. The progress of this hydrolysis is quicker than that of zirconium chloride and was measured by determinations of electrical conductivity. Complete hydrolysis is effected very quickly at  $25^\circ$ , the end point being reached after eighteen hours.

Colloidal solutions of zirconium hydroxide are readily obtained by dialysing an aqueous solution of the acetate. A. McK.

### Zirconium Salts and Colloidal Zirconium Hydroxide.

ARTHUR MÜLLER (*Zeitsch. anorg. Chem.*, 1907, 52, 316—324. Compare Mandl, *Abstr.*, 1904, i, 135; Ruer, *Abstr.*, 1905, ii, 256, 863).—Colloidal zirconium hydroxide was obtained as a strongly opalescent solution (1) by adding successively small amounts of *N*-ammonia to an aqueous solution of the nitrate as long as the precipitate first formed dissolves on shaking and warming slightly; (2) by dissolving the freshly precipitated, well-washed hydroxide in an aqueous solution of the nitrate. As regards coagulation, it behaves like other positively charged colloidal solutions, multivalent anions having the greatest effect.

It is shown that commercial zirconium nitrate is not a salt of constant composition. While its solutions are being evaporated to

obtain it in the solid state, it undergoes hydrolytic decomposition, the nitric acid escaping, so that the salt consists of a mixture of nitrate and oxide in varying proportions. It dissolves to form a distinctly opalescent, partly colloidal solution. The same is probably true of other zirconium salts.

From the above considerations it seems probable that many of the basic salts described as being obtained by the action of various salts on solutions of zirconium salts are really adsorption compounds of the salts and colloidal zirconium hydroxide. G. S.

**Preparation of the Oxysulphides of Zirconium and Thorium.** OTTO HAUSER (*Zeitsch. anorg. Chem.*, 1907, 53, 74—77).—The oxysulphides of zirconium and thorium, ZrOS and ThOS, can be obtained readily by heating the respective sulphates, carefully dried, to low redness in a current of dry hydrogen sulphide and cooling in the same gas.

The zirconium compound is light yellow and has D 4.87, whilst the thorium compound has D 6.44; under certain conditions both are spontaneously inflammable in air. G. S.

**Vanadium Compounds.** THOMAS F. RUTTER (*Zeitsch. anorg. Chem.*, 1907, 52, 368—396).—The first part of the paper contains a detailed account of work already published (Abstr., 1906, ii, 366) on the electrolytic preparation and properties of vanadous and vanadic salts. The contention of Marino (Abstr., 1906, ii, 617) that the copper test for vanadous salts is to be preferred to the author's silver sulphate test (*loc. cit.*) because silver salts are reduced by vanadic salts, is not valid, since it is now shown that copper salts are also reduced by vanadic salts in acid solution under certain conditions. The exact conditions requisite for obtaining satisfactory results in testing qualitatively for vanadous and vanadic salts are discussed.

The *E.M.F.* (reduction respectively oxidation potential) of bi-, ter-, quadri-, and quinque-valent vanadium salts has been measured, and the behaviour of these salts towards numerous oxidising and reducing agents has also been investigated qualitatively. From a comparison with other reducing agents, it is shown that the relative reaction velocities cannot be foretold from the properties of the reacting substances.

The rate of reaction between vanadic and silver sulphate in acid solution has been measured quantitatively; the velocity is greatly increased by iron and copper salts. In the latter case the reaction is very slow at first, but afterwards the rate increases rapidly. This preliminary disturbance is independent of the order in which the reagents are mixed and is connected with the precipitation of silver in the amorphous form. G. S.

**Vanadium Pentoxide as an Accelerator of Oxidation.** ALEXANDER NAUMANN, LUDWIG MOESER, and ERNST LINDENBAUM (*J. pr. Chem.*, 1907, [ii], 75, 146—147).—The oxidation of sucrose to oxalic acid by means of nitric acid takes place below 70° more rapidly and completely in presence of small amounts of vanadium pentoxide. This

may be demonstrated by adding nitric acid, D 1.4, to sucrose in two tubes and to one of these a small amount of sodium vanadate. When heated in the water-bath at  $50^{\circ}$ , the sample containing the vanadium changes from yellow to green in consequence of the formation of the blue tetroxide and evolves nitrous fumes, the evolution of gas continuing after the tube is removed from the bath. The brown fumes are evolved much more slowly by the second tube. Above  $70^{\circ}$ , oxalic acid is oxidised by nitric acid in presence of vanadium pentoxide, forming carbon and water. Contrary to statements in the literature, the solubility of oxalic acid in water is diminished by addition of nitric acid, the minimum solubility at  $15^{\circ}$  being in nitric acid, D 1.30.

Similarly, the oxidation of ethyl alcohol to aldehyde and acetic acid by air, of potassium iodide by hydrogen peroxide in neutral solution, and of stannous to stannic salts by nitric acid or potassium chlorate and hydrochloric acid, are accelerated by addition of vanadium pentoxide, or of a vanadate respectively. On the other hand, addition of vanadium pentoxide causes no marked acceleration of the rate of oxidation of ferrous or mercurous salts by nitric acid or potassium chlorate and hydrochloric acid. The oxidation of ferrous salts by nitric acid is a reversible reaction, the nitric oxide or nitrous acid formed by the oxidation reducing the ferric salt. The oxidation takes place quantitatively if carbamide is added, whilst a solution of ferric chloride gives a blue precipitate with potassium ferricyanide on addition of potassium nitrite and hydrochloric acid.

The vanadium pentoxide must act as an accelerator, by giving up oxygen, to the oxidisable substance, being itself re-formed at expense of the oxidising agent.

G. Y.

**Bismuthous Compounds.** I. WALTER HERZ and ARTHUR GUTTMANN (*Zeitsch. anorg. Chem.*, 1907, 53, 63—77).—Bismuthous oxide,  $\text{BiO}$ , has been prepared by reduction of bismuth hydroxide with a stannous salt in alkaline solution, as described by Schneider (Abstr., 1899, ii, 227; 1900, ii, 212), and identified by comparison with the same salt prepared by Tanatar's method (Abstr., 1901, ii, 553), the contention of Vanino and Treubert (Abstr., 1898, ii, 485, 598), that bismuthous oxide cannot be prepared by the method suggested by Schneider, being thus disproved.

Further, Schneider obtained bismuthous sulphide,  $\text{BiS}$ , by heating the corresponding oxide in a current of hydrogen sulphide and the authors have now confirmed this observation, although Aten (Abstr., 1906, ii, 11) could obtain no evidence of the existence of the compound in question from a study of the freezing point curve of the system bismuth-sulphur.

G. S.

**Quinquevalent Bismuth.** EDGAR B. HUTCHINS, jun., and VICTOR LENHER (*J. Amer. Chem. Soc.*, 1907, 29, 31—33).—It has been shown by previous workers that bismuth is capable of existing in combination with oxygen in a higher state of valency than the tervalent (compare Gutbier, Abstr., 1906, ii, 174, 234, 551, 679). Experiments have now been made to obtain pentahaloids of bismuth, but without success.

When bismuth trichloride is treated with solid or liquid chlorine it undergoes no change. Impure bismuth pentoxide dissolves in dilute hydrochloric acid at  $-10^{\circ}$  with evolution of chlorine. If a solution of bismuth chloride in hydrochloric acid is saturated with chlorine at  $-10^{\circ}$  and ammonium chloride is added, on concentrating the solution over sulphuric acid, the salt,  $\text{BiCl}_3 \cdot 2\text{NH}_4\text{Cl}$  (Déherain, *Compt. rend.*, 1862, **54**, 726), is produced. On passing chlorine into a solution of the salt,  $\text{CsICl}_2$  (Wells and Penfield, *Amer. J. Sci.*, 1892, **43**, 27), and bismuth trichloride, the compound,  $2\text{BiCl}_3 \cdot 3\text{CsCl}$  (Brigham, *Abstr.*, 1892, 788), is obtained. Similarly, when bromine is added to a hot solution of caesium tribromide and bismuth tribromide in hydrobromic acid, the double salt,  $2\text{BiBr}_3 \cdot 3\text{CsBr}$ , is formed as a yellow precipitate. E. G.

**Treatment of Gold, Platinum, and Silver Residues.** KLUT (*Pharm. Zeit.*, 1907, **52**, 168—169).—*Gold*.—Any gold in solution is separated by treating the alkaline solution with ferrous sulphate; the precipitate obtained is added to the solid residues, which, after washing, are digested with nitric acid and once more thoroughly washed. The residue is warmed with hydrochloric acid (1.124), and nitric acid (1.153) added until all the gold has dissolved; the solution, after evaporating until on cooling it solidifies, is diluted, filtered, and the filtrate evaporated until all nitric acid is driven off. A solution of ferrous sulphate is added in large excess to the dilute solution of gold chloride, the whole heated on a water-bath for several hours, the precipitate filtered off, washed thoroughly with hydrochloric acid, finally with water, dried, and then incinerated in a crucible.

*Platinum*.—Solutions containing platinum are treated with ammonium chloride and the ammonium platinichloride added to the solid residues; these, after moistening with water, are mixed with about an equal quantity of oxalic acid and dried at  $100^{\circ}$ . The dry mixture is heated in a covered crucible, at first gently and then strongly for some time, then washed thoroughly, digested with nitric acid to remove any silver present, washed again, then heated several hours with hydrochloric acid, finally washed thoroughly on an ash-less filter paper, and the whole incinerated.

*Silver*.—After precipitating all silver from solution as chloride, the solid is boiled with an excess of sodium hydroxide solution and dextrose added in small portions until the precipitated silver dissolves completely in nitric acid; the silver is then filtered off, washed thoroughly, and dried. W. H. G.

**Alloys of Palladium and Lead.** RUDOLF RUER (*Zeitsch. anorg. Chem.*, 1907, **52**, 345—357. Compare Heycock and Neville, *Trans.*, 1892, **61**, 888).—From an investigation of palladium-lead alloys by Tammann's system of thermal analysis, controlled by microscopic observations, the existence of the compounds  $\text{PdPb}_2$ ,  $\text{PdPb}$ ,  $\text{Pd}_2\text{Pb}$ , and  $\text{Pd}_3\text{Pb}$  has been established, and there is evidence of the formation of a fifth compound.

The freezing point curve shows two maxima at  $454^{\circ}$  and 20% and  $1219^{\circ}$  and 61% by weight of lead respectively, corresponding with the

compounds  $\text{PdPb}_2$  and  $\text{Pd}_3\text{Pb}$ ; two eutectic points at  $265^\circ$  and 5% and  $1200^\circ$  and 66% of palladium respectively, and three breaks at  $495^\circ$ ,  $596^\circ$ , and  $830^\circ$  respectively. The breaks at  $495^\circ$  and  $830^\circ$  indicate the existence of the compounds  $\text{PdPb}$  and  $\text{Pd}_2\text{Pb}$ , which decompose below their respective melting points; the formula of the fifth compound, indicated by the break at  $590^\circ$ , has not been established definitely, but it contains between 37.5% and 40.7% of lead. From 60—66% and 77—100% of palladium mixed crystals separate.

Alloys containing 20—90% of palladium are harder than their components, and this property attains its maximum at 65% of the metal just mentioned. Alloys containing 17.5—60% of palladium are very brittle; above the latter point, however, they become much tougher.

G. S.

**Palladium Hydroxylamines.** SIMON ZEISEL and A. NOWAK (*Annalen*, 1907, 351, 439—449. Compare Alexander, *Annalen*, 1881, 246, 239; Uhlenhuth, *Abstr.*, 1900, ii, 485).—Palladium forms two compounds with hydroxylamine. One of these, formed in colourless needles by the action of hydroxylamine hydrochloride and sodium carbonate on palladous chloride, can be isolated as the free base, in which state it is analogous to Uhlenhuth's platinum base, and consequently, according to Werner's view, must have two hydroxyl groups

attached directly to the metallic atom,  $\begin{array}{c} \text{OH} \\ \text{NH}_3\text{O} \diagup \text{Pd} \diagdown \text{NH}_3\text{O} \\ \text{HN}_3\text{O} \diagdown \text{Pd} \diagup \text{NH}_3\text{O} \\ \text{OH} \end{array}$ ; the

colourless, crystalline chloride of this base is ionised, consequently its chlorine atoms must lie in the second sphere of the molecule, outside of the complex nucleus, and it must be a derivative,

$\left[ \begin{array}{c} \text{NH}_3\text{O} \diagup \text{Pd} \diagdown \text{NH}_3\text{O} \\ \text{NH}_3\text{O} \diagdown \text{Pd} \diagup \text{NH}_3\text{O} \end{array} \right] \text{Cl}_2$ ,  
of the labile base,  $\left[ \begin{array}{c} \text{NH}_3\text{O} \diagup \text{Pd} \diagdown \text{NH}_3\text{O} \\ \text{NH}_3\text{O} \diagdown \text{Pd} \diagup \text{NH}_3\text{O} \end{array} \right] (\text{OH})_2$ , which on formation changes immediately into the stable modification.

The second palladium compound of hydroxylamine is isolated only in the form of its chloride,  $\text{Pd}(\text{NH}_3\text{O})_2\text{Cl}_2$ , which exists in two modifications obtained on treating the base,  $\text{Pd}(\text{NH}_3\text{O})_4(\text{OH})_2$ , with a small amount of dilute hydrochloric acid as a yellow, granular precipitate and in long, slender, yellow needles respectively.

The further investigation of these chlorides has been rendered fruitless by their instability.

G. Y.

**Iridium Compounds.** EBERHARD RIMBACH and F. KORTEN (*Zeitsch. anorg. Chem.*, 1907, 52, 406—415).—The solubility in water of iridium ammonium chloride,  $(\text{NH}_4)_2\text{IrCl}_6$ , has been determined from  $14.4^\circ$  to  $70^\circ$ ; at  $14.4^\circ$  and  $39.4^\circ$ , 100 grams of the solvent dissolve 0.699 and 1.226 grams of the salt respectively.

*Rubidium iridium chloride*,  $\text{Rb}_2\text{IrCl}_6$ , occurs in microscopic octahedral crystals, very slightly soluble in water. *Iridium pyridine chloride*,  $\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_6$ , and *iridium aniline chloride*,  $\text{Ir}(\text{C}_6\text{H}_5\text{N})_2\text{Cl}_6$ , are obtained by interaction of their components in aqueous solution;



the former occurs in black needles, the latter as a black, amorphous mass. Attempts were made to prepare iridium thiocyanate, alone or as a component of a double salt, but without success.

*Iridium sulphate*,  $\text{Ir}(\text{SO}_4)_2$  (Berzelius, 1828), occurs as a yellowish-brown, amorphous mass; on heating with strong sulphuric acid, the solution becomes green, owing to reduction to the sesquisulphate,  $\text{Ir}_2(\text{SO}_4)_3$ . From the latter solution, iridium alums have been obtained in green crystals on adding alkali sulphates (compare Marino, Abstr., 1905, ii, 43).

*Potassium iridium cyanide*,  $\text{K}_3\text{Ir}(\text{CN})_6$ , and the corresponding *barium* salt, unlike the similarly constituted platinum compounds, show no tendency to combine with free halogens. Conductivity measurements show that they are derived from a stable tribasic acid,  $\text{H}_3\text{Ir}(\text{CN})_6$ . The crystallographic characters of the potassium salt are also quoted.

The compound,  $\text{Ir}_2(\text{CN})_{12}\cdot\text{Cu}_3(\text{NH}_3)_6\cdot 4\text{H}_2\text{O}$ , obtained by the action of ammonia on copper iridium sesquicyanide, occurs in well-formed, lustrous, blue crystals, which slowly give up water and ammonia on exposure to air. A silver compound,  $\text{Ir}(\text{CN})_6\cdot\text{Ag}_3(\text{NH}_3)_2\cdot 3\text{H}_2\text{O}$ , obtained by the action of ammonia on silver iridium sesquicyanide, occurs in colourless, lustrous crystals, which slowly decomposes on exposure to light.

G. S.

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## Mineralogical Chemistry.

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**Analyses of Norwegian Pyrites.** EYVIND BOEDTKER (*Chem. Centr.*, 1906, ii, 1863; from *Rev. Gén. Chim.*, 1906, 9, 323—326).—Norwegian pyrites is much used for the production of sulphur and copper, and in value ranks next to Spanish pyrites. In forty-three analyses the sulphur varies from 37·65 to 49·26% (mean 44%), and the copper from 0·14 to 3·62% (mean 2%). The following are two detailed analyses:

	S.	Cu.	Fe.	Mn.	Co.	Ni.	Zn.	Pb.	Bi.	As.	Ag.
I.	43·03	2·504	39·54	0·064	trace	—	0·419	—	trace	0·006	0·00148
II.	42·59	1·490	40·11	0·032	0·114	trace	0·720	trace	—	nil	0·00042

	CaO.	Sr, Ba.	MgO.	P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	C.	SiO <sub>2</sub> (silicates).	O (calc.).
I.	3·66	trace	0·43	0·028	1·94	—	7·58	0·89
II.	2·76	trace	0·70	0·041	2·97	trace	7·16	1·58

L. J. S.

**Composition of Lengenbachite.** ARTHUR HUTCHINSON (*Min. Mag.*, 1907, 14, 204—206).—Analysis of this new mineral (described by R. H. Solly in 1905), from the Binnenthal in Switzerland, gave:

Pb.	Ag.	Cu.	Fe.	As.	Sb.	S.	Total.	Sp. gr.
57·89	5·64	2·36	0·17	13·46	0·77	19·33	99·62	5·85

This agrees with the formula  $6\text{PbS}, (\frac{3}{5}\text{Ag}, \frac{2}{5}\text{Cu})_2\text{S}, 2\text{As}_2\text{S}_3$  or  $7\text{RS}, 2\text{As}_2\text{S}_3$ .

L. J. S.

**Artificial Formation of Magnetite and Sillimanite.** P. P. SUSTSCHINSKY (*Trav. Soc. Nat., St. Pétersbourg*, 1906, 37, pp. 1—9 *Russ.*, 9—14 *Ger.*)—A description is given of a crystalline glaze, which had been accidentally formed on a porcelain plate by the melting of iron-pyrites contained in the clay of the seggar in which the plate was baked. Where the molten iron-pyrites had dropped on the plate, dark brown spots were formed, and a microscopical examination of these in thin section proved the presence of skeletal groups of magnetite octahedra and needles of sillimanite.

L. J. S.

**New Method of Representing Van't Hoff's Investigations on Oceanic Salt Deposits. II.** ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1907, 52, 358—367).—The paper contains a further development of the author's graphic method of treating these problems (compare *Abstr.*, 1906, ii, 833), and is illustrated by numerous diagrams.

G. S.

**Graphitic Iron in a Meteorite.** WIRT TASSIN (*Proc. U.S. National Museum*, 1906, 31, 573—574).—A septarian nodule, extracted from a sample of the Cañon Diablo meteoric iron, consists of septa of metal like that of the rest of the mass, whilst the interseptal veins contain crystalline graphite, amorphous carbon, troilite, and a carbide of iron having the following composition :

Fe.	Ni.	Co.	Si.	C.	P.	Total.	Sp. gr.
88.84	4.00	trace	2.00	4.35	0.87	100.06	6.910

This has the form of irregular, angular, and foliated masses, which are strongly magnetic, of a dark steel-grey colour, with metallic lustre, and soft enough to leave a mark on paper ; in its characters it thus differs from cohenite.

L. J. S.

**Composition and Structure of the Hendersonville (North Carolina) Meteorite.** GEORGE P. MERRILL, with analysis by WIRT TASSIN (*Proc. U.S. National Museum*, 1907, 32, 79—82).—This meteoric stone was found in 1901, but probably fell about 1876 ; its original weight was about 6 kilos. It consists of enstatite, a monoclinic pyroxene, and olivine, with metallic particles. The structure is chondritic, and is suggestive of a partial recrystallisation of fine detrital material. Analyses are given of the metallic portion and of the silicates soluble and insoluble in dilute hydrochloric acid ; from these the composition of the whole is calculated as :

Fe.	Ni.	Co.	S.	P.	SiO <sub>2</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .
2.37	0.21	0.01	1.61	0.012	46.06	14.33	2.20	0.23
Residue								
(chromite).								
CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.			Total.		
2.13	28.62	0.10	0.96		0.51	99.352		

The corresponding mineralogical composition is : nickel-iron, 2.59 ; troilite, 4.43 ; schreibersite, 0.08 ; chromite, 0.80 ; olivine, 40.48 ; pyroxenes, 51.62%.

L. J. S.

## Physiological Chemistry.

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### Effect of Carbohydrates on Resistance to Lack of Oxygen.

WALES · H. PACKARD (*Amer. J. Physiol.*, 1907, 18, 164—180. Compare Abstr., 1906, ii, 95).—If *Fundulus* embryos are supplied with carbohydrates which can be digested and absorbed, their length of life in lack of oxygen is increased. The general conclusions are stated to confirm A. P. Mathew's highly speculative views on the nature of protoplasmic respiration.

W. D. H.

**Influence of Digitalis, Strophanthus, and Adrenaline on the Velocity of the Blood Stream.** CHARLES WALLIS EDMUNDS (*Amer. J. Physiol.*, 1907, 18, 129—148).—The members of the digitalis group accelerate the blood stream, except in large doses, when retardation occurs. The former effect may in part explain the good effects the drugs produce. Adrenaline slows the blood current.

W. D. H.

**Physiology of Glands. VIII. Physico-chemical Relations of Different Substances in the Blood.** LEON ASHER and R. ROSENFELD (*Biochem. Zeitsch.*, 1907, 3, 335—358).—Buffa's method of partial freezing is not in itself capable of settling the question whether serum is a true solution. Simple solutions of sodium chloride give analytical results from the frozen and not frozen portions which do not agree with theory; this is also the case for solutions containing colloid constituents.

Sodium chloride is free in solution in the serum; it passes out by diffusion against water or against blood poor in salt. The time relationships of this action are the same as with simple salt solutions. There is no ground for the statement that in inanition the sodium chloride is more firmly united in the blood. Similar results were obtained with sugar, which is therefore also in simple solution in the blood.

W. D. H.

**Blood-Coagulation. VIII. LEO LOEB** (*Beitr. chem. Physiol. Path.*, 1907, 9, 185—204. Compare Abstr., 1906, ii, 372).—The time relationship of the action of tissue-coagulins, dialysed muscle extract, and thrombin on invertebrate blood, shows in all cases a direct proportionality between the time of coagulation and the amount of reagent added. It was found difficult to investigate the action of serum because of the difficulty of finding an indifferent reagent for purposes of dilution. Calcium can be replaced by strontium, barium, and in some cases by magnesium, sodium, and other cations. Calcium seems to play a double part in the clotting process, or two different varieties of calcium compound are necessary; one of which is only necessary in small amount, and this can only be replaced by strontium and barium; this probably enters into combination with the coagulin. The second and larger quantity is

necessary for the change of fibrinogen into fibrin in the presence of a coagulin. Coagulin is not a kinase, but acts independently of thrombin on fibrinogen.  
W. D. H.

**Iron in the Colouring Matter of Blood and its Absorption of Light.** HANS ARON (*Biochem. Zeitsch.*, 1907, 3, 1—25. Compare this vol., i, 266).—The ratio of the coefficients of light extinction,  $\epsilon/\epsilon'$ , for the fresh blood of horses, calves, dogs, rabbits, and cats, varies considerably. This is probably due to the presence of a second colouring matter in the blood, namely, methaemoglobin. It is shown that specimens of fresh blood which have a low value for  $\epsilon/\epsilon'$  give a much higher value when they are left for some time and then aerated. This is attributed to the presence of methaemoglobin in the blood; when kept in the absence of air this became reduced to haemoglobin, which is then oxidised to oxyhaemoglobin during aeration. Similar processes can occur in the organism. When the fresh blood is poor in oxygen, a reduction of the blood can take place, and it is found that the amount of methaemoglobin is smaller than under normal condition. Methaemoglobin is also probably present in the blood as it circulates in the organism. The amounts are extremely small except in certain pathogenic cases.

Numerous experiments have been made to determine the relationship between the amount of blood colouring matter estimated spectrographically and the percentage of iron. After loss of a considerable amount of blood and partial recovery, the amount of iron is less than would be expected from the amount of colouring matter present, indicating that probably a new colouring matter with a smaller percentage of iron has been formed.  
J. J. S.

**Psychical Secretion of the Stomach.** HEINRICH BOGEN (*Pflüger's Archiv*, 1907, 117, 150—160).—The observations were made on a child three and a half years old, on whom a gastric fistula had been made to relieve stenosis of the oesophagus. Just as Pawloff showed in his experiments on dogs, the mere presentation of food calls forth secretion of gastric juice; mental conditions such as grief and pain hinder the secretion. The latent period varies with different kinds of food shown (meat, 4.75; milk, 9 minutes). The quantity of secretion, its duration and acidity, vary with the strength of the stimulus.  
W. D. H.

**The Influence of Morphine and Opium on the Secretion of the Stomach and Pancreas.** ADOLF BICKEL and LUDWIG PINCUSOHN (*Sitzungsber. K. Akad. Wiss., Berlin*, 1907, 217—233).—Morphine causes first inhibition and then increase of both juices. Opium, on the other hand, stimulates the secretion of gastric juice, but paralyses the pancreas. The question is discussed whether in the case of morphine, the increased pancreatic flow is secondary to the gastric secretion leading to the formation of secretin.  
W. D. H.

**The Action of Rennet on Concentrated Solutions of the Products of Peptic Digestion.** D. LAWROFF (*Zeitsch. physiol. Chem.*, 1907, 51, 1—32).—The action of rennet (or if rennet and pepsin are

regarded as the same substance, the prolonged action of pepsin) converts the products of gastric digestion into substances that have been named plasteins or coaguloses; the latter term is adopted in the present work. The precipitated substance is regarded as evidence of the reversible action of pepsin, and the yield is greatest in concentrated solutions which are faintly acid. The substances that yield coaguloses are also obtained from the products of action of acids and alkalis on proteins, and fall into two main groups, those of the proteose and those of the mono-amino-acid-group. The coaguloses themselves differ a good deal, and their reactions are of the protein type; in some cases the percentage of nitrogen is low. Their differentiation into classes is not yet possible.

W. D. H.

**Ferment Actions. I. Coferment of Lipase.** ARTHUR S. LOEVENHART. **II. Inhibiting Effect of Sodium Fluoride on Lipase.** ARTHUR S. LOEVENHART and GEORGE PEIRCE. **III. Effect of Bile on the Hydrolysis of Esters by Pancreatic Juice.** ARTHUR S. LOEVENHART and C. G. SOUDER. **IV. Are the Animal Enzymes Concerned in the Hydrolysis of Various Esters Identical?** ARTHUR S. LOEVENHART (*J. Biol. Chem.*, 1907, 2, 391—395; 397—413; 415—425; 427—460).—Magnus's coferment for liver lipase consists of bile salts; but bile salts only assist in the hydrolysis of amyl salicylate, and not in that of ethyl butyrate and other esters. Sodium fluoride inhibits the action of such enzymes markedly, but in varying degrees. There is a quantitative relationship between the enzymes and the fluoride; the fluoride does not destroy the enzymes or react with the esters, neither is its action due to precipitation of calcium. It either reacts with the enzyme or more probably with an intermediate product formed in the action of the enzyme on the *zymolyte* (a new term suggested instead of substrate).

Bile salts, lecithin, and bile accelerate the action of pancreatic juice on all the esters studied, including olive oil. Details are given of the degree of acceleration, which varies considerably in different cases. The bile salts appear to be mainly responsible, partly, but not altogether, on account of their solvent action. Various lipolytic enzymes exhibit both differences and similarities, which are described in full. There is probably only one ester-splitting enzyme in the liver, and another (a different one) in the pancreas.

W. D. H.

**Enzymes of the Pancreas.** KARL MAYS (*Zeitsch. physiol. Chem.*, 1907, 51, 182—184).—A continuation of the polemical discussion that has arisen in reference to Vernon's work on this subject. W. D. H.

**Absorption of Protein in the Dog's Stomach.** SERGEI SALASKIN (*Zeitsch. physiol. Chem.*, 1907, 51, 167—181).—A criticism of London's work and methods, which are regarded as too complicated for the deduction of correct physiological conclusions. The writer believes that the absorption of the products of protein digestion occurs in the stomach.

W. D. H.

**Absorption from the Peritoneal Cavity.** H. GIDEON WELLS and LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1907, 18, 136—163).—Some views of Exner on the rôle adrenaline plays in hindering absorption by the lymphatics are questioned. No evidence was discovered that a finely-divided suspension of mineral oil is absorbed from the peritoneal cavity of the dog either by the blood or lymph. W. D. H.

**Metabolism in Inanition. I. Acid Formation.** M. BÖNINGER and L. MOHR. **II. Intestinal Putrefaction.** R. BAUMSTARK and L. MOHR (*Chem. Zentr.*, 1907, i, 55—56, from *Zeitsch. exp. Path. Ther.*, 3, 675—687; 687—690).—The excretion of the acetone group of substances increases on the first day of hunger; so also does that of ammonia. The ammonia formed is insufficient to neutralise the acids. The origin of acetone substances is mainly fat and fatty acids.

The only source of the urinary indican found was the indole formed in the intestine. W. D. H.

**Assimilation of Phosphoric Acid and Calcium from Calcium Phosphates by Growing Animals.** ALBIN KÖHLER, FR. HONCAMP, and P. EISENKOLBE (*Landw. Versuchs-Stat.*, 1907, 65, 349—380. Compare *Abstr.*, 1905, ii, 265).—Further experiments with lambs showed that precipitated tricalcium phosphate and dicalcium phosphate are about equal in food value. The amount of phosphoric acid supplied was 1.5 gram instead of 3 grams as previously employed. N. H. J. M.

**Fate of Radium after its Introduction into the Animal Organism.** GUSTAVE M. MEYER (*J. Biol. Chem.*, 1907, 2, 461—480).—Radium introduced by any channel finds its way into all the tissues; its excretion continues for a long time in the urine and largely with the fæces; its removal by lungs or skin was not examined. In its distribution and elimination it resembles metals of the alkaline earth series.

W. D. H.

**Ethyl Alcohol and Ethyl Esters in the Animal Body.** FELIX REACH (*Biochem. Zeitsch.*, 1907, 3, 326—334).—The old statement that animal organs and tissues contain small amounts of alcohol is confirmed. Small amounts of ethyl esters are present also.

W. D. H.

**Fluorine in the Shells of Molluscs.** P. CARLES (*Compt. rend.*, 1907, 144, 437—438).—The liquid obtained by dissolving oyster shells in dilute hydrochloric acid does not contain fluorine. When, however, the shells are calcined, finely powdered, boiled for two hours in water, made alkaline with potassium carbonate, and the resulting liquid filtered and cautiously neutralised with acetic acid in the presence of barium chloride, a precipitate is obtained which appreciably etches glass under the conditions previously described (this vol., ii, 129). It is preferable, however, to treat the crushed shells with about five times their weight of water, add sufficient acetic acid (together with a little barium chloride) to dissolve them, and estimate the fluorine in the

filtrate (which contains the greater quantity), and in the residue (after dissolution in dilute hydrochloric acid) by precipitation with barium chloride in neutral or ammoniacal solution and treatment of the precipitated barium fluoride as in the preceding method.

The shells of fresh Arcachon oysters and mussel shells from the same basin contain 0.012% fluorine (ten times as much as in sea water), and fossil oyster shells from Sainte Croix-du-Mont contain 0.015%. The author concludes (1) that fluorine is easily evolved from fluorides dissolved in water when mixed with hydrochloric acid and a carbonate; (2) that the alkaline earth fluorides are more soluble in acetic acid than is generally believed, and (3) that oysters and mussels assimilate alkali earth fluorides from sea water for the consolidation of their shells.

E. H.

**The Organic Substance in the Skeletal Tissues of Anthozoa.** I. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1907, 51, 33—63).—In the investigation of *Gorgonia* and related animals, iodine was found to be a constant constituent of the skeletal material; the amount of iodine varied from 0.05% to 8.92%. In contradiction of former observers, bromine is also constantly present, its amount varying from 0.23% to 4.2%. Bromogorgonic acid is probably analogous to iodogorgonic acid. The amount of chlorine is usually insignificant. The haloids are in organic combination. The amount of sulphur was about 1%, thus putting the substance out of the keratin group. The variations described do not appear to depend on climate, composition of the sea water, age of the animal, or to be related to the physical characters (colour, texture, hardness, elasticity, &c.) of the skeleton.

W. D. H.

**The Influence of Alcohol on Hydrolysing Enzymes.** BERNHARD SCHÖNDORFF and C. VICTOROFF (*Pflüger's Archiv*, 1907, 116, 495—516).—Seegen's statement that glycogen disappears from livers treated with alcohol is incorrect. If the liver is finely divided and immediately treated with at least twice its volume of 96% alcohol, its percentage of glycogen remains unchanged. The same is true for muscle, but the greater difficulty of rapidly mincing muscle must be taken into account. The diastatic ferment is not killed by the alcohol; on removal of the alcohol; its activity is undiminished. Cooling to  $-21^{\circ}$  for five days does not destroy the ferment. At the room temperature the glycogen diminishes in muscles; thus dog's muscle lost 17% of its glycogen in forty-five minutes, and ox muscle 33% in eighty-five minutes.

W. D. H.

**Crab Extract.** D. ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. Nahr. Genussem.*, 1907, 13, 180—184).—A sample of crab extract was found to contain considerable quantities of tyrosine, leucine, arginine, and lysine, but the two characteristic bases present in meat extracts, creatine and creatinine, were absent.

W. P. S.

**Chemical and Biological Investigation of Surviving Organs.** WILHELM WIECHOWSKI. **The Uricolytic Ferment of Ox-Kidney and Dog's Liver.** W. WIECHOWSKI and HUGO WIENER. The



**Products of Fermentative Uric Acid Decomposition in Animal Organs.** W. WIECHOWSKI (*Beitr. Chem. Physiol. Path.*, 1907, 9, 232—246; 247—294; 295—310).—The first paper deals with methods, drying, mincing, extraction, use of antiseptic (toluene), &c. The ferment which destroys uric acid was obtained from the dry powdered organ; it is an oxydase which is only active in neutral or faintly alkaline media. It is destroyed at 50°. The presence of 0.08% thymol inhibits its action somewhat, as also do toluene, fluorides, or various extractives in the organs investigated (ox-kidney and dog's liver); calcium chloride and potassium acetate have no harmful effect on it, but proteolytic ferments, urea, alcohol, and ammonium sulphates have. It is contained in the cells, not in the plasma of the organs. As a result of its activity, urea was never found, but the uric acid is oxidised quantitatively into allantoin *in vitro*.  
W. D. H.

**Excretion of Amino-acids and Total Nitrogen during In-anition.** THEODOR BRUGSCH and RAHEL HIRSCH (*Chem. Zentr.*, 1907, i, 55; from *Zeitsch. exp. Path. Ther.*, 3, 638—644).—Particulars are given as to the fall in total nitrogen excreted in two cases of fasting. In one case, it was greater than in another. The amino-acids of the urine were not increased; glycine was not detected. The assimilation for alanine was lowered, but glycine and leucine were well assimilated.  
W. D. H.

**Hippuric Acid Synthesis and Benzoic Acid Excretion in Dogs.** THEODOR BRUGSCH and RAHEL HIRSCH (*Chem. Zentr.*, 1907, i, 57; from *Zeitsch. exp. Path. Ther.*, 3, 663—674).—The power of synthesising hippuric acid is less in dogs than in rabbits. If benzoic acid is given to a dog, the greater part is excreted unchanged in the urine, and part as an unidentified compound.  
W. D. H.

**Occurrence of Pyridine Methochloride in Urine and its Relation to Tobacco Smoking and Coffee Drinking.** FRIEDRICH KUTSCHER and ALBERT LOHMANN (*Zeitsch. Nahr. Genussm.*, 1907, 13, 177—179).—From the bases occurring in human urine, pyridine methochloride has been isolated and identified. The theory is advanced that its occurrence is due to either tobacco smoking or coffee drinking, as pyridine is known to be present in tobacco smoke and in aqueous decoctions of roasted coffee. In confirmation of this, it has been shown that the administration of pyridine to dogs is followed by the presence of pyridylmethyammonium compounds in the urine.  
W. P. S.

**Excretion of Phosphoric Acid during Experimental Acidosis in Rabbits.** R. FITZ, C. L. ALSBERG, and LAWRENCE J. HENDERSON (*Amer. J. Physiol.*, 1907, 18, 113—122).—If rabbits are fed with acids, the urinary phosphoric acid is at first increased, and then decreased. This supports the theory that phosphates are primarily concerned with neutralising acid and removing it from the body.  
W. D. H.

**Katabolism of Fatty Acids in Diabetes. II.** JULIUS BAER and LÉON BLUM (*Chem. Zentr.*, 1907, i, 185; from *Arch. exp. Path. Pharm. J.*, 56, 92—100).—Fatty acids containing four carbon atoms in a straight chain ( $\alpha$ - and  $\beta$ -methylbutyric and  $\alpha$ - and  $\beta$ -ethylbutyric acids) are converted by the diabetic organism into hydroxybutyric acids. Those containing a similar chain of three or five carbon atoms are not. Ethylmalonic acid and methylsuccinic acid have no effect on the excretion of hydroxybutyric acid; leucine, tyrosine, and phenylalanine increase it.  
W. D. H.

**Experimental Diabetes after Extirpation of the Pancreas in Selachians.** V. DIAMARE (*Chem. Zentr.*, 1907, i, 359; from *Zentr. Physiol.*, 20, 617—620).—The blood of Selachian fishes is free from dextrose, but after extirpation of the pancreas, the blood of *Torpedo marmorata* reduces Fehling's solution, and aqueous extracts of the kidney contain sugar.  
W. D. H.

**Gout. VII. Relationship Between Uric Acid and Amino-acids.** HEINRICH KIONKA and ERNST FREY (*Chem. Zentr.*, 1907, i, 58; from *Zeitsch. exp. Path. Ther.*, 3, 597—603. Compare *Abstr.*, 1905, ii, 742).—After adding uric acid to living blood, the presence of glycine can be detected by its conversion into the  $\beta$ -naphthalenesulphonyl derivative, and microscopic examination. There does not appear to be an essential difference in the excretion of the amino-acids in gouty cases, and normal persons; at most the insufficiency can only be relative.  
E. W. W.

**Metabolism of Phosphoric Acid and Calcium in Osteomalacia under the Influence of Phosphorus Treatment.** GERHARD HOTZ (*Chem. Zentr.*, 1907, i, 55; from *Zeitsch. exp. Path. Ther.*, 3, 605—632).—Phosphorus treatment in two cases influenced calcium metabolism beneficially as long as it was continued.  
W. D. H.

**The Behaviour of Iodine in Tuberculous Animals.** OSWALD LOEB and LOUIS MICHAUD (*Biochem. Zeitsch.*, 1907, 3, 307—314).—Tuberculous tissues absorb iodine compounds in increased measure. This is regarded as a support to Jakoby's hypothesis that remedial agents link themselves to the diseased tissues. The iodine is present in organic combination which is not insoluble in alcohol.  
W. D. H.

**Lactic Acid in the Urine of Pernicious Vomiting of Pregnancy.** FRANK B. UNDERHILL (*J. Biol. Chem.*, 1907, 2, 485—487).—A case of pernicious vomiting in pregnancy is recorded with an analysis of the urine. The high percentage of ammonia at the expense of the urea (noted also in previous cases) is due to an effort to correct excessive formation of organic acids. Lactic acid was found in the urine, and was separated as zinc para-lactate.  
W. D. H.

**Physiological Action of Tetramethylarsonium Iodides.** EMIL BURGI (*Chem. Zentr.*, 1907, i, 152; from *Arch. exp. Path. Pharm.*, 56, 101—113).—See this vol., i, 302.

**Local Action of Cocaine and Allied Substances on Motor Nerves.** A. LÄWEN (*Chem. Zentr.*, 1907, i, 182; from *Arch. exp. Path. Pharm.*, 56, 138—160).—Isotonic solutions of cocaine, novococaine, alypine, and stovaine, were applied to a frog's sciatic nerve; within an hour the excitability dropped to less than half. By indifferent fluids, these materials can be washed out completely; this occurs most rapidly with novococaine. After stovaine the original excitability never returned.  
W. D. H.

**Acid Poisoning. II.** HANS EPPINGER (*Chem. Zentr.*, 1907, i, 55; from *Zeitsch. exp. Path. Ther.*, 3, 530—538).—A rabbit can be made to exhibit tolerance towards acids by increasing the protein in its diet; a dog loses its natural tolerance by reduction of its protein food. In rabbits, subcutaneous administration of the protein has a similar effect. The products of protein cleavage when given in the diet possibly neutralise the acids given. It is not established, however, that giving amino-acids by the mouth, or urea subcutaneously, will relieve the coma of diabetes.  
W. D. H.

**Toxolecithide of Bee Poison.** J. MORGENROTH and U. CARPI (*Chem. Centr.*, 1906, ii, 1854; from *Berl. klin. Woch.*, 43, 1424—1425).—The solution obtained by treating freshly extracted bee stings and the drops of poison adhering to them with equal parts of a physiological sodium chloride solution and glycerol has a hæmolytic action on different kinds of blood, and the effect is considerably increased by the addition of very small quantities of lecithin, the quantity of the latter is insufficient to have any injurious action. The neutral solution of the prolecithide of the bee poison is not as stable as that of cobra poison, but the toxolecithide is very little affected by change of temperature. The filtrate, obtained by treating a mixture of 1.5 c.c. of the original solution of bee poison with an equal vol. of 5% lecithin solution and filtering at 37° after twenty-four hours, gives a flocculent precipitate on the addition of 22 c.c. of absolute alcohol and 150 c.c. of ether; the precipitate forms a clear solution in physiological sodium chloride solution. When the poison is treated in a similar way, but without the addition of lecithin, a very small precipitate is obtained which has not a hæmolytic action. The hæmolytic action of the mixture of the poison and lecithin is decreased by cholesterol. It is apparent, therefore, that bee poison contains a substance (prolecithide) which resembles the poison of snakes and scorpions and combines with lecithin to form a peculiar toxolecithide.  
E. W. W.

## Chemistry of Vegetable Physiology and Agriculture.

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**Denitrification of Soil.** GASPARE AMPOLA and S. DE GRAZIA (*Gazzetta*, 1906, 36, ii, 893—905. Compare Abstr., 1905, ii, 194).—Further experiments have confirmed those of Ampola (*loc. cit.*) on the relative values as manures of calcium and sodium nitrates, and of green material, stable manure and straw. Experiments with sheep, cow, and horse manures show that the first is the most and the last the least useful. Stable manure has practically the same action as straw alone. The supposed dangers attending the use of stable manure are unfounded, provided that it is employed in as putrid a condition as possible and that the application of nitrate is delayed until the organic matter has undergone decomposition. T. H. P.

**Nitrogenous Nutrition of Yeast.** HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1907, 3, 121—286).—The paper is divided into three parts. Part 1 deals in full with the kind of nitrogenous combination necessary for the action of yeast, and the results have already appeared in a preliminary communication (this vol., ii, 44). Part 2 deals with the influence of nitrogenous nutriment on fermentation, growth, and nitrogenous metabolism of the yeast. The experiments, which are throughout of an exhaustive kind, were made with three kinds of yeast. If peptone is employed, increasing concentration leads to increased growth and ferment activity. If leucine, asparagine, or ammonium sulphate are used, fermentation diminishes with increasing concentration. The highest economic factor, that is quickest fermentation and least nitrogenous metabolism, was obtained with asparagine. A combination of asparagine and ammonium sulphate at the most favourable minimum of 0.008% nitrogen gave the greatest ferment action of all combinations, except in the case of peptone. High concentration of leucine acts unfavourably on killed yeast (zymase). The optimum of cell-growth and fermentation go together in the case of peptone, but not with the other substances; the most favourable percentage of nitrogen for growth being here 0.03 instead of 0.008. In estimating nitrogenous metabolism, the nitrogen in the surrounding liquid must be taken into account as well as that in the dried yeast. Yeast obtains its energy supply not only from fats and carbohydrates, but also by the fission of nitrogenous substances leading to the evolution of carbon dioxide.

The third part of the paper deals with the question of the by-products, glycerol, succinic acid, and especially fusel oil. These are regarded as pure excreta of no more use to the yeast in its metabolism; the general conclusion regarding fusel oil is that no fermentation occurs without the presence of amino-acids which yield fusel oil in the fermenting fluid, and therefore no fermentation takes place without the simultaneous formation of fusel oil. W. D. H.

**Influence of Manganese Salts on Alcoholic Fermentation.** E. KAYSER and H. MARCHAND (*Compt. rend.*, 1907, 144, 574—575).—When manganese sulphate is added to fruit musts, which are to be fermented with yeast, there is an increase in the amount of alcohol, glycerol, and acids formed, but the initiation of fermentation occurs later the greater the amount of manganese sulphate added. Manganese lactate and acetate produce practically the same effect as the sulphate when added in equivalent quantity, but the phosphate and succinate lead to the production of less alcohol and more glycerol. With manganese nitrate, fermentation sets in rapidly, and the amount of sugar consumed is about the same as when manganese sulphate is added. The addition of potassium nitrate to the must leads to a smaller consumption of sugar than when yeast is used alone.

T. A. H.

**Migration of Soluble Principles in Plants.** GUSTAVE ANDRÉ (*Compt. rend.*, 1907, 144, 383—386. Compare this vol., ii, 291).—The soluble matters of artichoke roots and roots of *Phytolacca* increase in the relation of 1:1.5 in three or in two and a half months; the roots are, therefore, reserve organs. In the stems of artichoke the increase in soluble matter is still greater, whilst there was a loss in the stems of *Phytolacca*. The leaves of artichoke remained almost constant, the production of sugar being coincident with an equal migration to the stems and roots. In the case of *Phytolacca*, the migration of soluble substances from the leaves was in excess of the production; in this case the migration was not only towards the roots as seed production had commenced.

N. H. J. M.

**Starch Meal.** W. H. BLOEMENDAL (*Chem Zentr.*, 1907, i, 176—177; from *Pharm. Weekblad.*, 43, 1249—1265).—The composition of the different kinds of starch meal given below was found to agree with the formula  $(C_6H_{10}O_5)_x$ , and the following constants are also quoted in the abstract:

	D in water.	D in 96% alcohol.	Ash.	Water.	Heat of combustion.
<i>Amylum solani</i> .....	1.458	1.488	0.26	19.88	4000 cal.
„ <i>oryzæ</i> .....	1.498	1.485	0.58	13.23	4001 „
„ <i>tritici</i> .....	1.476	1.484	0.40	15.95	4004 „
„ <i>marantæ</i> ...	1.474	1.495	0.22	16.61	4027 „

Owing to the difficulties of the determination of the density the figures in the first two columns can only be regarded as approximate.  $\beta$ -Amylose is the chief component of starch meal; the quantity of  $\alpha$ -amylose varies from 8.3% to 17%, and amyloextrin and other products of hydrolysis are also present. The difference between the two kinds of amylose depends on a difference in the content of water and  $\alpha$ -amylose which does not give a blue coloration with iodine readily passes into  $\beta$ -amylose which gives a blue coloration.  $\alpha$ -Amylose is insoluble in water, and a solution of starch therefore contains only  $\beta$ -amylose; the solution is unstable, and deposits a substance which resembles the original starch, but in which the proportion of  $\alpha$ - and

$\beta$ -amylose is different. It is possible that the two amyloses are chemically identical and the difference merely dependent on a different arrangement of the pseudo-crystalline needles. The presence of amyloextrin is indicated by the red coloration which is formed on addition of iodine solution, and this substance was detected in starch meal from *Chelidonium majus*, *Gentiana lutea*, *Iris germanica*, *Phalænopsis spec.*, *Serapias lingua*, and *Stanhopea oculata*, but it was not found in a commercial sample of *Amylum marantæ*. E. W. W.

**Presence of Formaldehyde in Green Plants.** G. KIMPLIN (*Compt. rend.*, 1907, 144, 148—150).—When a concentrated solution of hydrogen sodium sulphite containing an excess of *p*-methylamino-*m*-cresol is introduced by means of a capillary tube into a leaf of *Agave mexicana*, exposed to light for a short time until the solution has penetrated, a red precipitate is formed indicating the presence of formaldehyde. The precipitate is seen by immersing a section of the impregnated portion of the leaf in absolute alcohol, and examining a portion in a drop of water.

A number of aldehydes and aldehydic compounds were treated with *p*-methylamino-*m*-cresol. Various colorations (green, yellow, and reddish-brown), generally very unstable, were obtained, whilst formaldehyde gives a permanent red colour. N. H. J. M.

**Detection of Formaldehyde in Plants.** GINO POLLACCI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 199—205. Compare Abstr., 1900, ii, 160).—A criticism of work on the presence of formaldehyde in leaves, and the methods used for its detection in them. T. H. P.

**Phytochemical Observations Regarding Hydrocyanic Acid.** H. G. F. ZIJNEN WARTEL (*Pharm. Weekblad.*, 1907, 44, 178—180).—By experiments on the leaves of *Prunus laurocerasus*, the author proved that heating to 60° does not prevent the complete decomposition of the glucoside by the enzyme present. In addition to the glucoside, *Prunus laurocerasus* contains traces of free hydrogen cyanide. The presence or absence of light during germination has no influence upon the amount of hydrogen cyanide present in shoots of *Linum usitatissimum*, and the use of nitrogenous and non-nitrogenous nutriment (such as peptone and sugar) with a view to stimulate its production did not yield positive results.

By means of amygdalin, the presence of emulsin or a related enzyme has been detected in *Rosaceæ*, in many *Papilionaceæ*, and in varieties of *Vicia*, *Lathyrus*, *Cytisus*, and *Orobis*, but not in *Lupinus* and *Trifolium*. A positive reaction was also yielded by *Ribes Americanum*, *Deutzia gracilis*, various *Liliaceæ* and *Juncaceæ*, and certain *Gramineæ* and *Cyperaceæ*.

The potato is poisoned by a solution of potassium ferrocyanide containing one-fiftieth of a gram-molecule per litre, and by one of mercuric cyanide of one-tenth this strength. Potassium ferricyanide, potassium thiocyanate, potassium cyanide, potassium silver cyanide, and chloral hydrocyanide were also more or less injurious to the plants examined,

On the other hand, solutions of amygdalin containing one-tenth of a gram-molecule per litre were innocuous to potatoes and sugar-beet.

A. J. W.

**Formation and Distribution of Essential Oil in a Perennial Plant.** EUGEN CHARABOT and G. LALOUE (*Compt. rend.*, 1907, 144, 152—154).—The plant, *Artemisia absinthium*, was examined: (1) September 26, 1904, long before the flowering period; (2) July 10, 1905, when flowering commenced; (3) August 4, 1905, and (4) September 2, 1905, the end of the flowering period. At the first period when leaves preponderate, the roots do not contain any essential oil, whilst the leaves contain more than the stems. At the second period, the stems predominate; the roots then contain more essential oil than the stems, and the proportion in all parts of the plant is increased. At the third period, the stems still predominate, and the accumulation of the essence in the roots is still more evident. By the end of the flowering period the proportion of leaf becomes relatively greater, owing to renewed leaf production.

The odoriferous substances are produced most actively at the beginning of the development of the plant, whilst they are consumed during the period of fructification. In practice it is desirable to prevent the fructification of the flower, or else to extract the essence before this is accomplished.

N. H. J. M.

**Successive Distributions of the Terpenic Compounds Amongst the Different Organs of a Living Plant.** EUGÈNE CHARABOT and G. LALOUE (*Compt. rend.*, 1907, 144, 435—437. Compare Abstr., 1904, ii, 365, 581, 634; 1905, ii, 112, 549; 1906, ii, 385).—(1) Long before the appearance of the first inflorescence it is found that wormwood (*Artemisia absinthium*) yields an essence containing only traces of thujone. The essential oil contained in the stem is more soluble than that in the leaf. The essence of wormwood from the middle of France, extracted either from the wild or the cultivated plant, differs considerably in composition from those of the Parisian region and from the American essence; the latter are richer in thujone and poorer in combined thujol than the former. (2) When the first inflorescence appears, an essence is found in them less soluble than that in the leaves, as has already been found with sweet basil at a corresponding stage. The highest proportion of ethers is found in the essence from the roots, that from the stems contains the next lower proportion, then comes that from the inflorescences, and finally that from the leaves. The essence from the leaves contains the greatest amount of thujone, that from the stems only traces. At the beginning of the inflorescence the ethers accumulate in the root, whilst the proportion of thujone becomes relatively great. (3) During fructification the weight of the essence diminishes in the leaf and in the inflorescence. Analysis shows that the quantity of thujol in the inflorescence increases although the amount of essence diminishes. (4) On completion of fructification, new shoots bring a fresh quantity of essence. The essence disappears in the dried inflorescences, but whilst in the preceding stage the relatively soluble thujol increased, it now undergoes the

greatest diminution. This is explained, as in the case of sweet basil, by the partial return of the essential oil to the green organs when the function of the flower is complete. E. H.

**Glycolytic Enzymes in Vegetable Organisms.** JULIUS STOKLASA, ADOLF ERNEST, and KARL CHOCENSKÝ (*Zeitsch. physiol. Chem.*, 1907, 50, 303—360).—In most cases anaerobic metabolism in the organs of seeds appears to be identical with alcoholic fermentation, as does the anaerobic breathing of frozen organs of the same plants and of beet-root and potatoes. The freezing of plant tissues does not appear to affect the ratio—aerobic/anaerobic breathing. The process of freezing does not destroy zymase or lactacidase, but they cannot be isolated from the frozen tissues.

Peat and coal undergo autoxidation, and the evolution of carbon dioxide is partially due to autoxidation and partially to enzymatic action.

Details are given for the isolation of the crude enzymes and for the detection of the various fermentation products, including lactic acid, ethyl alcohol, and acetic acid.

The general conclusion drawn is that plant cells contain enzymes which induce lactic and alcoholic fermentations; these enzymes resemble zymase and lactacidase respectively. These are regarded as primary processes, secondary reactions consist in the degradation of the primary products by enzymatic action in the presence of oxygen. These secondary reactions produce acetic acid, methane, formic acid, and hydrogen, which can undergo further oxidation to carbon dioxide and water. J. J. S.

**Glycolytic Enzymes in Vegetable Organisms.** JULIUS STOKLASA, ADOLF ERNEST, and KARL CHOCENSKÝ (*Zeitsch. physiol. Chem.*, 1907, 51, 156—157. Compare preceding abstract).—The existence of glycolytic enzymes in the seedlings of plants other than those previously investigated is described. Zymase leads to the appearance of lactic acid, and lactacidase to that of alcohol and carbon dioxide. W. D. H.

**Composition of Vegetable Juices from Stems and Leaves.** GUSTAVE ANDRÉ (*Compt. rend.*, 1907, 144, 276—278).—The amounts of ash and total nitrogen were determined in the juices expressed under different degrees of pressure from the stems and leaves of Jerusalem artichoke and *Phytolacca decandra* at four different periods of growth (compare this vol., ii, 122). N. H. J. M.

**Eriodictyon Glutinosum.** GUSTAV MOSSLER (*Annalen*, 1907, 351, 233—254. Compare Power and Tutin, *Abstr.*, 1906, ii, 835).—A number of substances have been stated by previous authors to occur in *Eriodictyon glutinosum*, but have not been chemically characterised. The present investigation was undertaken in consequence of the increasing use of the drug.

On distillation in a current of steam, eriodictyon yields a distillate the odour of which indicates the presence of small quantities of an



ethereal oil, which, however, could not be isolated. The *fat* extracted by means of light petroleum, crystallises from alcohol in leaflets, m. p.  $54^{\circ}$ ; has the acid number, 33.1—33.4; the hydrolysis number, 102.1—102.5, and the iodine number, 91—91.5; and on hydrolysis with alcoholic potassium hydroxide, yields an unsaturated acid,  $C_{15}H_{28}O_2$ , m. p.  $47-48^{\circ}$ , b. p.  $250-270^{\circ}/20$  mm., which forms a lead salt soluble in ether, and a dibromide,  $C_{15}H_{28}O_2Br_2$ . The portion of the fat not hydrolysed by potassium hydroxide consists of a saturated hydrocarbon, m. p.  $66^{\circ}$ , b. p.  $270-280^{\circ}/15$  mm. The analytical and other data do not yet suffice to indicate the exact formula; it lies between the limits  $C_{27}H_{56}$  and  $C_{31}H_{64}$ .

Treatment of the residue from the light petroleum extraction with ether leads to the isolation of chlorophyll, resinous substances, and eriodictyonone,  $C_{15}H_7O(OH)_4 \cdot OMe$ , m. p.  $214-215^{\circ}$  (corr.), which crystallises from alcohol, gives a deep red coloration with traces of alcoholic ferric chloride, reduces moist silver oxide or Fehling's solution, and remains unchanged when boiled with 4% sulphuric acid. The tetra-acetyl derivative,  $C_{15}H_7O(OAc)_4 \cdot OMe$ , crystallises from a mixture of alcohol and ether in stout, colourless prisms, m. p.  $158^{\circ}$  (corr.). The tetrabromide,  $C_{16}H_{14}O_6Br_4$ , formed in chloroform-ethyl acetate solution, crystallises in white prisms, m. p.  $204^{\circ}$ , decomposes at  $207^{\circ}$ , and readily loses hydrogen bromide. The oxime,  $C_{16}H_{14}O_5 \cdot NOH$ , m. p.  $192-194^{\circ}$ , has not been purified. The oxime of the tetra-acetate,  $OMe \cdot C_{13}H_7(OAc)_4 \cdot NOH$ , m. p. about  $182^{\circ}$ , crystallises from alcohol.

Oxidation of eriodictyonone with potassium permanganate in dilute sodium hydroxide, by means of chromic acid in glacial acetic acid, or by fusion with potassium hydroxide, leads to the formation of tars or to complete destruction of the molecule. On distillation with zinc dust, it yields a yellow, viscid oil with an odour of naphthalene.

When distilled alone at  $110-150^{\circ}/40$  mm., eriodictyonone yields cresol and a small amount of a crystalline substance, m. p.  $81^{\circ}$ . G. Y.

**Active Substances of Tephrosia Vogelii.** MAURICE HANRIOT (*Compt. rend.*, 1907, 144, 150—152).—Macerated leaves of *Tephrosia Vogelii* are used in Madagascar and the East Coast of Africa for the purpose of paralysing fishes, which are then picked off the surface of the water. Fresh leaves are much more active than dried leaves.

When an alcoholic extract of the leaves is distilled with steam, a sparingly soluble oily substance, tephrosal, passes over. The residue is evaporated in a vacuum, extracted with chloroform, and precipitated with ether. The filtered liquid is treated with potassium hydroxide, the ether distilled off, and the residue, tephrosin, crystallised several times from boiling acetone and washed with ether.

*Tephrosal*,  $C_{10}H_{16}O$ , is a liquid having a very strong odour. The cold aqueous solution reduces ammoniacal silver nitrate and cupropotassium solutions, and reddens magenta decolorised by hydrogen sulphite.

*Tephrosin*,  $C_{31}H_{25}O_{10}$ , the toxic substance of *Tephrosia*, forms small, brilliant prisms, m. p.  $187^{\circ}$ , volatile at high temperatures, with partial decomposition. It distils in a vacuum without decomposition. Its solution in chloroform when treated with bromine, yields a compound, m. p.  $133^{\circ}$ , very soluble in ether.

N. H. J. M.

**Amount of Solanine in Potatoes and the Influence of Soil Cultivation on the Production of Solanine.** F. VON MORGENSTERN (*Landw. Versuchs-Stat.*, 1907, 65, 301—338).—Potatoes used for feeding contain on the average 0·0058% solanine; table potatoes, 0·0125%; and potatoes used for both purposes, 0·0115%. Greater amounts would probably give to potatoes the sharp taste which is acquired by too long exposure to light; potatoes which have thus become green are very rich in solanine. Yellow potatoes were found to contain 0·0078% solanine, whilst red potatoes contained 0·0119%. Potatoes from a dry sandy soil and a moist humus soil contained respectively 0·0133 and 0·0045% of solanine. The amount of solanine does not seem to increase when potatoes are stored, the apparent gains being due to loss of water and carbon dioxide.

During the growth of potatoes there is a tendency for the solanine to migrate from the older to the newer parts; at the same time the percentage amount in the plant diminishes.

The chief rôle of solanine seems to be the protection of the growing and sensitive portions of the plant; it also hinders the immediate diosmosis of the sugar produced during assimilation. N. H. J. M.

**Injurious Nitrogen in Sugar-Beet.** KARL ANDRLÍK (*Zeitsch. Zuckerind. Böhm.*, 1907, 31, 277—284. Compare Abstr., 1906, ii 388).—The chief cause of the production of injurious nitrogenous matters in beet is deficiency of rain, and in very dry seasons the amount of injurious substances may be two or three times as great as in normal seasons. Exclusive nitrogenous manures, both as nitrate and ammonia, distinctly favour the accumulation of injurious substances in the roots; farmyard manure has no injurious effect, and the injury caused by nitrates may be reduced by application of potassium manure and superphosphate. N. H. J. M.

**Composition, Digestibility, and Food Value of Sugar-Beet Sections.** FR. HONCAMP (*Landw. Versuchs-Stat.*, 1907, 65, 381—406).—Sugar-beet sections obtained in Steffen's hot juice process have the following composition. Dry matter, 91·41; crude protein, 7·05; crude fat, 0·39; non-nitrogenous extract, 68·47; sugar, 36·88; crude fibre, 11·82; and ash, 4·24%. In conjunction with nitrogenous food the sections are very suitable for feeding. They can be used in greater amount than molasses foods which have to be employed with care owing to the large amounts of salts they contain.

Hansson (*Tidskr. Landtm.*, 1906, No. 41; and *Mitt. deut. landw. Ges.*, 1906, 21, 465) has recently found that feeding with 1 kilo. of the sections yielded exactly the same amount of milk as 10 kilos. of ordinary sugar-beet sections. The duration of the experiments was, however, far too short for the results to be considered conclusive.

N. H. J. M.

**Is the Darkening of Beet-Juice Produced on Exposure to the Air Due to the Presence of Tyrosine or Homogentisic Acid in the Juice?** ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1907, 50, 508—524. Compare Reinke, Abstr., 1883, 880).—Not merely the pulp and juice of the beet but also those of the potato and dahlia

tubers became dark coloured on exposure to the air. The amount of tyrosine which can be isolated from beet-juice is so extremely minute that it cannot be the cause of the coloration, this is confirmed by the fact that practically the same amount of tyrosine can be extracted after the darkening of the colour has occurred. No trace of homogentisic acid could be extracted from the juice. J. J. S.

**Relation of Calcium Salts to the Assimilation of Nitric Nitrogen.** W. W. JERMAKOFF (*Bied. Zentr.*, 1907, **36**, 102—105; from *J. exper. Landw.*, 1905, **6**, 431).—Leaves of vine, *Paulownia imperialis*, was supplied during twenty-four hours with 0.2% solutions of calcium and potassium nitrate respectively. At the end of the experiment determinable amounts of nitrates were found in the leaves supplied with potassium nitrate, and only traces in the leaves which had calcium nitrate. In a second experiment all the leaves received potassium nitrate for twenty-four hours; the leaves were then cut in half, and the one set of halves kept for a second twenty-four hours in solutions of calcium chloride, magnesium chloride, and potassium chloride respectively, and in water alone. The results showed that the nitrate accumulated during the first twenty-four hours mostly disappeared when subsequently supplied with calcium chloride, but not in presence of magnesium and potassium chlorides; and the conclusion is drawn that nitrates are only assimilated in presence of calcium. It is suggested that free nitric acid is formed, and that this acts on dextrose, producing ammonia and oxalic acid; the ammonia being utilised for protein formation and the oxalic acid precipitated as calcium salt.

N. H. J. M.

**Influence of the Non-protein Nitrogen Compounds of Foods on Milk Production.** AUGUST MORGEN, CARL BEGER, and F. WESTHAUSSER (*Landw. Versuchs-Stat.*, 1907, **65**, 413—440. Compare Abstr., 1906, ii, 563).—Amides cannot take the place of proteins, but have more effect than carbohydrates. The experiments will be continued.

N. H. J. M.

**Presence of Aldehydes in Cheese, and their Rôle in the Production of Bitterness.** AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1907, **144**, 333—335).—Aldehyde was frequently found in cheese, the greatest amount being in cheese having a bitter taste. Bitterness may be produced artificially by exposing cheese to the action of aldehyde vapour, and is attributed, like the bitterness of some wines, to the formation of an aldehyde-resin.

N. H. J. M.

**Soils from the Northern Portion of the Great Plains Region : Distribution of Carbonates on the Second Steppe.** FREDERICK J. ALWAY and GUY R. McDOLLE (*Amer. Chem. J.*, 1907, **37**, 275—283. Compare this vol., ii, 126).—Determinations of carbon dioxide have been made showing the distribution as well as the total amount of carbonates present in the soils of the second steppe. The samples taken represent complete sets of one foot sections to a depth of six feet.

The amount of carbonates in the surface soils is, in all cases, less than that in the subsoil. The subsoil, judged by the content of carbon dioxide, is of two distinct types; the first, boulder clay, containing 7·5% to 12% of carbon dioxide, whilst the second, a clay of lacustral origin, contains 1·25% to 4·0%.

The higher the proportion of carbonates, the lower is the hygroscopic coefficient, this relationship being strongly marked.

H. M. D.

**Carbon Disulphide Treatment of Soils.** BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1907, ii, 18, 56—74. Compare Abstr., 1906, ii, 486; and Moritz and Scherpe, *Arb. biol. Abt. k. Gesundheitamtes*, 4, 123—155).—Plot experiments with rye showed an increase of 40—50% of grain and 30—40% of straw due to application of carbon disulphide.

Experiments made to show the number of germs in the soil showed that the application of carbon disulphide resulted in a considerable increase in the numbers. As pointed out, however, it is not the number which is of importance but the activity.

The full discussion of the results is postponed until the after-effect of carbon disulphide has been sufficiently investigated.

N. H. J. M.

**Calcium Carbonate Concretions.** EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1907, 65, 471—479).—Concretions obtained from the deeper layers of the loamy soil near Kaiserslautern had the following percentage composition:

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	CaCO <sub>3</sub> .	MgO.	MgCO <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>3</sub> .
1·048	1·262	0·203	55·294	0·178	1·890	4·204	0·157	0·090	34·824

Absorption experiments made with 50 grams of the finely-powdered concretion in each case showed that 0·1904 gram of K<sub>2</sub>O, 0·0592 gram of N (as ammonia), and 0·5200 gram of P<sub>2</sub>O<sub>5</sub> were absorbed by 100 grams of substance in forty-eight hours. Concretions in their natural state (not ground) absorbed 0·756 gram of P<sub>2</sub>O<sub>5</sub> in four days.

N. H. J. M.

**Physiological Behaviour of Dicyanodiamide with Regard to its Value as Manure.** RENATO PEROTTI (*Centr. Bakt. Par.*, 1907, ii, 18, 50—56).—Higher plants are only injured by solutions containing 3 per thousand or more dicyanodiamide, different plants having varying powers of resisting its action. Lower organisms (spirogyra and bacteria) are more resistant than higher plants.

Calcium cyanamide is far more injurious than dicyanodiamide and in a state of much greater dilution. The manurial value of calcium cyanamide seems to depend on its conversion into dicyanodiamide.

N. H. J. M.

**Can the Availability of Bone Meal Phosphoric Acid be Increased by Application of Ammonium Sulphate?** OSKAR BÖTTCHER (*Landw. Versuchs-Stat.*, 1907, 65, 407—411).—Ammonium sulphate, owing to its physiological acidity, considerably increased the availability of bone meal for oats growing in a humus, sandy loam. Sodium nitrate was without effect.

It is considered doubtful whether similar results would be obtained in field experiments, as the amount of ammonium sulphate employed would be less.

So-called fermented bone meal is not more available than steamed bone meal.  
N. H. J. M.

**Influence of Calcium and Magnesium Manuring on Phosphate Manure.** F. WESTHAUSER and WILLY ZIELSTORFF (*Landw. Versuchs-Stat.*, 1907, 65, 441—447).—The results of pot experiments with white mustard showed that water-soluble phosphoric acid, applied at the rate of 100 kilos. per hectare, was rendered insoluble by small amounts of calcium carbonate and still more by magnesium carbonate. Calcium sulphate slightly increased the yield. When phosphoric acid is applied in the form of basic slag, moderate amounts of calcium and magnesium carbonates, or lime and magnesia, increased the yields. Large amounts are, however, injurious, magnesium being more so than calcium.  
N. H. J. M.

**Action of Straw Manure on the Fertility of Soils.** LORENZ HILTNER and L. PETERS (*Bied. Zentr.*, 1907, 36, 155—159; from *Arb. k. biol. Anstalt. Land-Forstwirts.*, 1906, 5).—Lupins and oats were grown in lupin and potato soils (9 kilos.) to which lupin straw (90 grams), potassium nitrate (1 gram), and potassium and phosphoric acid manures were added. No great differences were noticed in the case of lupins, whilst the growth of oats was retarded in presence of lupin straw. The second year of the experiment, oats were sown in all the pots, and it was found that the yield was greater after lupins than after oats. The after effect of lupin straw on oats after lupins was very favourable, increasing the yield, on the average, 50·9%; so that the whole effect (first and second years) of lupin straw was good. The best results were obtained with straw and nitrate together. In the case of oats after oats, the after effect of lupin straw was less decidedly favourable (the average gain was 19·2%), and insufficient to make good the loss, due to straw, in the first year.

Field experiments in 1900 and 1901 with lupins, seradella, robinia, peas, and beans gave similar results. The straw was only injurious to lucerne. The favourable action of robinia, the straw of which is very woody, was particularly marked.

Extract of straw greatly increased the yield of mustard; it is therefore to the insoluble matter of the straw that injurious effects must be attributed.  
N. H. J. M.

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### Analytical Chemistry.

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**Use of Textile Fibres in Analytical Microchemical Analysis of Inorganic Substances.** FRIEDRICH EMICH [and, in part, JULIUS DONAU] (*Annalen*, 1907, 351, 426—438. Compare Abstr., 1902, ii, 45, 351 ; Donau, Abstr., 1904, ii, 684).—This is a description of a new

method of microchemical analysis in which the formation of a precipitate or coloration is not observed under the microscope, but is carried out in textile fibres which are examined afterwards microscopically. As these fibres can be removed readily from one reagent into another, the interference which commonly occurs in microscopical crystallisation of mixtures is avoided.

The delicacy of the microchemical test for each substance is expressed by a factor,  $E$ , termed the "equivalent sensitiveness"; this is the maximum number of c.c. in which 1 gram-equivalent of the substance is dissolved when the amount contained in 1 c.c. of the solution can be just detected. Thus, boron trioxide, of which 0.0000006 m.g. can be detected, has  $E_{\text{BO}_3} = 0.000001 \text{ c.c.} \times 59/3 \text{ grams} / 0.000000006 \text{ gram} = 33,000 \text{ c.c.}$

Such microchemical tests are much more delicate than even spectroscopic tests; thus the minimum amount of borax which can be detected microchemically is 0.001  $\mu\text{g.}$ , or of boron, 0.0001  $\mu\text{g.}$ , whereas the minimum limit for the spectroscopic detection of boric acid is 2  $\mu\text{g.}$  (Murano, *Abstr.*, 1902, ii, 355).

Microchemical thread tests and the corresponding factors,  $E$ , are given for boron and the more important of the heavy metals.

G. Y.

**Preparation of Standard Sulphuric Acid.** FREDERIC W. RICHARDSON (*J. Soc. Chem. Ind.*, 1907, 26, 78—79).—A known quantity of the acid is neutralised with barium hydroxide and the resulting barium sulphate weighed. The method of procedure is as follows. Five c.c. of dilute sulphuric acid of known sp. gr. are weighed in a platinum basin and neutralised by the addition of clear, saturated barium hydroxide solution, phenolphthalein being used as indicator. The solution is then evaporated, the residue is ignited, and weighed. Knowing the sp. gr. of the acid, it is easy to calculate the quantity of barium sulphate which ought to be obtained and to check the amount found by the weight of the residue. The acid solution may then be diluted to the required strength.

W. P. S.

**Succinic Acid as a Standard in Alkalimetry and Acidimetry.** ISAAC K. PHELPS and J. L. HUBBARD (*Amer. J. Sci.*, 1907, [iv], 23, 211—213).—The authors confirm the fact that succinic acid is admirably adapted for volumetric work, but the best ways of obtaining it in a pure condition have not been recorded. The following methods give good results. Twenty c.c. of pure ethyl succinate are boiled with 200 c.c. of water and 3 drops of nitric acid for four hours in a reflux apparatus, and the concentrated liquid is allowed to crystallise; the product is then purified by recrystallisation from water, and dried in the air or over sulphuric acid. Another way of preparing the pure acid is to boil pure succinic anhydride with water, or the commercial acid may be purified by recrystallisation, preferably from water containing a little nitric acid. The pure acid should melt in an open capillary tube at 182.3°.

L. DE K.

**A New Reaction for Free Hydrochloric Acid in Stomach Contents.** FRIEDRICH SIMON (*Chem. Centr.*, 1906, ii, 1883 ; from *Berl. Klin. Woch.*, 43, 1431).—A pinch of pure dry guaiacum resin is dissolved in a test tube in 10 parts of sweet spirits of nitre and 40 parts of alcohol, and 5 c.c. of the filtered stomach contents is carefully poured down the sides. In the presence of free hydrochloric acid, a dirty white ring is formed, which after a few seconds turns distinctly blue, or green if the amount of acid is very small. The reaction is favoured by heating the contents slightly. Lactic acid also causes a blue ring, but only if present to the extent of at least 1.25%.  
L. DE K.

**Detection of Chlorates in Urine.** HERMANN HILDEBRANDT (*Chem. Centr.*, 1906, ii, 1881 ; from *Vierteljahrschr. ger. Med. öffentl. Sanitätswesen*, 32, 81—89).—The urine is acidified with pure nitric acid and silver nitrate solution is added so long as a precipitate is formed. On adding sodium nitrite and, if necessary, some more silver nitrate, the chlorate is reduced to chloride, and precipitated as silver chloride, which is then collected and weighed.  
L. DE K.

**Estimation of Iodine in Pharmaceutical Preparations such as Ointments, &c.** ERWIN RUPP and J. KOST (*Pharm. Zeit.*, 1907, 52, 125—126).—The process described previously by Rupp and Horn (*Abstr.*, 1906, ii, 895) may be applied to the estimation of iodine in ointments in the following manner. Five grams of the sample are melted in about 50 c.c. of boiling water and a few grams of hard paraffin are added to cause the fatty constituents of the ointment to solidify on cooling. The solid cake of fat is broken up, when cold, and the aqueous solution is poured through a filter; the latter is then washed with water until the filtrate measures 100 c.c. Fifty c.c. of the filtrate are taken for the estimation of the iodine by the process mentioned above.  
W. P. S.

**New Method of Estimating Fluorine.** ERNST DEUSSEN [and HEINRICH KESSLER] (*Monatsh.*, 1907, 28, 163—172).—See this vol., ii, 265.

**Detection of Thiosulphates in Foods in the Presence of Sulphites.** AUGUST GUTMANN (*Zeitsch. Nahr. Genussm.*, 1907, 13, 261—264).—The test proposed is based on the conversion of the thiosulphate into sulphite and thiocyanate by the action of potassium cyanide; the reaction is quantitative and proceeds according to the equation:  $\text{Na}_2\text{S}_2\text{O}_3 + \text{KCN} = \text{Na}_2\text{SO}_3 + \text{KSCN}$ . In testing meat, 50 grams of the finely-divided sample are boiled with about 100 c.c. of 50% alcohol, the mixture being rendered slightly alkaline with sodium hydroxide. After cooling, the alcoholic solution is filtered, and the filtrate evaporated (but not to dryness) with the addition of 3 c.c. of 10% potassium cyanide solution. The residual solution is taken up with about 20 c.c. of 50% alcohol, the solution is acidified with dilute sulphuric acid, filtered, and the filtrate tested with ferric chloride solution. A red coloration indicates the presence of a thiosulphate in the meat. The test may be made quantitative by comparing the



coloration obtained with that produced by a known weight of thiocyanate.

W. P. S.

**Action of Nascent Hydrogen on Certain Metallic Compounds in Presence of Oxygenated Derivatives of Arsenic.** DIOSCORIDE VITALI (*Boll. Chim. Farm.*, 1907, 46, 89—93. Compare Abstr., 1905, ii, 354).—The use of copper sulphate or platinum tetrachloride as a means of facilitating the dissolution of purified zinc in dilute acid may give rise to considerable error in the estimation of arsenic by Marsh's apparatus. The copper (or platinum) initially separated combines with some of the arsenic to form an arsenide which is decomposed only slowly by the acid to form hydrogen arsenide. To obtain accurate results, it is necessary to use only a small quantity of the catalyst and to prolong the action of the acid until the solution and the precipitated copper do not show the least trace of arsenic by the Vitali test (*Boll. Chim. Farm.*, 1899, 224); much zinc should be used and, as zinc also combines with arsenic, enough acid should be used to dissolve the whole of the zinc. If salts of other metals are present in the solution, the metal in many cases is precipitated, owing to the reducing action of the hydrogen, and combines with arsenic, forming an arsenide which is only slowly decomposed; this is true of lead, nickel, gold, bismuth, cadmium, and silver.

The reducing action of zinc in presence of acid may be used to estimate copper in copper salts, the copper formed in the reduction being weighed as oxide. It is necessary, of course, that other metals reducible by zinc should be absent in such cases and that the zinc be pure. A similar process can be applied to the estimation of gold, platinum, and silver.

W. A. D.

**Detection of Arsenic in Foods or Organs.** CASIMIR STRYZOWSKI (*Chem. Centr.*, 1906, ii, 1778; from *Pharm. Post*, 39, 677—678).—One gram of the solid substance or 5—10 grams of a semi-liquid one are rubbed with 10 c.c. of water, and 1 gram of magnesium oxide and 0.5—1 c.c. of nitric acid are added. The whole is evaporated to dryness in a 25 c.c. porcelain crucible and gradually burnt to white ash. The residue, which contains any arsenic present, is dissolved in dilute sulphuric acid and tested as usual.

L. DE K.

**Estimation of Arsenic, Copper, Lead, and Zinc in Wines.** A. HUBERT and F. ALBA (*Chem. Centr.*, 1906, ii, 1872—1873; from *Mon. Sci.*, [iv], 20, ii, 799—802).—Two hundred to one thousand c.c. of the sample are mixed with one-fifth of the volume of pure nitric acid, and the liquid is added from a dropping funnel to 20—50 c.c. of sulphuric acid which has been heated to boiling in a Kjeldahl flask. The volume of the acid should not increase sensibly during the boiling, which may take from forty minutes to three hours according to the volume of wine operated on. Finally, the acid is boiled down to 5—10 c.c. When cold, the residue is diluted with an equal volume of water and a portion of it is examined quantitatively for arsenic in the Marsh apparatus. The remainder is evaporated in a platinum dish until the bulk of the acid is expelled; the residue is diluted, neutralised with

ammonia, then again slightly acidified with nitric acid, heated at 60—70°, and submitted to electrolysis, when the copper separates as metal at the cathode, and the lead at the anode as peroxide. The acid liquid still contains any zinc which may be present, which is then precipitated with ammonia and ammonium sulphide. L. DE K.

**Estimation of Hydrofluosilicic Acid in Presence of Hydrochloric Acid and Sodium Chloride in Sewage.** S. KOHN and LEO WESSELY (*Chem. Zeit.*, 1907, 31, 204).—The method is based on the fact that 1 mol. of hydrofluosilicic acid = 6 mols. of sodium hydroxide, but that the hydrochloric acid liberated on adding sodium chloride = 2 mols. only.

A measured quantity of the liquor is titrated hot with *N*-sodium hydroxide with phenolphthalein as indicator. The titration is then repeated after precipitating the acid with brine. If  $m$  = number of c.c. of alkali used in the first and  $n$  = number of c.c. in the second titration, then the c.c. of alkali required for the neutralisation of the hydrofluosilicic acid =  $3n - m/2$ . L. DE K.

**Formula for the Calculation of the Calorific Value of Fuels.** E. IENOBLE (*Bull. Soc. Chim.*, 1907, [iv], 1, 111—114).—Goutal has shown that the calorific value ( $P$ ) of a coal is equal to  $82C + aV$ , where  $C$  is the percentage of ash-free coke,  $V$  the percentage of moisture-free volatile matter, and  $a$  a coefficient, which has the value 145, 130, 117, 109, 103, 98, 94, 85, or 80 when the corresponding value of  $V'$  is 5, 10, 15, 20, 25, 30, 35, 38, or 40;  $V'$  is given by the relation  $100V/C + V'$ . It is shown that this formula may be reduced to the simpler form  $P = 82C + 73.66V + (98CV)/(C + 7V)$ , and that similar results are obtained by the use of the still less complex equation  $P = 87.4(100 - k)$ , where  $k$  is the sum of the percentages of moisture and of ash, the latter calculated on the dry coal. Both these formulæ give approximately accurate results when applied to coal of medium quality, but are inapplicable when the calorific value of the fuel is over 8500 cal. T. A. H.

**Simplified Analysis of the Metals of the Fifth Group in the Presence of Magnesium.** A. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 769—773).—When equivalent quantities of magnesium carbonate and tartaric acid are mixed, magnesium tartrate,  $\text{MgC}_4\text{H}_4\text{O}_6$ , separates in the cold after two days, but the acid salt,  $\text{Mg}(\text{C}_4\text{H}_5\text{O}_6)_2$ , mentioned by Dulk could not be obtained (*Annalen*, 1832, 2). If compounds of the type  $\text{MgR}_2$  are added to sodium hydrogen tartrate,  $\text{NaC}_4\text{H}_5\text{O}_6 \cdot \text{H}_2\text{O}$ , a precipitate separates only after about a week; when, however, a potassium salt is present, potassium hydrogen tartrate is at once precipitated. In the course of analysis, having removed barium, strontium, and calcium, concentrated sulphuric or hydrochloric acid is added, and the solution evaporated, ignited, and redissolved in a small quantity of water. If a small portion shows the presence of magnesium, another portion is tested for potassium by adding sodium hydrogen tartrate. Before testing for sodium by means of potassium antimonate,  $\text{KSbO}_3$ , it is necessary to remove magnesium

by the addition of potassium hydroxide. The following numbers have been obtained for the solubility of anhydrous sodium hydrogen tartrate in water. One hundred grams of solution contains 4.14 grams at 0.5°, 4.87 at 2.5°, 6.10 at 16.6°, 6.34 at 18°, 6.84 at 23°, 8.42 at 30°. Z. K.

**Analytical Characters of Barium and Strontium.** HENRI BAUBIGNY (*Bull. Soc. Chim.*, 1907, [iv], 1, 55—61).—The criticisms of Caron and Raquet (this vol., ii, 52) on the method devised by the author for the separation of barium and strontium (*Abstr.*, 1895, ii, 114) are replied to and it is pointed out that since barium chromate is appreciably soluble in dilute acetic acid, the method of separation described by these authors (*loc. cit.*) does not secure complete precipitation of the barium; experimental data supporting this conclusion are given. T. A. H.

**Influence of Ammonium Salts on the Titration of Zinc with Sodium Sulphide.** V. HASSEIDTER (*Bull. Soc. Chim. Belg.*, 1907, 20, 373—374).—As a result of his experiments, the author states that the presence of an excess of ammonium salts causes the brown coloration on the lead test paper to appear sooner than it would do were ammonium salts absent; in other words, less sodium sulphide is required to complete the titration. W. P. S.

**Analysis of Zinc Ores.** JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1907, [iv], 1, 61—63. Compare this vol., ii, 131).—The ore is digested with hydrochloric acid, and the mixed sulphides, precipitated from the solution so obtained by hydrogen sulphide, are digested with sodium sulphide. The sulphide solution is acidified with hydrochloric acid and the washed precipitate oxidised with nitric acid and aqua regia, if necessary. In the product, arsenic is first estimated as ammonium magnesium arsenate, and then antimony as the sulphide, a correction being applied to the weight of the latter for the small amount of arsenious sulphide included with it and derived from the ammonium magnesium arsenate which remains in solution. In the portion of the original sulphide precipitate, which is insoluble in sodium sulphide, lead is estimated as the sulphate, copper electrolytically as the metal, and in the residue, cadmium as the sulphate. This last may contain traces of lead, copper, and zinc.

From the acid filtrate collected from the original sulphide precipitate, iron, manganese, and aluminium are precipitated together as the oxides by means of hydrogen peroxide and ammonia. From this mixture, iron and aluminium are precipitated together by means of ammonium succinate in presence of sodium acetate, and after incineration the aluminium is determined by fusion with potassium hydroxide. The manganese in solution is precipitated as  $Mn_2O_4$  by means of hydrogen peroxide and ammonia.

The liquid remaining after the elimination of the three foregoing metals is boiled to remove excess of ammonia and to cause the separation of a small amount of alumina still retained. It is then cooled and treated with hydrogen sulphide after the addition of a few drops of ammonia solution to separate the zinc, which is weighed as sulphide.

From the filtrate, calcium is precipitated as the oxalate and weighed as the sulphate, and magnesium is precipitated in the usual manner as magnesium ammonium phosphate. T. A. H.

**Analysis of Lithopones.** A. COPPALLE (*Ann. Chim. anal.*, 1907, 12, 62—65).—A modification of Drawe's method (*Zeitsch. angew. Chem.*, 1902). Instead of estimating the zinc sulphide from the difference between the total zinc and the oxide soluble in acetic acid, the author prefers determining the sulphide from the sulphuric acid formed on oxidation.

Attention is called to the possible presence of kaolin which would augment the weight of the insoluble matter (barium sulphate), also to the frequent presence of small quantities of barium carbonate; this may be estimated by boiling a separate portion of the sample with dilute hydrochloric acid and precipitating the barium with sulphuric acid. Its weight should be deducted from the total barium sulphate, as during the oxidation process the barium carbonate is converted into sulphate. L. DE K.

**Electrolytic Estimation of Lead.** GEORG VORTMANN (*Annalen*, 1907, 351, 283—293).—From the statements of previous authors it might be thought that the electrolytic estimation of lead as the peroxide gives satisfactory results except only in presence of arsenic, selenium, manganese, and bismuth. This, however, is not the case, as is shown in the present paper, in which details of seventy-five estimations are given. The following conclusions are drawn as to the conditions under which trustworthy results may be obtained.

The current density may vary within wide limits. The lead must be in the form of the nitrate, the solution must contain sufficient free nitric acid to prevent the deposition of metallic lead, and, of other elements, only copper may be present. In the presence of sulphuric, selenic, or chromic acid, the precipitation must be repeated as the results of the first are high. If arsenic or phosphoric acid is present, the peroxide is incompletely precipitated; separation may be effected by precipitation as metallic lead, solution in nitric acid, and precipitation of the peroxide; this procedure is not recommended. If other metals are present, the results are usually high, and can be depended on only when constant on reprecipitation. G. Y.

**Potassium Ferrocyanide and Ferricyanide as Reagents for Metals in Ammoniacal Solutions.** DIOSCORIDE VITALI (*Chem. Centr.*, 1906, ii, 1780; from *Boll. Chim. Farm.*, 45, 665—666).—In ammoniacal solution, potassium ferrocyanide gives a green colour with copper, a peach coloration and precipitate with bismuth, a green precipitate with cobalt, a white precipitate with silver, a white precipitate with zinc, a white precipitate with cadmium, and a red coloration and yellow precipitate with platinum.

Potassium ferricyanide gives with copper a green coloration, with bismuth a reddish-brown coloration, with cobalt a brown precipitate, with zinc no precipitate, with cadmium no precipitate, and with platinum a green coloration with yellow precipitate. L. DE K.

**Action of Potassium Ferri- and Ferro-cyanide on Ammoniacal Solutions of Certain Metallic Salts.** HERMANN GROSSMAN (*Chem. Zeit.*, 1907, 31, 37—38).—The author contradicts several statements made by Vitali (preceding abstract) and shows that the ferro- and ferri-cyanide tests for copper, nickel, cobalt, and silver in ammoniacal solution are untrustworthy.  
W. H. G.

**Estimation of Copper.** W. H. FOSTER (*Proc. Camb. Phil. Soc.*, 1907, 14, 90—97).—The method described is a modification of Schwarz's method for estimating copper, differing from it in the use of ferric sulphate instead of ferric chloride, titration of the reduced salt with potassium permanganate and employment of the double carbonate of copper and potassium instead of the tartrate. This method, using dextrose as the reducing agent, gives good results when copper alone is present, but it cannot be applied to mixtures of copper and those metals with which it is usually associated in alloys and ores. Hydroxylamine or phenylhydrazine cannot be employed as reducing agents in place of dextrose.  
W. H. G.

**Titration of Mercurous Salts with Potassium Permanganate.** D. L. RANDALL (*Amer. J. Sci.*, 1907, [iv], 23, 137—140).—Mercurous sulphate may be readily titrated with potassium permanganate. As, however, the reaction is irregular towards the end, it is necessary to add to the solution, which should contain free sulphuric acid, a decided excess of permanganate. The liquid is now decolorised by adding standard ferrous sulphate and the titration with permanganate continued.

The process is also applicable to mercurous nitrate. In this case the liquid may be safely acidified with nitric acid, provided no more than 3% of this is used.  
L. DE K.

**Estimation of Manganese in Water.** HEINRICH LÜHRIG and W. BECKER (*Pharm. Centr.-h.*, 1907, 48, 137—142).—Of several methods tried, that described by Knorre (*Abstr.*, 1902, ii, 108) was found to be the most trustworthy for the estimation of small quantities of manganese in water. For detecting the presence of traces of manganese, the authors employed a modification of Marschall's process, in which the water to be tested is heated with nitric acid, silver nitrate, and ammonium persulphate. A pink permanganate coloration is obtained if as little as 0.0001 gram of manganese per litre is present.  
W. P. S.

**Analysis of Products of the Iron Industry containing High Proportions of Chromium.** GINO GALLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 58—67).—All the methods which have been proposed for the analysis of iron alloys containing large proportions of chromium are difficult and tedious to carry out, as they require the metal to be brought into a fine state of division and then to be fused, in some cases more than once, with an oxidising agent; if the fusion is effected in a platinum or nickel crucible, the latter is appreciably attacked, whilst

if a silver crucible is used, the development of heat is often sufficient to fuse the crucible.

Such alloys can be readily brought into solution by the author's electrolytic method, which consists in passing the current from the alloy suspended in a 15% potassium chloride solution rendered faintly alkaline with potassium hydroxide to a platinum wire used as a negative pole. The most suitable temperature is 80—85°, at which 1 gram of the metal can be dissolved in four hours with an *E.M.F.* of 8—10 volts and a current of 0.5 ampere. By this means the whole of the iron is precipitated as ferric hydroxide, whilst the chromium is left in solution as potassium chromate. The potassium ions appearing at the negative pole react with water causing an evolution of hydrogen; in order to prevent the latter from reducing the chromate, the platinum wire is placed inside a Pukal's porous pot. The chromium may be estimated in an aliquot part of the liquid by rendering the latter slightly acid with hydrochloric acid, boiling to expel the last traces of chlorine, and adding it to a mixture of 1—2 grams of potassium iodide in a small quantity of water with 5 c.c. of dilute hydrochloric acid (1:5); the iodine separated according to the equation:  $2K_2CrO_4 + 6KI + 16HCl = 10KCl + 2CrCl_3 + 8H_2O + 6I_2$ , is then measured by titration with standard sodium thiosulphate solution.

Any nickel or manganese present is precipitated as hydroxide with the ferric hydroxide and may be determined by the ordinary methods. This precipitate also contains all the phosphorus, while the sulphur remains in the solution; methods are described for their determination.

T. H. P.

**Quantitative Separation of Tin from Manganese Iron and Chromium by Electrolysis.** NICOLAI A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 764—769. Compare Abstr., 1906, ii, 199).—Ferrous and manganous oxalates are similar in properties to the corresponding nickel and cobalt salts, and, like the latter, the metals are not deposited on the electrodes when a current is sent through their solution. Since tin is easily deposited in this way, it can thus be separated qualitatively from solutions of these salts. The method of procedure is similar to that for nickel and cobalt. The results are accurate for manganese, chromium, and ferrous salts, but satisfactory results for ferric salts have not yet been obtained.

Z. K.

**Estimation of Antimony and Tin in Babbit-Metal, Type-Metal, or other Alloys.** WILSON H. LOW (*J. Amer. Chem. Soc.*, 1907, 29, 66—74).—The alloys, or the sulphides of tin and antimony obtained in due course, are heated with sulphuric acid, if necessary, with addition of a little potassium sulphate until the metals are converted into sulphates. If iron is present, the alloy must be oxidised first with nitric acid, and after expelling this completely by evaporation with sulphuric acid and potassium sulphate, a little tartaric acid is added, and the heating continued until the carbon has disappeared. The mass which now contains the antimony as antimonious, and the tin as stannic, sulphate, is dissolved in dilute hydrochloric acid, and the antimony is

titrated with standard permanganate. Previous addition of some tartaric acid does no harm. The liquid is now mixed with excess of hydrochloric acid and a little metallic antimony in a current of carbon dioxide, and when cold, the tin is titrated with standard iodine with starch as indicator. The presence of lead and copper does not interfere.

*Standardisation of the Solutions.*—0.1202 Gram of pure antimony and 0.1190 gram of tin are heated with 10 c.c. of sulphuric acid and 3 grams of potassium sulphate. The mass is dissolved in 50 c.c. of water and 10 c.c. of hydrochloric acid, 110 c.c. of water are added and the permanganate is run in, 50 c.c. of strong hydrochloric acid are added, the liquid is boiled in a current of carbon dioxide, with 1 gram of antimony to reduce the tin, and the iodine solution is then checked.

L. DE K.

**Colorimetric Estimation of Titanium in the Presence of Iron.** P. FABER (*Chem. Zeit.*, 1907, 31, 263—265).—When hydrogen peroxide is added to a titanium sulphate solution, a yellow or yellowish-red coloration is produced, and a colorimetric method for the estimation of titanium has been based on this fact. In some cases, however, when the titanium has been obtained in solution by fusion with potassium hydrogen sulphate, the colorations given by duplicate portions of the sample are not of the same intensity. The author shows that this is due to the formation of more or less basic sulphate during the fusion, and that it may be overcome by dissolving the fused mass in dilute sulphuric acid. The presence of iron salts renders the method unworkable, but the addition of phosphoric acid does away with the influence of the iron salts; phosphoric acid must also be added to the standard comparison solution, as it slightly alters the tint of the coloration.

W. P. S.

**Estimation of Gold in Auriferous Sand by the Wet Way.** ALBERT FOURNIER (*Compt rend.*, 1907, 144, 378—381).—The following method is recommended for sands containing much iron. The sand is mixed intimately with 5% of manganese dioxide, digested with pure cold hydrochloric acid for twenty-four hours, and then heated on a water-bath until the liquid becomes quite clear. The liquid is decanted from the residue which is washed with acidified water, and evaporated nearly to dryness on a water-bath. The still acid liquid is precipitated by alcohol at 95°. After vigorous shaking, the liquid is left for forty-eight hours and then filtered by decantation. The alcoholic filtrate contains all the chlorides soluble in alcohol, it is heated on a water-bath and submitted to a current of pure hydrogen sulphide during a lengthy period varying with the amount of sand taken. The insoluble sulphides are washed with boiling, very dilute hydrochloric acid, then with pure water until free from hydrogen chloride; then digested on a water-bath with pure hydrochloric acid free from nitric acid. The residue after washing is treated with hydrochloric acid together with a few drops of nitric acid, and evaporated to dryness. This process is repeated with hydrochloric acid and with water. The solution obtained may be reprecipitated with hydrogen sulphide if the presence of traces of iron is suspected,

or may be treated directly for the separation and isolation of the precious metals. E. H.

**New Method of Estimating Ammonia in Water.** ALBERT BUISSON (*Compt. rend.*, 1907, 144, 493—495. Compare Abstr., 1906, ii, 704).—When sodium carbonate is added to a solution of any ammonium salt (2 mols.) containing mercuric chloride, the whole of the ammonia is precipitated as a white, amorphous compound (Gerresheim, Abstr., 1879, 438).

The author finds that with a constant quantity of ammonium salt, increasing the amount of mercuric chloride from the minimum (5 mols. of mercuric chloride to 2 mols. of ammonium salt) up to 0.5 gram per litre does not alter the composition of the precipitate. When larger quantities of mercuric chloride are used, the precipitate is no longer of constant composition, but contains mercuric oxychloride. Analysis of the precipitate of constant composition corresponds with the formula  $\text{CO}_3(\text{Hg}_5\text{N}_2\text{Cl}_2)_2\text{O}, 3\text{H}_2\text{O}$ . When heated at  $100^\circ$  it loses  $3\text{H}_2\text{O}$  and becomes yellow.

To estimate ammonia in water, the following procedure is recommended. One litre of the water, made alkaline with 5 c.c. of 15% sodium carbonate solution, is distilled at such a rate that rather more than 100 c.c. are condensed in one and a half hours. The distillate is received in 10 c.c. of 1% hydrochloric acid, diluted to 1 litre, treated with 10 c.c. of a 5% solution of mercuric chloride, precipitated by 10 c.c. of 15% sodium carbonate solution and left for twenty-four hours. The precipitate is collected on a filter of glass wool previously tared, washed with 5 c.c. of water, dried at  $100^\circ$ , and weighed. The weight of the precipitate multiplied by 0.03 gives the weight of ammonia. If the quantity of ammonia is very small (less than 0.001 gram) the distillate is not diluted, and then only 1 c.c. of each solution is employed. Quantities of ammonia varying from 0.0001 to 0.012 gram, the amount occurring in natural waters, can be estimated very accurately by the method. E. H.

**Spanish Oil of Thyme.** JOSEPH RODIE (*Bull. Soc. chim.*, 1907, [iv], 1, 236—239).—With a view to devising a simple means of detecting sophistication in the oil, the specific gravities, "phenol" contents (thymol or carvacrol, or both), and the solubilities in 65%, 70%, and 80% alcohol of upwards of forty samples have been determined and are tabulated and shown graphically in the original.

From the results, the conclusion is drawn that oils having a specific gravity greater than 0.950, and which are soluble in 65% alcohol, may safely be regarded as containing over 60% of "phenol." Those with a specific gravity between 0.922 and 0.950, which are soluble in 70% alcohol, may be accepted as containing from 40% to 60% of "phenol," especially if they are also soluble in 65% alcohol. Oils which are insoluble in 70% alcohol and have a specific gravity less than 0.922 should be regarded with suspicion. T. A. H.

**Esterification of *tert.*-Terpenic Alcohols, especially Linalool, and Estimation of this Alcohol in Volatile Oils.** VICTOR BOULEZ (*Bull. Soc. chim.*, 1907, [iv], 1, 117—120).—The linalool, or the



volatile oil containing it, is diluted with five times its weight of turpentine oil and the mixture gently boiled with acetic anhydride and sodium acetate during three hours. Under these conditions, acetylation of the linalool is complete, and there is no secondary decomposition. The estimation of the linalyl acetate formed is carried out in the usual manner, a correction being applied for the small quantity of acetyl ester formed from the turpentine oil. This method, with perhaps slight modification, may be applicable to the acetylation and estimation of other alcohols of the same type, such as geraniol and terpineol.

T. A. H.

**Pathological-Chemical Notes.** [Detection of Cholesterol Esters, Carbamide, Urobilin and Bilirubin, and of Sugar.] ERNST SALKOWSKI (*Chem. Centr.*, 1906, ii, 1851—1852; from *Arb. Path. Inst., Berlin*).—I. *Occurrence and Detection of Esters of Cholesterol*.—By boiling 4 grams of epidermis with 93% alcohol, 0.1504 gram of cholesteryl palmitate was obtained in the form of a snow-white, silky mass, m. p. 77—78° (compare Hürthle, *Abstr.*, 1896, ii, 485), which consisted of matted needles. The ester was separated from the fats by treatment with alkali hydroxide, the action being stopped before the cholesterol ester was attacked. From solutions containing 0.5 and 0.25 gram of the palmitate in 50 grams of palm fat, 0.224 and 0.0618 were obtained respectively. The palmitate gives the Liebermann and the Neuberg-Rauchwerger reactions, but is not attacked by sulphuric acid and iodine, probably because it is not wetted by the mixture. In the case of the crude ester which has not been recrystallised by adding alcohol to the ethereal solution, the particles become very slowly red or violet and a dirty green or blue coloration is only formed after twenty-four hours. Chloroform and sulphuric acid give a dull red coloration.

II. *Detection and Estimation of Carbamide in Fluids and Organs of the Body*.—In order to estimate the carbamide in fluids, the residue from the last alcoholic extraction is treated when cold with nitric acid (D 1.2), the mixture allowed to remain for twenty-four hours, the fats and fatty acids removed from the precipitate by washing with absolute alcohol and ether, and the carbamide finally weighed as nitrate or as free carbamide after treating the nitrate with barium carbonate. Contamination with hypoxanthine is detected by the formation of a gelatinous precipitate of hypoxanthine silver when silver nitrate is added to the ammoniacal solution of the nitrate. The quantity of hypoxanthine corresponding with that of the silver contained in the precipitate is subtracted.

III. *Detection of Urobilin and Bilirubin in presence of each other in the Contents of the Small Intestine*.—The contents of the small intestine are concentrated on the water-bath and then extracted with alcohol. To the turbid aqueous solution which remains on evaporation, sodium carbonate solution is added until alkaline, and then calcium chloride; the bile colouring matters are carried down by the precipitate, whilst the urobilin remains in solution. The precipitate is covered with alcohol and a small quantity of hydrochloric acid, warmed, filtered, and the filtrate finally boiled. The solution may have a slight green

tint, but usually remains yellow, and does not give the reaction of bile-colouring matter. In order to detect the presence of urobilin, the solution is acidified with hydrochloric acid and extracted with chloroform, the extract shaken with water, filtered, and examined spectroscopically. When a few drops of an alcoholic or aqueous solution of zinc chloride are added, the chloroform solution becomes rose-red and acquires a green fluorescence (Wirsing). When an intensely yellow solution of urobilin in chloroform is gently shaken with an equal volume of nitric acid, D 1.18—1.2, the acid becomes bluish-violet to purple and the chloroform blue. The nitric acid shows an absorption band between the yellow and the red and a second between the green and the blue, whilst the chloroform solution has often a faint band in the red or between the yellow and the red. The colour of the acid gradually changes to red and yellowish-red, whilst that of the chloroform disappears. In the case of lutein, the nitric acid remains colourless and the chloroform solution gradually becomes so.

IV. *Detection of Minute Quantities of Sugar in Urine by means of Phenylhydrazine.*—Five c.c. of urine to which 0.5 c.c. of glacial acetic acid has been added are treated with 20 drops of phenylhydrazine and to the mixture after boiling for one minute, 5 drops of a 15% solution of sodium hydroxide are added. A volume of water equal to three-quarters of the volume of the liquid is added, the mixture again heated until it just begins to boil, and then allowed to remain for a day. A loose, sulphur-yellow precipitate is formed, which appears under the microscope to consist of double clusters of slender needles. Lactose and maltose do not give this reaction.

E. W. W.

**Delicate Reaction for Carbohydrates.** HENRY J. H. FENTON (*Proc. Camb. Phil. Soc.*, 1907, 14, 24—26).—It has been shown (Fenton and Gostling, *Trans.*, 1898, 554; 1901, 361) that the formation of  $\omega$ -bromomethylfurfuraldehyde by the action of hydrogen bromide affords a characteristic test for ketohexoses, and that its formation by aldoses could not be detected. By the following method the merest trace of  $\omega$ -bromomethylfurfuraldehyde may be detected, and, since by this means its production from aldoses has been proved, this test may serve for the identification of all hexoses or compounds which yield hexoses on hydrolysis.

A minute quantity of the solid to be examined is moistened with water, mixed with a drop or two of phosphorus tribromide dissolved in toluene, gradually heated on a water-bath to 90—100°, and kept at this temperature until the mixture has turned dark coloured. It is then cooled, stirred with a little alcohol and a few drops of ethyl malonate, and finally made alkaline by the addition of alcoholic potash. On diluting the mixture with a large volume of water, a blue fluorescence is apparent. Sugars in dilute aqueous solution may also be detected by pouring 2—3 c.c. of the solution on to an excess of calcium chloride to form a pasty mass, and treating this in the manner described above.

W. H. G.

**Colour Reactions of Carbohydrates with Indole and Scatole.** F. WEEHUIZEN (*Chem. Zentr.*, 1907, i, 134; from *Pharm. Weekblad.*, 43, 1209—1210).—Dextrose (glucose), lactose, saccharose, starch, and

cellulose, when heated with strong hydrochloric acid and scatole, all yield a beautiful violet and permanent coloration; this reaction still showed in a dilution of 1:300000. Indole causes a brownish-red coloration.

L. DE K.

**Colour Reaction of Pentoses.** MANFRED BIAL (*Biochem. Zeitsch.*, 1907, 3, 323—325).—The author defends his methods against Sachs's criticisms (this vol., ii, 135).

W. D. H.

**Estimation of Methylpentoses.** ADOLF JOLLES (*Annalen*, 1907, 351, 38—43. Compare Abstr., 1906, ii, 203; Votoček, Abstr., 1899, ii, 701; Ellett and Tollens, Abstr., 1905, ii, 210).—Methylpentoses are estimated volumetrically in the same manner as pentoses, the conversion into methylfurfuraldehyde taking place quantitatively when methylpentoses are distilled with hydrochloric acid in a current of steam. In the results obtained with rhamnose, the error lies between +1.2% and -0.97%.

In a mixture containing pentoses and methylpentoses, the total sugar is determined by distillation with hydrochloric acid and titration with sodium hydrogen sulphite and iodine solutions; in a second sample, the methylpentoses are precipitated by addition of alcohol and saturated aqueous baryta at 0°, and the pentoses determined in the filtrate. With mixtures of arabinose and rhamnose, the error for the pentose was 0.4—1.05%, and, for the methylpentose, -0.8% to -1.8% of the total quantity of sugar.

G. Y.

**The Relative Value of Almén's and Worm-Müller's Tests for Sugar.** OLOF HAMMARSTEN (*Pflüger's Archiv*, 1907, 116, 517—532). EDUARD PFLÜGER (*ibid.*, 533—542. Compare this vol., ii, 137).—Further polemical discussion in which both authors adhere to their original views.

W. D. H.

**Reducing Substances and their Estimation in Sugars and Sugar Products.** HENRI PELLET (*Chem. Zentr.*, 1907, i, 71; from *Zeitsch. Ver. Rübenzuck. Ind.*, 1906, 1012—1022).—The author uses Fehling's solution as modified by Violette; when used for the gravimetric estimation of a reducing sugar the liquid should not be boiled but heated for three minutes at 85—88°, as at a higher temperature other substances may exert a reducing action. In order to free the filter completely from copper tartrate, washing with a 1% solution of Rochelle salt has been recommended, but as this causes a loss of cuprous oxide the author prefers making a correction which according to circumstances may amount to 3—7 mg.

The Clerget process for the estimation of crystallisable sugar in presence of other reducing substances is at the present the only available method.

The reducing sugars in cane and beet products are identical; some molasses, however, contain substances which reduce the Fehling solution on prolonged boiling.

L. DE K.

**Detection of Cane-Sugar in Milk and Cream.** W. H. ANDERSON (*Analyst*, 1907, 32, 87—88).—A test, proposed originally

by Cayaux (*Pharm. Centr.-h.*, 1898, **39**, 503), is stated to be rapid and accurate; it consists in boiling a mixture of 15 c.c. of milk, 0.1 gram of resorcinol, and 1 c.c. of concentrated hydrochloric acid. If cane-sugar is present, a fine red coloration is produced, whilst pure milk remains almost unchanged, only turning a brown colour on continued boiling. The test will detect the presence of 0.2% of cane-sugar.  
W. P. S.

**A Rapid Method for the Detection of Lactose and Galactose in Urine.** RICHARD BAUER (*Zeitsch. physiol. Chem.*, 1907, **51**, 158—166).—The method depends on the appearance of a precipitate of mucic acid when the urine is evaporated down with nitric acid.  
W. D. H.

**Detection and Estimation of Raffinose.** RUDOLF OFNER (*Zeitsch. Zuckerind. Böhm.*, 1907, **36**, 326—328).—About 50 grams of the sugar (when 1% or more of raffinose is present) is shaken for fifteen minutes with about 150 c.c. of methyl alcohol and a few drops of potassium alum solution, filtered, and washed with methyl alcohol. The filtrate is evaporated until syrupy and heated for three hours on a water-bath with 50 c.c. of 3% sulphuric acid. It is then neutralised with barium carbonate, decolorised with blood carbon, evaporated to about half its volume, treated with 96% ethyl alcohol (2 vols.) and 1 c.c. of *α*-phenylmethylhydrazone, and heated in a reflux apparatus on a water-bath for half an hour. After treatment with blood charcoal and filtration, the hydrazone separates in silky crystals when 2% or more raffinose is present; otherwise it may be necessary to start the separation by adding 2—3 mg. of galactose phenylmethylhydrazone. The filtered hydrazone is washed successively with alcohol, water, alcohol, and ether.

Raffinose may be determined in a similar manner. The details will be given later on.  
N. H. J. M.

**New Chemical Test for Strength in Wheat Flour.** THOMAS B. WOOD (*Proc. Camb. Phil. Soc.*, 1907, **14**, 115—118).—An investigation on the conditions which influence the volume of the loaf produced by a given weight of flour. It is found that the volume of the loaf is due to the amount of sugar at the disposal of the yeast, the addition of sugar to the flour producing an increase in volume; consequently, indications of this particular component of "strength" in wheat flour may be obtained, either by estimating the quantity of sugar present as such and of the sugar formed by incubating the mixture of flour and water at such a temperature and for such time as is commonly used in baking, or by mixing the flour with yeast and water and measuring the carbon dioxide evolved during fermentation.  
W. H. G.

**Assay of "Formalin."** NICOLAAS SCHÖORL (*Chem. Centr.*, 1906, ii, 1873—1874; from *Pharm. Weekblad.*, **43**, 1155—1162).—Three grams of the sample are mixed with 50 c.c. of *N*-alkali and 50 c.c. of neutralised 3% hydrogen peroxide, and the whole is heated for fifteen

minutes on the boiling water-bath. When cold, the liquid is titrated with *N*-acid, using phenolphthalein as indicator. L. DE K.

**Acidimetry of Urine according to the Moritz and to Freund-Lieblein Methods.** WALTER VÖLKER (*Chem. Zentr.*, 1907, i, 194; from *Arch. Klin. Med.*, 88, 302—313).—The author states that the process recommended by Freund and modified by Lieblein (separation of primary from secondary phosphates by means of barium chloride) is utterly untrustworthy. In Moritz's process for the estimation of the acidity in urine, the volumetric estimation of the phosphoric acid is rendered more accurate by the addition of sodium chloride, and the injurious action of the calcium salts is prevented by addition of normal sodium oxalate. L. DE K.

**Mineral Acids in Vinegar.** F. D. RATCLIFF (*Analyst*, 1907, 32, 82—84).—It appears from the results given that whilst Hehner's method will not detect the addition of a small amount of mineral acid to vinegar, the method described by Richardson and Bowen (*J. Soc. Chem. Ind.*, 1906, 25, 836) gives too high results, and actually finds what is not there. The author asserts that the practice of adding mineral acid to vinegar has long since ceased, and that it is waste of time to work out new methods for detecting this class of adulteration. W. P. S.

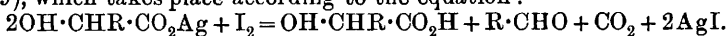
**New Reaction for Formic Acid.** EZIO COMANDUCCI (*Gazzetta*, 1906, 36, ii, 793).—The following reaction for formic acid is not given by formates, formaldehyde, acetaldehyde, crotonaldehyde, methyl or ethyl alcohol or glycerol, acetic, propionic, butyric, valeric, lactic, oxalic, succinic, malic, tartaric, citric, benzoic, salicylic, or phthalic acid.

About 2.5 c.c. of the liquid to be tested are diluted with an equal volume of water, and to the solution are added 15 drops of concentrated (1:1) sodium hydrogen sulphite solution; the liquid is then shaken and gently heated, the appearance of a reddish-yellow coloration indicating the presence of formic acid.

This reaction, which is sensitive to 0.5—1.0% of formic acid, may be employed to detect the presence of the acid in methyl alcohol, glycerol, or acetic acid. T. H. P.

**A New Test for Lactic Acid.** W. THOMAS (*Zeitsch. physiol. Chem.*, 1907, 50, 540—541).—Vournasos has described a new test (formation of *isonitrile*) for lactic acid (*Abstr.*, 1902, ii, 264), which Croner and Cronheim state is better than Uffelmann's for the detection of that substance in the gastric contents. This view is not confirmed, and another test is introduced. It consists in heating the gastric contents with a few drops of 30% chromic acid solution for ten minutes on the water-bath. A reddish-brown colour is given by traces of lactic acid; this does not occur with hydrochloric acid, butyric acid, acetic acid, acetone, or alcohol. W. D. H.

**Chemical Recognition of some Physiologically Important Substances.** [Alcohol. Lactic Acid. Amino-acids.]—REGINALD O. HERZOG (*Annalen*, 1907, 351, 263—266).—A new test for lactic acid, for which no characteristic reaction has been described previously, is based on Herzog and Leiser's investigation of the action of iodine on the silver salts of  $\alpha$ -hydroxy-fatty acids (*Abstr.*, 1901, i, 499), which takes place according to the equation :



Small amounts of lactic are recognised by the odour of the acetaldehyde evolved, or the aldehyde may be collected in water and tested for with sodium nitroprusside and piperidine.

$\alpha$ -Amino-acids, which are important as hydrolysis products of the proteins, are converted by careful treatment of their hydrochlorides with silver nitrite into the corresponding  $\alpha$ -hydroxy-acids, which are tested for in the same manner as lactic acid.

The following method is suggested for the estimation of alcohol in aqueous solution. The solution is added drop by drop at intervals of some seconds to 20 c.c. of a solution of 1 gram of potassium permanganate in 500 c.c. of concentrated sulphuric acid, until the point is reached at which the wine-red solution changes to violet on addition of a further drop of the reducing solution. The end point is seen most easily by comparison of two samples to one of which a drop more of the alcoholic solution has been added. The process is applicable to solutions containing 1—0.5% of alcohol. G. Y.

**Estimation of some of the Organic Acids occurring in Fruits.** GUNNER JØRGENSEN (*Zeitsch. Nahr. Genussm.*, 1907, 13, 241—257).—The following is an outline of the method used by the author in estimating the organic acids occurring in wines and fruit juices. The solution is neutralised, lead acetate and alcohol are added, and the precipitate is collected on a filter, washed, and decomposed by means of hydrogen sulphide. The filtrate from the lead sulphide is concentrated by evaporation, neutralised with potassium hydroxide, and a portion of the tannate, together with some sulphate and phosphate, precipitated by the addition of alcohol. This precipitate is separated by filtration; the filtrate is acidified with acetic acid and the tartaric acid thrown down as potassium hydrogen tartrate; after removing the alcohol from the filtrate and acidifying the latter with hydrochloric acid, the succinic acid is extracted from the solution with ether. The residual solution is now neutralised and treated with barium chloride, whereby the sulphuric and phosphoric acids and some tannin are precipitated. The filtrate from this precipitate is mixed with a small quantity of alcohol and barium citrate, which is thus precipitated, is collected on a filter. The addition of a large volume of alcohol to the filtrate results in the precipitation of the barium malate. These two barium salts are further purified by reprecipitation, and the quantity of the acids estimated from the barium contained in the respective salts. The quantity of the tartaric and succinic acids is estimated by titration of the fractions obtained as described above.

The following quantities (grams per 100 c.c.) were obtained on applying the method to various samples of wine and fruit juices.

Red wine: tartaric acid, 0.128—0.206; succinic acid, 0.042—0.059; citric acid, none; malic acid, 0.032—0.089. Port wine: tartaric acid, 0.090; succinic acid, 0.036—0.052; citric acid, none; malic acid, 0.083—0.142. Sherry: tartaric acid, 0.078—0.133; citric acid, 0.006—0.014; malic acid, 0.047—0.071. Madeira: tartaric acid, 0.051—0.157; succinic acid, 0.013—0.052; citric acid, none; malic acid, 0.037—0.061. Raspberry juice: tartaric acid, succinic acid, and malic acid, none; citric acid, 0.50—1.04. Cherry juice: tartaric acid, none; succinic acid, traces; malic acid, 0.39—0.91.

W. P. S.

**Estimation of Uric Acid by Direct Precipitation.** MEISENBURG (*Chem. Centr.*, 1906, ii, 1880—1881; from *Arch. Klin. Med.*, 87, 424—436).—Satisfactory results are obtained by mixing 180 c.c. of urine with 5 c.c. of hydrochloric acid and rotating for forty-eight hours. In order to facilitate the precipitation, a known weight of uric acid (about 0.1 gram) is added and allowed for.

L. DE K.

**Sources of Error in the Toxicological Detection of Hydrocyanic Acid.** DOMENICO GANASSINI (*Chem. Centr.*, 1906, ii, 1783—1784; *Boll. Chim. Farm.*, 45, 745—748. Compare Abstr., 1905, ii, 867).—Minute traces of hydrogen cyanide may be formed when during the usual distillation with tartaric acid the blood or other organs get overheated. Proteins and their derivatives, such as xanthines and also hæmatin, yield hydrogen cyanide at 200°. The distillation should therefore be always conducted in a current of steam.

L. DE K.

**Estimation of Hydrocyanic Acid in the Seeds of Phaseolus lunatus.** EMILE KOHN-ABREST (*Chem. Zentr.*, 1907, i, 69—70; from *Mon. Sci.*, [iv], 20, 11, 797—798. Compare Abstr., 1906, ii, 625).—Fifty grams of the crushed seeds are macerated in a closed flask with 500 c.c. of water for four hours at 37° or twenty-four hours at the ordinary temperature, 10 c.c. of hydrochloric acid are added to prevent frothing, and 150 c.c. are distilled off on a sand-bath. After adding 50 c.c. of hydrochloric acid to the residue, another 300 c.c. are distilled. The distillates are rendered alkaline with potassium hydroxide, a slight excess of Seltzer water is added, and the hydrogen cyanide titrated with *N*/10 iodine. One c.c. of iodine = 0.00135 gram HCN. The first distillate contains about 2/3 of the total amount present.

White Birma beans yield 0.00891—0.02079%, coloured beans, 0.01075—0.01269%, of hydrogen cyanide.

L. DE K.

**Detection of Salicylic Acid in Wines and Foods.** DIOSCORIDE VITALI (*Chem. Centr.*, 1906, ii, 1782—1783; from *Boll. Chim. Farm.*, 45, 701—708).—Wine is shaken with four times its bulk of pure toluene which dissolves any salicylic acid present without taking up the least trace of other acids. Preserved tomatoes, &c., are acidified with hydrochloric acid, evaporated to syrupy consistency, and extracted with absolute alcohol. The alcoholic extract is evaporated and the residue dissolved in a little water and then shaken with toluene. The

toluene is then tested for salicylic acid by shaking with 1 c.c. of dilute ferric chloride.

The author gives an additional test for salicylic acid. If a trace of copper sulphate is added so as to leave the liquid colourless the residue on evaporation will have a green colour. L. DE K.

**Simple Fat-Extraction Apparatus.** GEORGE S. FRAPS (*Amer. Chem. J.*, 1907, 37, 85—87).—A modification of Knorr's apparatus (Wiley's "Principles and Practice of Agricultural Analysis," 1st ed., 3, 44—47) which has the advantages of being of simpler construction and less expensive. For details, reference must be made to the description and diagrams in the original. E. G.

**Decomposition of Iodoform and Chloroform in Certain Vegetable Oils.** SERGEI F. POPOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1114—1119).—Under the action of a high temperature, the oxygen of the air, and of light, iodoform decomposes according to the equations:  $4\text{CHI}_3 + 5\text{O}_2 = 4\text{CO}_2 + 2\text{H}_2\text{O} + 6\text{I}_2$ ;  $4\text{CHI}_3 + 3\text{O}_2 = 4\text{CO} + 2\text{H}_2\text{O} + 6\text{I}_2$ ;  $2\text{CHI}_3 + \text{O}_2 = 2\text{COI}_2 + 2\text{HI}$ ; similarly, chloroform undergoes decomposition as follows:  $4\text{CHCl}_3 + 5\text{O}_2 = 4\text{CO}_2 + 2\text{H}_2\text{O} + 6\text{Cl}_2$ ;  $2\text{CHCl}_3 + \text{O}_2 = 2\text{COCl}_2 + 2\text{HCl}$  (Schoorl and van den Berg, *Abstr.*, 1906, i, 57, 474, 481).

The author shows that, owing to this decomposition, the use of chloroform as a solvent for vegetable oils leads to low values being obtained for the iodine numbers. Thus, insolation of cacao butter with chloroform or iodoform causes the iodine value to fall from 35.7 to about 32, whilst insolation with ether has little or no effect on the butter in this direction. Also, the iodine number of linseed oil is diminished from 170—145 (or from 170—118) when the oil is subjected to insolation in presence of chloroform (or iodoform).

With solutions of iodoform in chloroform, the percentage amount of iodine yielded by a constant weight of iodoform increases with the dilution of the solution (compare Schuyten, *Abstr.*, 1901, i, 3). T. H. P.

**Determination of the Saponification Number of Lubricating Oils containing Saponifiable Fats.** HERMAN SCHREIBER (*J. Amer. Chem. Soc.*, 1907, 29, 74—75).—Five grams of the sample are treated with 25—50 c.c. of *N*/2 alcoholic potassium hydroxide and 25 c.c. of benzene. Should it be necessary to double the amount of benzene, a little more pure alcohol should be added so as to obtain a clear solution on warming. The flask is then attached to an air condenser and placed on an iron plate resting on a steam-bath. After half an hour's boiling, the saponification will be complete and the undecomposed alkali is then titrated as usual. L. DE K.

**Physico-Chemical Constants of Fats.** D. SIDERSKY (*Ann. Chim. anal.*, 1907, 12, 59—62).—A useful table showing the usual constants of a large number of fats and oils. The author recommends the determination of every one of the constants in fat analysis.

L. DE K.

**The Refraction of Fats and Fatty Acids.** R. K. DONS (*Zeitsch. Nahr. Genussm.*, 1907, 13, 257—261).—From the results recorded, it is seen that the refraction of the insoluble fatty acids of



butter varies within as wide limits as does that of the butters themselves. The difference between the refractions of butter fats and of the insoluble fatty acids of the same butters is practically constant, lying between 10.4 and 12.0. This difference in the case of cocoanut oil and its fatty acids is 16.9, and, although of some aid in the detection of cocoanut oil in butter, will not indicate small quantities of this adulterant. With lard, the difference is 13.1, a figure closely approaching that yielded by butter.

W. P. S.

**Water in Butter.** JULES WAUTERS (*Bull. Soc. Chim. Belg.*, 1906, 20, 365—373).—In the writer's opinion the sale of butter containing an excessive amount (over 18%) of water ought to be prohibited, and the actual addition of water to butter ought, in any case, to be considered an adulteration. Samples of butter intended for analysis ought to be preserved in special vessels in order to prevent the evaporation of the water, and the portion of the sample used for the estimation of the water should be taken from the centre of the pat, and not from the whole pat after re-mixing.

W. P. S.

**A Comparison and Criticism of the Methods for the Detection and Estimation of Cocoanut Oil in Butter.** THOMAS R. HOBGSON (*Chem. News*, 1907, 95, 121—122).—The only trustworthy process for the detection of cocoanut oil in butter is considered by the author to be the estimation of the iodine number. The saponification number was found to be of no practical value, but the Reichert-Wollny number may show some indications of the presence of cocoanut oil if the amount in the sample is large. The method proposed by Wijsmann and Reijst (*Abstr.*, 1906, ii, 402) is a good qualitative test, but as a quantitative method it fails entirely. Thorp's method (*Abstr.*, 1906, ii, 588) is of considerable value as a confirmatory test, and the extraction and identification of phytosterol affords good evidence of the presence of vegetable oil in a sample.

W. P. S.

**Njave Butter.** KONRAD WEDEMEYER (*Chem. Rev. Fett. Harz. Ind.*, 1907, 14, 35—36).—Njave butter, or Njari oil, is obtained from the seeds of one of the *Sapotaceæ*; and is similar to shea butter, which is yielded by another member of the *Sapotaceæ* family. The seeds weigh from 10 to 15 grams each, of which about one-third is due to the hard shell, and yield about 50% of fat. The constants of the fat are:  $D_{40}^{20}$  0.8979; Reichert-Meissl number, 1.2; saponification number, 185.3; iodine number, 56.1; Maumené number, 55°; acid number, 38.1; acetyl number, 13.4;  $n_D^{40}$  1.4606; unsaponifiable matter, 3.66%; insoluble fatty acids, 96.1%. The fatty acids have m. p. 46.6°. The residue of the seeds, after the fat has been extracted, contains 19.74% of protein substances.

W. P. S.

**Applicability of Bomer's Phytosteryl Acetate Reaction to the Detection of the Adulteration of Animal with Vegetable Fats.** FRANS M. JAEGER (*Chem. Weekblad.*, 1907, 4, 1—10. Compare *Abstr.*, 1899, ii, 191, 192, 259; 1902, i, 30, and ii, 184; 1906, i, 742).—The value of Bömer's test as a qualitative and as a quantitative

method is criticised. The number of phytosterols in plants is smaller than hitherto supposed, the chief being ordinary phytosterol, m. p. 136°, which is present as an isomorphous mixture with other phytosterols, and therefore cannot be separated by fractional crystallisation. From Calabar fat, Windaus and Hauth (this vol., i, 128) have isolated phytosterol and stigmasterol, m. p. 170°. The author gives melting-point curves for mixtures of phytosteryl and stigmasteryl acetates with cholesteryl acetate from 0—100%, and concludes that Bömer's reaction is valuable as a qualitative test, but does not yield trustworthy quantitative results.

A. J. W.

**Phenolphthalein in Urine.** GRÜBLER (*Chem. Zentr.*, 1907, i, 137; from *Pharm. Post.*, 39, 689).—Urine containing phenolphthalein is distinguished from urine containing chrysophanic acid or santonin as follows. With barium hydroxide it gives a colourless precipitate and a violet-red filtrate, with sodium carbonate at once a reddish-violet coloration, whilst on heating with sodium hydroxide and zinc dust the liquid is decolorised owing to formation of phenolphthalein. On adding lead acetate and then sodium hydroxide to the filtrate, a violet-red coloration is noticed, which fades gradually.

L. DE K.

**Reactions of Santonin.** C. REICHARD (*Pharm. Zeit.*, 1907, 52, 88—89).—If a little solid sodium hydroxide is added to an alcoholic solution of santonin, and the mixture heated, a bright red coloration is produced; after a few hours the colour changes to yellow. When ammonia is used in place of sodium hydroxide, a feeble red coloration is obtained on heating, the mixture becoming colourless on cooling. Sulphuric acid does not react with santonin in the cold; on warming, an intense blue coloration is formed, which on further heating changes to yellow. Nitric acid gives no reaction with santonin even when heated. From this the author concludes that the yellow colour, which santonin assumes when exposed to air, is not due to oxidation. If a mixture of mercuric chloride, santonin, and sulphuric acid is heated, a yellowish-black coloration is obtained, whilst a mixture of mercurous nitrate and santonin, when moistened with sulphuric acid, immediately turns black. A bright blue colour is produced on adding a drop of sulphuric acid to a mixture of copper sulphate and santonin; on warming, the colour changes to blackish-red. A similar reaction is given by cuprous chloride, and a blue coloration is obtained if bismuth subnitrate is employed in place of the copper salts. Diphenylamine, santonin, and sulphuric acid do not react in the cold, but, on warming, the mixture is coloured an intense red; this changes to yellow at the end of about twelve hours, and afterwards passes into dark green.

W. P. S.

**A Property of Adrenaline.** B. KRULL (*Chem. Zentr.*, 1907, i, 131; from *Pharm. Weekblad.*, 43, 1208—1209).—A drop of solution of adrenaline (1:1000) when mixed with a drop of copper sulphate solution, of cherry-laurel water, and of ammonia, gives an unstable red coloration, but if a minute crystal of sodium hydrogen carbonate is used instead of the ammonia, the red colour is permanent. Pure

potassium cyanide may be substituted for the cherry-laurel water and alkali.

L. DE K.

**Sources of Error in the Kerner-Weller Assay of Commercial Quinine Sulphate.** PETRO BIGINELLI (*Chem. Centr.*, 1906, ii, 1692; from *Boll. Chim. Farm.*, 45, 253—260).—In applying the Kerner-Weller test, the quinine sulphate should be dried at 40—50° and exposed for some twelve hours to the air; it then contains 2H<sub>2</sub>O. The test, however, is not always to be depended on, so that it must be supplemented by other tests, such as the solubility in ether-chloroform mixture, &c.

L. DE K.

**Assay of Cinchona Barks.** FLORENCE (*Chem. Zentr.*, 1907, i, 130—131; from *Bull. Sci. Pharm.*, 13, 365—368).—*Rapid approximate method.*—Twelve grams of the powdered bark are treated with 120 grams of pure ether and 10 c.c. of 10% sodium hydroxide, and, after one hour, 10 c.c. of water are added and the ethereal liquid is filtered through cotton wool. The filtrate is then shaken with 30 c.c. of lime water to remove impurities. To 100 c.c. of the solution are then added 10 c.c. of water, and a *N*/10 ethereal solution of oxalic acid is added so long as a precipitate forms; this represents the total alkaloids in 10 grams of bark. Of the oxalates formed, the quinine salt is the only one insoluble in water, therefore it may be collected, dried, weighed, and calculated into sulphate.

*Accurate method.*—The bark is well shaken with 10% sodium hydroxide solution, and the mass is extracted in a suitable apparatus with a mixture of 4 parts of ether and 1 of chloroform; the extract is purified by repeatedly shaking with lime water, and this is then again shaken with pure ether. The ethereal solutions are evaporated in a tared dish and the residue represents total alkaloids. These are then dissolved in pure ether containing 20% of pure chloroform, 30 c.c. of water saturated with quinine oxalate are added, and the liquid is titrated with *N*/10 ethereal oxalic acid. The quinine oxalate is collected on a weighed filter, pressed dry, and weighed. It is then dried at 100° and weighed again. For each gram of moisture retained in the undried precipitate a deduction of 0.00069 gram of quinine oxalate is made.

L. DE K.

**Assay of Morphine. A Method of Extraction.** THOMAS TICKLE (*Pharm. J.*, 1907, 78, 162—164).—The essential point of the process consists in the use of *m*-cresol as a solvent for the alkaloid. In very weak solutions the cresol only takes up about twice as much of the alkaloid as does amyl alcohol, the aqueous layer becoming saturated with cresol and being a stronger solvent than water alone. This miscibility of the water and the solvent may be diminished by the addition of some other solvent, such as amyl alcohol. The process described by the author consists in liberating the alkaloid with sodium hydrogen carbonate, and extracting it with four successive quantities of a mixture containing 2 parts of recently distilled *m*-cresol and 1 part of amyl alcohol. The extracts, amounted to 30 c.c., are united, 15 c.c. of ether and 30 c.c. of light petroleum are added, and the

morphine is extracted from the mixture by repeated agitation with 1% acetic acid solution. The morphine acetate solution thus obtained is evaporated to dryness, the residue is dissolved in water and placed in a covered vessel side by side with an open beaker containing very dilute ammonia. The solution absorbs the ammonia and deposits the alkaloid in a crystalline state; the crystals are then dried at 110° and weighed. W. P. S.

**Estimation of Morphine in Opium.** L. PICARD (*Chem. Zentr.*, 1907, i, 138—139; from *Bull. Sci. Pharm.*, 13, 419—427).—*Modified Leger's ammonia method.*—Six grams of the dried sample are triturated with lime water, using altogether 48 c.c., and allowed to remain for two hours in the covered mortar. Fifteen minutes before the filtration, 0.5 gram of sodium salicylate is added; after stirring, the mass is pressed through linen and the liquid filtered through a quick filter. Thirty-six c.c. of the filtrate are mixed with 4 c.c. of ether, the liquid is neutralised with ammonia, and after adding a further six drops the whole is well shaken for ten minutes and left for twenty-four hours. The separated crystals of morphine are then collected on a weighed filter, washed with water containing ether, dried, and weighed.

To remove any narcotine the precipitate may be washed with a little benzene.

*Modified lime method.*—7.5 Grams of the dried sample are triturated with 3 grams of calcium hydroxide and 10 c.c. of water, another 65 c.c. of water are added, and the whole is left for two hours. The mass is pressed through linen, and the liquid is filtered. Fifty-three c.c. of the filtrate are mixed with 5 c.c. of strong alcohol, 15 c.c. of ether, and 1 gram of ammonium chloride, gently shaken and left for twenty-four hours. The crystals of morphine are collected on a double, tared filter, washed with 15 c.c. of ether, then with 10 c.c. of water, dried, extracted with 10—15 c.c. of chloroform, again dried, and weighed. L. DE K.

**Estimation of Morphine in Opium and Tincture of Opium.** EDWARD HENRY FARR and ROBERT WRIGHT (*Pharm. J.*, 1907, 78, 164—169).—The authors are convinced that the official, or "lime," process is for all practical purposes the best that has been devised for the estimation of morphine in opium. The quantity of filtrate taken as representing so much opium is, however, too large, and in the case of opium, not more than 102.5 c.c. of filtrate must be used for the estimation. It is preferable to take 8 grams of the opium, 2 grams of calcium hydroxide, and 80 c.c. of water; 51 c.c. of filtrate are then equivalent to 5 grams of opium. For the assay of strong tincture of opium, 40 c.c. are evaporated until the alcohol has been driven off, 1 gram of calcium hydroxide is added, the mixture is diluted to 42 c.c., and 25 c.c. (representing 25 c.c. of tincture) of filtrate are taken for the estimation. The same volume, 40 c.c., is taken in the case of standardised tincture of opium and liquid extract of opium, the first being diluted to 41.5 c.c. and the second to 41 c.c. The temperature given in the

Pharmacopoeia for drying the crude morphine is sufficient to ensure complete dehydration.

W. P. S.

**Alkaloid Reactions [Narcotine].** C. REICHARD (*Pharm. Centr.-h.*, 1907, 48, 44—51).—Narcotine dissolves immediately in strong sulphuric acid without appreciable change in colour. If to the solution is added mercurous nitrate, a black colour is obtained, which changes gradually to yellowish-red (thebaine remains black). On adding sodium arsenate and heating gently on a watch-glass, the edges turn black and, on cooling, purple-red or violet-red colorations are noticed in the mass; the colour is fairly permanent, thus distinguishing it from veratrine. A similar coloration is produced by sulphuric acid and stannous chloride. If a drop of saturated solution of methylamine hydrochloride is evaporated to dryness on a porcelain slab with a little narcotine and the residual mass heated somewhat more strongly, an intense yellow coloration will be noticed which does not fade on exposure to the air; this test distinguishes it from morphine. If diphenylamine and narcotine are dissolved in sulphuric acid and then warmed, the mass turns a dirty yellow; morphine turns a dark reddish-violet. Like narceine and papaverine, narcotine turns dark yellow when gently heating with crystallised boric acid. Several other reactions are described.

L. DE K.

**Estimation of Strychnine in Nux Vomica by the Nitric Acid Process.** M. H. WEBSTER and R. C. PURSEL (*Amer. J. Pharm.*, 1907, 79, 1—7).—After a number of experiments, the authors propose the following modification of the official American test.

The alkaloids obtained as directed are dissolved in 15 c.c. of 3% sulphuric acid, and to the solution are added 3 c.c. of a mixture of equal volumes of nitric acid (D 1.4) and water and then 1 c.c. of a 5% solution of pure sodium nitrite. After thirty minutes, during which time the liquid is stirred a few times, the destruction of the brucine is complete and the strychnine may then be recovered as usual by adding ammonia and extracting with chloroform.

L. DE K.

**Estimation of Tryptophan in Protein Cleavage Products.** PHÆBUS A. LEVENE and C. A. ROUILLER (*J. Biol. Chem.*, 1907, 2, 481—484).—Isolation of the tryptophan leads to appreciable loss. The method suggested for estimating it is based on the following observations. When bromine water is added, a purple coloration develops which with more bromine deepens to a maximum; at this stage a further drop of bromine water discharges the colour. Tyrosine, if present, interferes with the result, but the quantity present in the tryptophan fraction prepared by the method of Hopkins and Cole can be reduced to a mere trace by avoiding excess of mercuric sulphate solution. The presence of cystine is more important, and necessitates an estimation of that substance by sulphur determination, and a subsequent correction of the figures obtained by titration of the mixture of tryptophan and cystine.

W. D. H.

**Glyoxylic Acid Reaction for Tryptophan, Indole and Scatole.** HENRY D. DAKIN (*J. Biol. Chem.*, 1907, 2, 289—296).—Some differences are noted in the colour reactions of the three substances mentioned, but the main point discussed is whether Hopkins is right in attributing the Adamkiewicz reaction to glyoxylic acid. Glyoxylic acid was prepared in seven different ways, some of which exclude the presence of oxidising agents; in all cases it gave the tryptophan colour reaction. At the same time, Rosenheim's statement (*Abstr.*, 1906, ii, 508) that an apparently identical reaction is given by formaldehyde in the presence of sulphuric acid which contains oxidising agents is confirmed. No evidence of the conversion of formaldehyde into glyoxylic acid was obtained. Neither, on the other hand, was any evidence forthcoming that glyoxylic acid underwent such a decomposition as would lead to its yielding the same products as are obtained from the formaldehyde. In other words, no real decision on the point at issue is forthcoming.  
W. D. H.

**Precipitation of the Colouring Matters of Red Wines and the Detection of Foreign Colouring Matters.** FERDINAND JEAN and C. FRABOT (*Ann. Chim. anal.*, 1907, 12, 52).—A slight modification of Trillat's process. Fifty c.c. of the sample are mixed with 1 c.c. of 40% formaldehyde and 4 c.c. of hydrochloric acid, and heated for a few minutes on the water-bath until a precipitate begins to form. A slight excess of ammonia is then added and the heating continued until the free ammonia has disappeared.

Genuine wines give a colourless filtrate, whilst those which have been coloured artificially retain the colour of the dyes.  
L. DE K.

**Bearberry Leaves and the Microscopic Detection of Arbutin.** TUNMANN (*Chem. Zentr.*, 1907, i, 196; from *Pharm. Zentr.-h.*, 47, 945—946).—The preparation, freed from fatty matters by treatment with ether-alcohol, is placed for a few moments in dilute sulphuric acid (1:5) and then moistened with strong nitric acid. The cells containing arbutin exhibit under the microscope a dark orange or dark brown coloration. A gentle heating promotes the reaction. The arbutin is present and evenly distributed only in the leaves. The decoction richest in arbutin is obtained when the comminuted leaves are macerated in water for twelve hours before being boiled.  
L. DE K.

**The Guaiacum Test for Blood and Similar Reactions.** O. SCHUMM (*Zeitsch. physiol. Chem.*, 1907, 50, 374—493).—With certain precautions, described in full, the guaiacum test is applicable for the detection of blood, and is trustworthy. Special attention is directed to the detection of blood in fæces and in bile.  
W. D. H.

**Can Horseflesh be Detected by Glycogen Estimation?** WILHELM RUSCHE (*Pflüger's Archiv*, 1907, 116, 347—367).—Niebel's statement that horseflesh can be detected by its high amount of glycogen is stated to be fallacious.  
W. D. H.

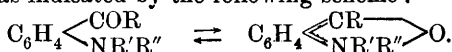
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## General and Physical Chemistry.

**Spectrochemistry of Nitrogen.** OTTO SCHMIDT (*Zeitsch. physikal. Chem.*, 1907, 58, 513—540. Compare Abstr., 1903, i, 681; 1905, i, 213).—The author has extended his earlier work (*loc. cit.*) in the direction of greater detail and accuracy, and arrives at the following results for the optical constants of the nitrogen atom and the  $N_2O$  group; the numbers given refer to the nitrogen atom, except those in the last three lines which refer to the  $N_2O$  group:

	$r_a$ .	$r_D$ .	$r_\gamma - r_a$ .
Primary aliphatic formylamines .....	2.51	2.64	0.12
"    "    urethanes .....	—	2.27	—
Secondary    "    formylamines .....	2.69	2.81	0.15
"    "    urethanes .....	2.25	2.31	0.10
Tertiary    "    formylamines .....	2.67	2.76	0.20
"    "    urethanes .....	2.51	2.51	0.10
Secondary aromatic formylamines .....	—	4.16	—
"    "    urethanes .....	—	3.45	—
Tertiary    "    formylamines .....	2.72	3.00	0.56
"    "    urethanes .....	2.50	2.57	0.36
Tertiary aliphatic nitrosoamines .....	7.92	8.06	0.55
"    aromatic    "    .....	8.65	8.97	1.43
Nitrosoalkylurethanes .....	8.18	8.25	0.61

It is further shown from a study of homologous aliphatic formylamines, urethanes, and nitrosoamines that the value of  $r_D$  for the  $\cdot CH_2 \cdot$  group is 4.663, somewhat greater than the value 4.603 given by Conrady. The atomic refraction and dispersion of nitrogen in the acid amides vary with the nature of the acid radicle which is linked to the nitrogen; they are sometimes smaller, sometimes greater, than in the corresponding amines. The phenomena observed with the derivatives of anthranilic acid and the methyl-*o*-aminobenzaldehydes may be satisfactorily interpreted by supposing that they are capable of tautomerism as indicated by the following scheme:



The relationships here involved are similar to those occurring in the case of the nitroanilines. J. C. P.

**Spectrum Analysis of the Light Emitted by Radium Bromide Crystals.** F. HIMSTEDT and GEORG MEYER (*Chem. Zentr.*, 1907, i, 617; from *Physikal. Zeitsch.*, 1906, 7, 762—764. Compare Abstr., 1906, ii, 62).—When the collimator tube was filled with dry air or helium the photographs of the spectra of the light from radium bromide crystals, not only showed the continuous spectrum of the phosphorescent light of the crystals, but also bands which proved that the gas about the crystals had emitted light; this was not the case, however, when carbon dioxide, carbon monoxide, or hydrogen was used. The effect is due to the action of the  $\alpha$ -rays on the gases. Radium emanation causes the nitrogen of air to form a band spectrum;  $\beta$ -rays have no effect. E. W. W.

**Band Spectra of Copper Halogen Salts.** RUDOLF DERICHSWEILER (*Chem. Zentr.*, 1907, i, 618; from *Zeitsch. wiss. Photograph. Photophys. Photochem.*, 4, 401—417).—The spectra of halogen salts of copper have been photographed from the yellow to the ultra-violet by using a small concave grating of 1 m. curvature. The salts were placed in a coal-gas oxygen flame, and in order to reduce the quantity of bromide or iodide which is dissociated, the salts were mixed with the corresponding ammonium salts; the dissociation of the iodide is greater than that of the bromide. The law that the squares of the molecular weights of nearly allied compounds vary inversely as the cubes of the differences of frequency in the case of those bands of the spectra of the compounds which correspond with one another when arranged in series was found to hold (compare Olmsted, this vol., ii, 210). E. W. W.

**Specific Rotations in Solution.** THOMAS S. PATTERSON and DAVID THOMSON (*Ber.*, 1907, 40, 1243—1259. Compare Patterson, *Abstr.*, 1906, ii, 61).—A reply to Walden (*Abstr.*, 1906, ii, 209), and a further criticism of that author's views.

Walden's statement that the molecular weight of methyl acetylmalate in methyl-alcoholic solution increases from 280.7 ( $c = 4.14$ ) to 350 in infinite dilution, is not in agreement with Beckmann's results. The present authors have determined the molecular weights of ethyl tartrate and methyl acetylmalate in methyl-alcoholic and in acetone solution, by the boiling point method, and have found them to increase slowly with increasing concentration. These esters have normal molecular weights also in benzene solution. On the other hand, the rotatory power varies with the solvent: ethyl tartrate in benzene,  $[\alpha]_D + 6.1^\circ$ ; in methyl alcohol,  $+11.5^\circ$ , and in acetone,  $+11.6^\circ$ ; methyl acetylmalate in benzene,  $[\alpha]_D - 32.5^\circ$ , in methyl alcohol,  $-24.7^\circ$ , and in acetone,  $-22.2^\circ$  (compare *Trans.*, 1902, 81, 1107). The results of a series of determinations of the specific rotations and molecular volumes of methyl acetylmalate in the homogeneous state and in chloroform, benzene, and methyl-alcoholic solutions at different temperatures, show that the temperature coefficient is approximately inversely proportional to the specific rotation at  $20^\circ$  (compare Frankland and Pickard, *Trans.*, 1896, 69, 140; Patterson and Frew, *ibid.*, 1906, 89, 338). The rotatory power of the ester,  $[\alpha]_D^{20} - 22.8^\circ$ , is increased by dilution with methyl alcohol,  $[\alpha]_D^{20} - 26^\circ$ , or with benzene,  $[\alpha]_D^{20} - 33^\circ$ , but is diminished by chloroform,  $[\alpha]_D^{20} - 16.5^\circ$ , whilst the molecular volume at  $20^\circ$ , 170.3 c.c., is diminished by solution in methyl alcohol, 165 c.c., or chloroform, 163 c.c., but is increased slightly by solution in benzene, 172 c.c.

That a relationship does or does not exist between the molecular weight of a compound in solution and its rotatory power cannot be decided from a consideration of Walden's work. G. Y.

**Phosphorescence.** HENRI BECQUEREL (*Compt. rend.*, 1907, 144, 671—677. Compare this vol., ii, 213).—Comparison of the spectra emitted by phosphorescent uranium salts (1) at atmospheric temperature and (2) at the temperature of liquid air, show that under the latter condition the brightest portions of the spectrum are displaced towards the less refrangible end. It is not certain that this displace-



ment is the result of new luminous movements, and it may be due to a brightening of bands existing feebly in the spectrum emitted at the atmospheric temperature. Coincidence of the reinforced bands with feeble bands occurs in the cases of several salts, and although the more refrangible portion of each band becomes brighter at the lower temperature the less refrangible portion tends to become feeble or disappear under this condition.

The light vibrations of the various bands in the emission spectra are polarised in different directions (compare Abstr., 1886, 189; Sohneke, *Ann. Phys. Chem.*, 1896, [ii], 58, 417, and Pochinnetto, Abstr., 1905, ii, 430), indicating diversity in the orientation of the different periodical movements of the same electron.

Of the substances examined, only the uranium salts exhibit the above phenomena, crystals of ruby, Iceland spar, various platino-cyanides, and chlorophane, showing only more or less marked enfeebling of portions of the continuous spectrum due to phosphorescence.

The natural fluorites are known to become phosphorescent when heated, and in this condition exhibit in the phosphoroscope spectra consisting of discontinuous bands occurring in particular orders for different rates of rotation of the discs of the apparatus (Becquerel *La Lumière*, vol. i, 360), and Urbain has identified a number of these bands with those given by various rare earths (Abstr., 1906, ii, 28, 359, 449), but all the bands characteristic of any particular rare earth do not appear for any one rate of rotation of the phosphoroscope discs.

When the natural fluorites have been once rendered phosphorescent by heating to a high temperature they do not become phosphorescent on a second heating, but they regain this property in part by (1) exposure to light in the phosphoroscope, (2) by the action of cathode rays, or (3) by the passage of an electric spark. The extent to which this property can be restored by exposure of the warmed mineral to the cathode rays emitted by radium reaches a maximum after a few days, and is not noticeably increased by exposure even for two years. The restorative action of light and the electric spark is similarly limited (Becquerel, Abstr., 1900, ii, 126), and in all three cases is probably due to the formation, or destruction, of compounds the return of which to the primitive condition is the cause of the light emitted by the phosphorescent substances, and in favour of this view it is mentioned that certain of the bands in the spectra given by the minerals to which the property of phosphorescence has been restored by means of radium rays are brighter than those emitted by the mineral in its primitive condition. Two kinds of effects appear to be produced by the exciting rays: the one temporary and destroyed spontaneously with the emission of light; the other persistent at a given low temperature, but destroyed at higher temperatures with the production of light. The difference in persistence of the bands due to different elements, both in the phosphoroscope and on the application of heat, indicates that these elements are concerned in the occurrence of both the "temporary" and "permanent" effects. In the case of the fluorites the production of the permanent effect is independent of the colour, which is not

necessarily due to the active constituents. Some colourless fluorites may become highly phosphorescent, and certain kinds which are decolorised by heating regain their colours on exposure to radium rays. This chemical explanation of phosphorescence in fluorites is not applicable to the case of uranium, where the phenomenon appears to be intimately connected with the movements of electrons in the atom of uranium. The different effects of a lowering of temperature, which in the one case modifies certain chemical actions and in the other appears to augment the elasticity of the medium in which the luminous vibrations occur, accentuates this difference. Phosphorescence is exhibited by uranic, but not by uranous salts.

T. A. H.

**Some Radioactive Problems.** HEINRICH GREINACHER (*Chem. Zentr.*, 1907, i, 529; from *Natur. Rundsch.*, 1906, 21, 671—674).—Lilienfeld's spectroscopic method (*Ann. Physik*, [iv], 1905, 16, 931), by means of which 2% of helium may be detected in a mixture of gases, has been used to determine whether polonium (from Marckwald) contains helium. Helium did not appear to be present, however, although each  $\alpha$ -particle is supposed to form an atom of helium. It is possible that only the radioactive emanations undergo this change, and that the solid elements are not affected.

Since polonium sublimes above 600°, it would be interesting to examine the spectrum obtained by evaporation in Geissler tubes of quartz.

The radioactivity of other elements and methods of examination are discussed in the original paper.

E. W. W.

**Atomic Transformations of Radioactive Substances.** AUGUSTO RIGHI (*Arch. Sci. phys. nat.*, 1907, [iv], 23, 247—264).—A summary of the present knowledge of the transformations of radioactive substances.

H. M. D.

**Influence of the Velocity of the  $\alpha$ -Particle on the Stopping Power of the Substance through which it Passes.** WILLIAM H. BRAGG (*Phil. Mag.*, 1907, [vi], 13, 507—516).—The experiments described in the paper show that the stopping power of a metal increases with the speed of the  $\alpha$ -particle, and the more so the higher the atomic weight of the metal.

J. C. P.

**Disintegration Constant of Radiothorium.** GIAN ALBERTO BLANC (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 291—296).—The author has determined the rate of decay of the activity of a radiothorium preparation isolated from the mud of Echaillon (compare Angelucci, *Abstr.*, 1906, ii, 594), and composed mainly of ferric hydroxide, the activity and emanating power being about 3000 times as great as that of an equal weight of thorium hydroxide in the condition of radioactive equilibrium. As the preparation had been extracted about six months before use, it had attained the state of radioactive equilibrium between the radiothorium and thorium X.

The activity was found to fall rapidly during some forty-three days, after which the diminution became slower and proceeded according to

the expression  $I_t = I_0 e^{-\lambda t}$ . From this formula, by application of the method of least squares, the disintegration constant was found to have the value  $\lambda = 9.4 \times 10^{-4}$ , the time being expressed in days. The characteristic time required for one-half the number of atoms existing in a certain mass of radiothorium to become disintegrated is 737 days. The highest value of such characteristic time previously known was 143 days, that of polonium or radium *F* (compare Curie, *Abstr.*, 1906, ii, 143).

The only explanation which can be suggested of the relatively rapid fall in activity occurring during about the first one and a-half months is the presence of another radioactive substance which disintegrates more rapidly than radiothorium. Further investigations are to be made on this point.

T. H. P.

**Electrical Potential and Nature of Alloys.** NICOLAI A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, i, 13—54. Compare *Abstr.*, 1903, ii, 212).—An historical and also a theoretical survey of the subject is given, curves being drawn showing the connexion between the composition and resulting potential for the various possible cases, that is, when either one of the metals is soluble in the other when they are both soluble in one another, or when they form definite chemical compounds, and so on. If an alloy of the metals  $M_1 M_2$  be taken (of which  $M_1$  is the less electropositive) the only really efficient electrolyte would be a mixture of  $M_1 X$  and  $M_2 X$ , and from Nernst's formula,  $E = RT/n \log P/p$ , it is deduced that  $M_1$  will not cause the separation of  $M_2$  from its solution, only when

$$\frac{\text{concentration of the } M_2 \text{ ions}}{\text{concentration of the } M_1 \text{ ions}} = \frac{\text{pressure of solution } M_2}{\text{pressure of solution } M_1}.$$

Now the pressure of solution of say zinc  $= 9.9 \times 10^{18}$  and of copper  $= 4.8 \times 10^{-20}$  atmos. Consequently, the copper contained in solution must be  $2 \times 10^{-38}$  times less than the zinc, or practically  $= 0$ . This will hold for most pairs of metals, hence the only solution which can be employed usually is  $M_1 X$ , and it will be necessary to compare the potential of an alloy with that of the less electropositive metal, and not the higher one as Laurie did. All this is proved experimentally, but when a salt,  $M_1 X$ , is employed the *E.M.F.* is often too small; it has therefore been found best to use an acid or alkali which gives sparingly soluble salts with the metals investigated. The *E.M.F.* changes gradually in time, usually in the same direction, this being due (1) to the fact that in most cases there is no electrolyte in relation to which the alloy will have a constant potential; (2) to the change in surface of the electrodes, owing to the formation of layers of gases; (3) to the slow alteration of the electrolyte, and so on. The curve representing this change in *E.M.F.* is asymptotic and tends to a certain maximum, after which it remains practically constant. By determining the latter values and by employing a modified form of apparatus for measuring the potential, far more constant and accurate numbers are obtained than was the case in Laurie's (*Trans.*, 1894, 65, 1030) and Hershkwitch's (*Abstr.*, 1898, ii, 582) experiments. In order to determine how far it is possible to judge of the chemical nature of an alloy by observation of the changes in its potential,

alloys were investigated, the chemical constitution of which could be well established by other methods. Thus, in the case of silver and selenium, the potential of the mixture is nearly constant and equal to that of pure silver, but when the metals are present in the proportions necessary for the formula  $\text{Ag}_2\text{Se}$ , there is a sudden drop in potential, after which further addition of selenium causes little change in potential. The same is observed for silver and tellurium. Copper and tellurium form the compounds  $\text{Cu}_2\text{Te}$  and  $\text{CuTe}$ , which give solid solutions with one another; the reddish-violet compound found in Colorado, and containing 43% of tellurium, is really one of these solutions. Thus, contrary to Hershkwitch's statement, it is observed that the potential curve can indicate more than one definite combination of the two metals forming an alloy. Lead and tellurium form the compound  $\text{PbTe}$ , which forms solutions with lead, but the potential only reaches a constant value after about twenty-four hours. Tin and tellurium form the compound  $\text{SnTe}$ . All the substances here identified have definite chemical properties which show them to be homologues of silver sulphide,  $\text{Ag}_2\text{S}$ , and of lead sulphide,  $\text{PbS}$ , respectively.

Z. K.

#### Potential Differences between Manganese and Lead Peroxide and various Aqueous and other Solutions.

LOUIS KAHLENBERG and ALONZO S. MCDANIEL (*Chem. Zentr.*, 1907, i, 220—221; from *Trans. Amer. Electrochem. Soc.*, 1906, 9, 365—373).—In order to compare the differences of potential of peroxides of lead and manganese in various solvents, the solutions must have a sufficiently high conductivity and must contain the same electrolyte; solutions of lithium chloride in acetone, pyridine, amylamine, and water were found to fulfil these conditions. The electrode, prepared by depositing the peroxide electrolytically on platinum, was immersed in a one-eighth normal solution which was connected with a normal mercurous chloride electrode. By applying a correction of  $-0.56$  volt, the true difference of potential between the electrode and the solution was obtained. In many cases, and especially in aqueous solutions, a constant *E.M.F.* was only attained after several days. The differences between the values for organic liquids or mixtures of such liquids with water and those for water are in every case greater for lead peroxide than for manganese peroxide. Larger potential differences are found for acetone than for water, but in pure pyridine and amylamine the constants are lower; manganese dioxide in water gives  $-0.978$ ; in acetone,  $-1.137$ ; in pyridine,  $-0.698$ , and in amylamine,  $-0.476$  volt. The presence of a small quantity of water has a great effect in the case of acetone, whilst for pyridine and amylamine the values increase but slowly as the quantity of water increases, so that the pure water constant is only attained when 90—100% of water has been added. When sulphuric acid is used instead of lithium chloride, the *E.M.F.* rises from  $-0.978$  to  $-1.566$  and from  $-1.196$  to  $-1.756$  volt for manganese and lead peroxides respectively.

Since Tower and Smith (*Abstr.*, 1896, ii, 142; 1897, ii, 45; 1900, ii, 331) have shown that Nernst's formula does not hold quantitatively for peroxide electrodes it has not been applied to the measurements.

The oxidation potentials of the peroxides of manganese and lead depend on the nature of the solvents and are less in basic solvents or in basic aqueous solutions than in pure water or in neutral solvents.

E. W. W.

**Photo-electric Fatigue.** WILHELM HALLWACHS (*Chem. Zentr.*, 1907, i, 605; from *Physikal. Zeitsch.*, 1906, 7, 766—770).—The formation of double electrical layers can only be considered as a secondary cause of the above phenomenon. Experiments with copper and cupric oxide in ordinary and in pure air have shown that ozone probably plays some part (*ibid.*, 1904, 5, 489). The same fatigue may occur in hydrogen as in air. The effects produced by evacuation, cooling, or heating point to the action of absorbed gas. The author has shown that the strong action of ozone depends neither on oxidation nor on contact electrical effects, and must therefore be due to a direct action on the electricity carrier; it is to be assumed that ozone has an extraordinary power of absorption for electrons.

E. W. W.

**Electrical Conductivity and Thermo-electric Power of Certain Compounds of the Heavy Metals.** KARL BÄDEKER (*Ann. Physik*, 1907, 22, 749—766).—For the determination of the electrical conductivity very thin layers of the substances examined were obtained by producing metallic mirrors on thin mica plates (0.01 millimetre thick) by cathodic disintegration and then subjecting the films to the action of vapours of various non-metallic substances. The compounds thus prepared appear under the microscope to be absolutely coherent, and this also agrees with their electrical behaviour. The thickness of the films was determined by weighing on a micro-balance, the thickness being of the order 100  $\mu\mu$ . The following values were obtained for the specific resistances at the room temperature. Cupric sulphide, 0.000125; cadmium oxide, 0.0012; silver sulphide at 200°, 0.0017; cuprous oxide, 40; cupric oxide, 400 (?); cuprous iodide, 0.045. With the exception of cuprous iodide, these compounds appear to conduct the current like the metals. In the case of the best conductor, cupric sulphide, the values of the temperature coefficient and of the ratio of the electrical to the thermal conductivity are very nearly the same as for the metals. On the other hand, cuprous iodide conducts electrolytically to an appreciable extent, and the increase in the conductivity with fall of temperature is much smaller than for the metals. Silver sulphide also conducts electrolytically below 175°, at which temperature it is transformed into a new modification which acts only as a metallic conductor. Measurement of certain thermoelectric combinations gave the following results between 0° and 100°: Cu—CuS, 7.33; CdO—Cu, 30; Cu<sub>2</sub>O—Pt, 480 micro-volts per degree.

H. M. D.

**Conduction of Electricity in Dilute Amalgams.** FRANZ SKAUPY (*Zeitsch. physikal. Chem.*, 1907, 58, 560—566).—If for an amalgam,  $c$  represents the number of gram equivalents of the metal per 100 grams of mercury,  $L$  the conductivity of the amalgam at 18° compared with that of mercury at the same temperature, and  $\lambda = (L - 1)/c$ , then the expression  $\lambda^2 c / \lambda_\infty (\lambda_\infty - \lambda)$  is a constant nearly

independent of dilution for amalgams containing lead, tin, bismuth, silver, and gold. In the case of zinc and cadmium amalgams, however, the value of the expression increases very markedly as the concentration increases. The equivalent conductivity at infinite dilution, that is  $\lambda_{\infty}$ , is approximately equal (mean value 0.8) for different metals, although to bring bismuth under this rule it must be assumed to be univalent. The experimental data used in establishing the foregoing conclusions are taken from the papers of Larsen (*Abstr.*, 1900, ii, 255) and others.

The foregoing conclusions can also be deduced theoretically from certain fundamental assumptions. Thus it is supposed (1) that substances exhibiting metallic conduction are partly dissociated into positive metal ions and negative electrons; (2) that the electrons are chiefly responsible for metallic conduction, their speed of migration being so much higher than that of the positive metal ions; (3) that the equilibrium between neutral molecules, ions, and electrons is governed by the mass action law; (4) that, in the case of amalgams, the metal is dissolved in diatomic form, but is largely dissociated into simple atoms, ions, and electrons.

J. C. P.

**Variation in the Conductivity of a Solution with Temperature.** FRIEDRICH KOHLRAUSCH (*Zeitsch. physikal. Chem.*, 1907, 58, 630—631).—A criticism of a statement made in a recent paper by Jones, Bingham, and McMaster (*ibid.*, 1906, 57, 314).

J. C. P.

**Abnormally High Values of Ionic Conductivity.** ARTHUR HANTZSCH and KENNETH S. CALDWELL (*Zeitsch. physikal. Chem.*, 1907, 58, 575—584. Compare Danneel, *Abstr.*, 1905, ii, 499).—Experiments are described showing that the conductivities of pyridonium salts in pyridine, of alkali formates in formic acid, and of alkali acetates in acetic acid, are much higher than the conductivities of alkali halides in the same solvents, although all the salts are dissociated to about the same extent in the different media. It seems to be a general rule that the conductivity of a salt which yields the same anion or the same cation as the medium in which it is dissolved is abnormally high. The explanation given for this phenomenon is similar to that already advanced by Danneel (*loc. cit.*).

J. C. P.

**Degree of Dissociation of Saturated Solutions of an Electrolyte in Various Solvents, and of Solutions in Partition Equilibrium.** JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1907, 58, 567—574).—Walden has recently shown (*Abstr.*, 1906, ii, 527) that the solubility of tetraethylammonium iodide in various ionising solvents is such that the degree of dissociation of the iodide has about the same value in each saturated solution. The author now proves that on thermodynamical grounds the degrees of dissociation of a given electrolyte when dissolved to saturation in various solvents must be approximately equal, and it is further pointed out that saturated solutions form a special division of the much more general class, in which the solutions are not saturated, but are in partition equilibrium. It is also shown that the ratio of the concentrations of a

given electrolyte when distributed between two solvents in partition equilibrium must be approximately the ratio of the dissociation constants of the electrolyte in the two solvents. This conclusion is none other than the Abegg-Bodländer relation between solubility and ionisation.

J. C. P.

**Anodic Solution of Copper and Mercury.** IWAN SHUKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, [viii], 1253—1257).—The most important factor in the mode of solution of the anode in the process of electrolysis is the behaviour of the electrolyte towards the products of solution formed. Thus in the case of copper, the cuprous salts readily form complexes with the electrolytes, sodium chloride, and hydrochloric acid, consequently a copper anode, in dissolving, produces mainly cuprous ions, especially if the current is weak and the solution is well stirred, with strong currents and without stirring, a considerable number of cupric ions are also formed, but the latter are diminished on stirring the solution. Mercury, on the other hand, gives complexes chiefly in the mercuric state, and consequently dissolves as such under the same conditions as are favourable to the formation of cuprous ions. With solution forming no complexes, copper dissolves chiefly in the cupric form, whilst with mercury,  $\frac{120}{121}$  of the total metal in solution is as mercurous, and  $\frac{1}{121}$  as mercuric, ions.

Z. K.

**Influence of Transverse Magnetisation on the Electric Conductivity of Metals.** LEO GRUNMACH and FRANZ WEIDERT (*Chem. Zentr.*, 1907, i, 605—606; from *Physikal. Zeitsch.*, 7, 729—740).—The change of resistance caused by magnetisation has been measured for silver, platinum, tantalum, cadmium, tin, gold, palladium, zinc, copper, lead, cobalt, nickel, and iron. Bifilar spirals of wire of 0.3 mm. diameter were used, the ends being soldered to copper strips and insulated by wax between ebonite plates; thinner wires were wound on mica and bedded in sealing-wax. The change of resistance caused by a magnetic fluid was measured directly by means of a galvanometer, the apparatus being arranged to give a differential effect. The para- and dia-magnetic metals showed an alteration of resistance which did not appear, however, to be connected with the magnetic susceptibility. The variations showed an initial acceleration as the strength of the field increased, but afterwards conformed to a linear function. In the cases of bismuth, cadmium, zinc, silver, gold, copper, tin, palladium, lead, platinum and tantalum, the change of resistance increased from the first-named to the last. The ferro-magnetic metals showed a different behaviour. The resistance of cobalt at once decreased, whilst that of iron had a considerable initial increase; it is doubtful, however, whether all kinds of iron would behave in the same way. The change of resistance was most marked in the case of nickel and least in that of iron. The initial increase of the resistance of nickel was very small.

E. W. W.

**Apparatus for Cryoscopic Determinations.** HENRI GIRAN (*Bull. Soc. chim.*, 1907, [iv], 1, 290—294).—An apparatus is described in which the cooling of the solution is brought about by the regulated

evaporation of methyl chloride. No figure is given, but the dimensions, method of using, and precautions to be observed are detailed in the original.  
T. A. H.

**A New Melting Point Apparatus.** JOHANNES THIELE (*Ber.*, 1907, 40, 996—997).—The apparatus figured consists of a glass tube 2 cm. in diameter and 12 cm. in length, the lower end of which is joined to its centre (like an inverted P) by a bent glass tube of 1 cm. diameter. Sufficient sulphuric acid is poured in to cover the upper opening of the bend, and the thermometer is adjusted with the bulb half way between the junctions of the bend with the main tube. Heat is applied to the bend, which causes circulation of the sulphuric acid. It is claimed that the rise in temperature is more even than in any other apparatus without mechanical stirring. If the rise in temperature is rapid, the small particles at the top of the capillary melt first and indicate approach to the melting point.  
G. Y.

**Specific Heat of Saturated Vapours.** JOHN P. DALTON (*Phil. Mag.*, 1907, [vi], 13, 536—542).—If  $\gamma_{\infty} = C_p/C_v$  at large volume, then theoretical considerations lead to the following results. (1) Saturated vapours of substances for which  $\gamma_{\infty} > 1.202$  have always a negative specific heat; (2) saturated vapours of substances for which  $\gamma_{\infty} < 1.202$  have a specific heat, which, as the temperature rises, is first negative, then positive, and finally negative again; (3) in the limiting case, where  $\gamma_{\infty} = 1.202$ , the two inversion points coincide, and the specific heat is then always negative except at one temperature, at which it becomes zero. Consideration of the experimental data available in the case of isopentane shows that the foregoing three propositions are confirmed in a general way, but that the limiting value of  $\gamma_{\infty}$  for normal saturated vapours is to be taken about 1.139 instead of 1.202. In the case of abnormal substances such as methyl alcohol, the limiting value of  $\gamma_{\infty}$  is much lower still.  
J. C. P.

**Specific Heats of Liquids which Solidify at very Low Temperatures.** ANGELO BATTELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 243—257).—The author has determined the specific heats of ether, toluene, ethyl bromide, light petroleum (b. p. 35—40°), ethyl and amyl alcohols, and carbon disulphide at various low temperatures. The substance was introduced in the solid state into a cylindrical Dewar's vacuum-jacketed vessel which had been cooled previously by means of a little liquid air, and after liquefaction its temperature was measured by two copper-constantan thermo-couples, one placed at the bottom and the other just below the surface of the liquid. A known amount of heat was then transmitted to the liquid by means of an electric current passing through a spiral of metallic wire. The change of temperature, after suitable correction, gives the specific heat.

The results obtained are as follow, the temperatures given being mean temperatures which vary 3° or 4° at most from the extreme temperatures.

For ether: 0.514 at -91.37°, 0.516 at -74.5°, 0.517 at -50.05°, 0.519 at -36.1°, and 0.523 at -21.3°.



For toluene: 0.353 at  $-92.02^{\circ}$ , 0.355 at  $-83.44^{\circ}$ , 0.357 at  $-71.52^{\circ}$ , 0.360 at  $-62.8^{\circ}$ , 0.365 at  $-47.37^{\circ}$ , 0.380 at  $-25.0^{\circ}$ .

For ethyl bromide: 0.195 at  $-105.47^{\circ}$ , 0.196 at  $-89.45^{\circ}$ , 0.199 at  $-66.32^{\circ}$ , 0.202 at  $-39.62^{\circ}$ , and 0.205 at  $-28.82^{\circ}$ .

Light petroleum (b. p.  $35-40^{\circ}$ ): 0.588 at  $-161.2^{\circ}$ , 0.592 at  $-126.91^{\circ}$ , 0.596 at  $-96.15^{\circ}$ , 0.601 at  $-74.15^{\circ}$ , 0.604 at  $-52.95^{\circ}$ , and 0.608 at  $-25.55^{\circ}$ .

Ethyl alcohol: 0.457 at  $-90.7^{\circ}$ , 0.459 at  $-82.67^{\circ}$ , 0.463 at  $-71.2^{\circ}$ , 0.486 at  $-38.37^{\circ}$ , and 0.497 at  $-27.97^{\circ}$ .

Amyl alcohol: 0.455 at  $-49.15^{\circ}$ , 0.462 at  $-40.2^{\circ}$ , 0.469 at  $-31.7^{\circ}$ , 0.473 at  $-27.3^{\circ}$ , 0.480 at  $-19.4^{\circ}$ , and 0.492 at  $-9.55^{\circ}$ .

Carbon disulphide: 0.195 at  $-95.75^{\circ}$ , 0.194 at  $-71.15^{\circ}$ , 0.196 at  $-59.4^{\circ}$ , 0.201 at  $-44.2^{\circ}$ , 0.213 at  $-26.54^{\circ}$ , 0.217 at  $-18.23^{\circ}$ , and 0.238 at  $+0.09^{\circ}$ .

The curves representing these values tend to become asymptotic to lines parallel with the axis of temperature. T. H. P.

### Variation of Specific Heats with Temperature and Density.

JOHN P. DALTON (*Phil. Mag.*, 1907, [vi], 13, 525—535).—The manner in which the specific heats are affected by deviations from the gas laws has been deduced from van der Waals' equation. The deductions made are confirmed by the values of  $C_p - C_v$  and  $C_p/C_v$  in the case of ethyl ether, calculated from available experimental data. As regards the variation of  $C_v$  with the volume in the case of ethyl ether the following deductions are made: (1) in the liquid state,  $C_v$  varies with the volume more than with the temperature, of which it is practically independent; (2) in the gaseous state and at large volumes,  $C_v$  is independent of the volume and becomes a function of the temperature only; (3) with increasing density,  $C_v$  at first increases; in the neighbourhood of the critical volume, it attains a maximum, and as the density is still further increased, it diminishes. Further confirmation of the results deduced from van der Waals' equation is supplied by available data for air and carbon dioxide. J. C. P.

**Inversion Temperature of the Joule-Kelvin Phenomenon for Air and Nitrogen.** KARL OLSZEWSKI (*Bull. Acad. Sci., Cracow*, 1906, 792—796).—The temperature has been determined at which a change in the sign of the heat effect takes place when air and nitrogen are allowed to undergo adiabatic expansion from a series of pressures ranging from 20 to 160 atmospheres to the ordinary atmospheric pressure. For the measurement of the small temperature differences an iron-constantan thermo-element, giving 1 mm. galvanometer scale deflection for  $0.2^{\circ}$ , was employed. The inversion temperature in the case of air falls from  $259^{\circ}$  at an original pressure of 160 atmospheres to  $124^{\circ}$  at 20 atmospheres. For nitrogen obtained from air, it falls from  $243^{\circ}$  at 159 atmospheres to  $163^{\circ}$  at 30 atmospheres. The observed variation of the inversion temperature with the initial pressure explains the fact that the liquefaction of air in the usual liquefying apparatus is not effected if the original pressure falls below 80 atmospheres.

H. M. D.

**The Law of Corresponding Limiting Curves, and especially the Behaviour of Diatomic Substances.** HANS HAPPEL (*Physikal. Zeitsch.*, 1907, 8, 204—209).—The author discusses the behaviour of

different types of substances in regard to the reduced equation of condition. When the reduced pressures of the saturated vapours are plotted as ordinates and reduced temperatures as abscissæ, the reduced vapour pressure curves obtained for the majority of tri- and poly-atomic substances are very nearly coincident. The curves for the monatomic substances, argon, krypton, xenon, and mercury are also close to one another, but deviate considerably from the first curve. Utilising the experimental data for oxygen, nitrogen, carbon monoxide, and hydrogen chloride, it is found that the reduced vapour pressure curves for the diatomic substances occupy an intermediate position. A similar dependence on the number of atoms in the molecule is exhibited by the value of  $RT_k/p_k v_k$ . For polyatomic substances of the fluorobenzene group the value of this factor is 3.75, for oxygen, nitrogen, and carbon monoxide it is 3.36, and the data for argon give 2.86 or 3.09 according to the method used in obtaining the value of  $v_k$ .

The author also discusses the bearing of the results on Eötvös's rule, according to which the temperature coefficient of the molecular surface energy has the same value for non-associated substances. It is pointed out that the value of the constant is different for the groups of substances which exhibit variable amounts of deviation from the reduced equation of condition, that is to say, for monatomic, diatomic, and polyatomic substances.

H. M. D.

**Saturation Constants, according to van der Waals' Equation.** JOHN P. DALTON (*Phil. Mag.*, 1907, [vi], 13, 517—524).—The author uses various available methods for the deduction of the saturation constants  $\theta$ ,  $\pi$ ,  $\omega_1$ , and  $\omega_2$ ; the calculated values of these constants are tabulated and tested by reference to (1) van der Waals' vapour pressure law:  $\log \pi = f(1 - 1/\theta)$ , and (2) Cailletet and Mathias' law of the rectilinear diameter.

J. C. P.

**Calorimetric Studies. I. Determination of Specific Heats of Pure Alcohols, of Mixtures of Water and Alcohols, and of Mixtures of Alcohols Alone.** EMIL BOSE [with A. MÜLLER] (*Chem. Zentr.*, 1907, i, 233—234; from *Nachr. k. Ges. Wiss. Göttingen*, 1906, 278—308).—In order to test the accuracy of Nernst's formula connecting heats of mixture and vapour tension of mixtures with those of the components, the specific heats of alcohols have been determined by the electrical method. By completely surrounding the calorimeter with a vessel through which water circulated at a constant temperature, the apparatus could be used at higher temperatures. A thermometric heating stirrer served the purposes of thermometer, stirrer, and heating spiral.

Whilst the older data for the specific heat of ethyl alcohol are expressed by the formula  $c = 0.5323 + 0.002518t$ , the authors' results are better represented by  $c = 0.5396 + 0.001698t$ , and for propyl alcohol by  $c = 0.5279 + 0.001692t$ ; the temperature coefficients being almost the same in both cases. For methyl alcohol,  $c = 0.5634 + 0.002715t - 0.0000376t^2$ , but the data are possibly less trustworthy,

owing to the volatility of the alcohol. The specific heat of mixtures of water with ethyl alcohol, propyl alcohol, and methyl alcohol respectively have been determined, as well as for mixtures of ethyl alcohol and propyl alcohol, ethyl and methyl alcohols, and propyl and methyl alcohols. Since the specific heat of a mixture of alcohols is very nearly equal to the value calculated from the specific heats of the components, the temperature coefficient of the heat of mixture must be very small.

E. W. W.

**Calorimetric Studies. II. Heat Toning of Mixtures of Alcohols and Water, and of Mixtures of Two Alcohols.** EMIL BOSE [with MARGRETE BOSE] (*Chem. Zentr.*, 1907, i, 234; from *Nachr. k. Ges. Wiss. Göttingen*, 1906, 309—334. Compare preceding abstract).—The heat toning of mixtures of ethyl alcohol and water at 0° is considerable, but decreases rapidly as the temperature is raised; at temperatures above 40° it is negative for mixtures in which the proportion of alcohol is the larger. For propyl alcohol and water the heat toning is negative even at 0°, and above 44° mixtures containing the lowest proportions of alcohol are formed with absorption of heat. In the case of the system, methyl alcohol and water, however, the heat effect does not change its sign. The heats of mixture of methyl and ethyl alcohols, methyl and propyl alcohols, and of ethyl and propyl alcohols are very small and are only slightly affected by temperature.

E. W. W.

**Calorimetric Studies. III.** EMIL BOSE (*Chem. Zentr.*, 1907, i, 234; from *Nachr. k. Ges. Wiss. Göttingen*, 1906, 335—350. Compare preceding abstracts).—The data obtained in the investigations described above are used to test the accuracy of the thermodynamic relationship, according to which the difference of the specific heats of the unmixed substances and of the mixture must be equal to the change of the heat of mixture with the temperature. In the case of the experiments made at 0°, the agreement is very good, but at higher temperatures it gradually becomes worse, especially in the case of mixtures of methyl alcohol and water; the divergence may, however, be due to errors caused by the volatility of the alcohols. From Nernst's formula it follows that in the simple case of mixtures of methyl alcohol and ethyl alcohol in which the curves of partial pressure and the vapour pressure curve of the mixture are straight lines, the heat of mixture is nearly *nil* for a small range of temperature, and the experimental results confirm this deduction.

E. W. W.

**The Hydrolytic Decomposition of Sodium Chloride as a Lecture Experiment.** FRIEDRICH EMICH (*Ber.*, 1907, 40, 1482—1483. Compare Spring, Abstr., 1885, 480).—A small amount of solid sodium chloride is introduced first into a red hot platinum crucible (*t* about 1100°) and then 1 c.c. of water which assumes the spheroidal state. After some thirty seconds about half the water has evaporated, and if the remaining drop of water is poured into 100 c.c. of a very dilute blue litmus solution, the presence of free acid (hydrochloric) in the water can be established. If the solid salt is dissolved in water before the

crucible has completely cooled, the solution can be shown to be alkaline. The alkaline reaction can also be shown by fusing a small amount of sodium chloride on platinum foil and allowing the flame to play on the salt. The moisture from the flame causes hydrolysis, and the solution of the salt in water is distinctly alkaline. J. J. S.

**Measurement of Surface Tension in Contact with Air.** TH. RENARD and PHILIPPE A. GUYE (*J. Chim. phys.*, 1907, 5, 81—112).—The capillary rise of various liquids has been measured in a vacuum according to Ramsay and Shield's method, and also in contact with the atmosphere. The calculated values of the molecular surface energy obtained from the two series of experimental data do not differ by more than 0.5%. The measurement in free air is recommended as being much simpler than the determination in evacuated apparatus, and values for the surface tension and the molecular surface energy as thus measured at a series of temperatures are given for benzene, toluene, *m*-xylene, mesitylene, cymene, chlorobenzene, *o*-cresol, *m*-cresol, anisole, phenetole, anethole, acetonitrile, propionitrile, butyronitrile, benzonitrile, aniline, dimethylaniline, pyridine, quinoline, ethyl, propyl, isobutyl and amyl alcohols, linalool, ethyl acetate, amyl acetate, methyl isobutyrate, ethyl hexoxymalate, methyl benzoate, acetone, methyl propyl ketone, methyl propyl ketoxime, and carbon tetrachloride. The method is not applicable to substances which oxidise readily or are hygroscopic, and is limited to temperatures below the boiling points of the various liquids. H. M. D.

**Surface Tension in the Critical Regions of Solutions.** G. N. ANTONOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1258—1266).—The two systems, aniline and amylene, isobutyric acid and water, have been investigated in detail. For temperatures above the critical, the surface tension, like the vapour pressure, is, within limits, independent of the concentration. For temperatures just below the critical, experiments show that, contrary to Ostwald's and Whatmough's supposition (*Abstr.*, 1902, ii, 125), the two layers have practically the same surface tension, however different their composition may be from one another. Curves are drawn showing the relation of surface tension to the temperature and also to composition. Z. K.

**Separation of Liquids into Layers under the Influence of Various Salts.** V. I. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, i, 78—102. Compare *Abstr.*, 1906, ii, 839).—Tables and curves are given showing the effect of various salts on the separation of solutions into layers at different temperatures, and also of the solubility of various fractions of butyric acid in water. It is pointed out that the results obtained in this investigation are in complete accordance with those obtained regarding the deviations of strong electrolytes from the law of mass action, the varying colours, &c., which all point to the association of the ions of the solute with the solvent. Z. K.

**Determination of the Reciprocal Actions of Substances in Solutions by their Vapour Pressures.** DMITRI P. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, i, 54—78).—When the solution

of one substance in another is accompanied by a fall in the vapour pressure it is usually ascribed to the formation of definite chemical compounds, but there are many solutions where, whilst all other facts indicate the occurrence of chemical reactions, there is a rise in the vapour pressure. For weak solutions the latter might be explained by assuming the polymerisation of the dissolved molecules, but this will not hold for concentrated solutions. In order to generalise all these phenomena, all solutions are regarded as subject to the same laws as those which govern the formation of chemical compounds, and the increase or decrease of the vapour pressure as being due to the reciprocal reaction of solute and solvent. The nature of these reactions can be determined by studying the change in the partial vapour pressures accompanying the change in constitution of the solution. Starting with the equation  $p = Px \pm Kf$  [where  $P$  = vapour pressure of the pure liquid  $x$ ,  $p$  = its partial vapour pressure, and  $f = x(1-x)$ ,  $x(1-x)^2$ , and so on], then it is found that for  $f = x(1-x)$ ,  $p - Px$  is a maximum when  $x = \frac{1}{2}$ , for  $f = x(1-x)^2$ ,  $p - Px$  is a maximum when  $x = \frac{1}{3}$ , and so on. For most solutions,  $p - Px$  is a maximum when  $x = \frac{1}{3}$ , and the relation of the partial pressure to the constitution will be represented by the equation I,  $p = Px + k_{11}Px(1-x)^2$ . The experimental values obtained for many pairs of liquids where no association takes place agree closely with those calculated from this equation; where, however, the association of molecules do occur, the experimental results are in accordance with the equation  $p = Px + k_1Px(1-x) + k_{11}Px(1-x)^2$ , and even for the non-associated solution still better results are obtained by introducing the term  $k_1x(1-x)$  into equation I, so that  $p = Px + K_1Px(1-x) + k_{11}Px(1-x)^2$ , in order to take account of the slight association which actually takes place in most cases. Thus the degree of association of any given solution can be determined by comparing the experimental partial vapour pressure with that which corresponds with formula I, and, given the vapour pressure and composition of any one solution, it is possible to calculate by equation I: (1) the vapour pressure of a solution at any concentration; (2) the partial pressure of the constituents. The magnitude of  $k_{11}$  depends on the nature of the two liquids. The experimental results for ethyl bromide and butyric acid correspond with the equation  $p = Px + k_1Px(1-x)$ . Equation I is also applicable to the solutions, aniline and amylene, isopentane and *n*-butyric acid, in the critical regions, at the critical point  $dp/dt = 0$ ;  $dk/dx = 0$  where  $t$  denotes the temperature. If  $p_{kp}$  denotes the critical partial pressure and  $x_{kp}$  stands for  $x$  at the critical point, then  $p_{kp} = 2x_{kp}^2/(3x_{kp} - 1)P$ , the calculated value of  $p_{kp}$  being very close to what might be expected from observations of the partial pressures just below and above the critical point. The simplest equation which represents  $k_{11}$  as a function of  $x$  and  $1-x$  is  $k_{11} = k_2[x^2 + n(1-x)^2]$ ;  $k_{11}$  and  $n$  vary with the temperature, and the more  $n$  approximates to unity, the lower is the critical temperature of the solution.

Z. K.

**Superfusion and Supersaturation.** LOUIS C. DE COPPET (*Ann. Chim. Phys.*, 1907, [viii], 10, 457—527)—In the theoretical part of the paper the author replies to certain objections raised by Ostwald (*Lehrb.*

*Allg. Chemie*, 1891, i, 966, 995—996) against the kinetic theory of superfusion and supersaturation (Abstr., 1876, 184) and shows (1) that the theory is not incompatible with the existence of the *metastable* state of a substance in fusion or solution; (2) that sodium salts form supersaturated solutions more readily than potassium salts, because they also more readily form hydrates, and (3) that more sparingly soluble salts do not so readily form supersaturated solutions as the more soluble salts, because the latter are usually dimorphous or exist in several hydrated forms.

The experimental part of the paper is occupied with a record of observations made during a period of thirty-three years on the temperatures at which superfused liquids or supersaturated solutions crystallised; on the relation between the mass of the superfused liquid or supersaturated solution and the mean duration of the superfusion or supersaturation, and on the effect of shaking such solutions. The experiments were conducted on superfused phenyl salicylate, and supersaturated solutions of sodium bromide, and sodium sulphate. Known weights of the liquids were sealed in tubes of varying diameter and length, placed in a room with a north aspect in which the mean difference between the maximum and minimum daily temperature was  $0.8^{\circ}$ , and examined daily for a period of several months during the years 1873—1874 and 1900—1906.

Phenyl salicylate, m. p.  $42.6^{\circ}$ , can remain superfused at the ordinary temperature during several years; the temperature limits between which spontaneous crystallisation occurs are  $7^{\circ}$  and  $25^{\circ}$ ; the mean duration of superfusion is generally longer in specimens which have been superfused at temperatures above  $100^{\circ}$  than in those at above  $80^{\circ}$ ; small quantities remain superfused for a longer period than larger quantities, and shaking does not induce crystallisation in the superfused liquid.

Solutions of sodium bromide saturated with the hydrate  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  at  $30^{\circ}$  crystallise spontaneously at temperatures between  $5^{\circ}$  and  $16^{\circ}$ ; at temperatures above  $19^{\circ}$  it is in the metastable state; solutions saturated with  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  at  $39.7^{\circ}$  crystallise more readily than the dilute solution. Mechanical shaking does not provoke crystallisation in either of the solutions.

Solutions of sodium sulphate saturated with  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  at  $19.3^{\circ}$ , or with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  at  $31^{\circ}$ , deposit crystals of the heptahydrate between  $5^{\circ}$  and  $13.4^{\circ}$ , and it changes to the metastable state at  $14$ — $15^{\circ}$ ; the decahydrate crystallised from the solution in one case at  $23^{\circ}$ , but in solutions saturated with the decahydrate at  $31^{\circ}$  the decahydrate only crystallised once in twenty-five years. The addition of sodium chloride (one-twentieth gram-mol.) to saturated solutions of sodium sulphate tends to diminish the mean duration of supersaturation, whilst the addition of potassium chromate, cupric chloride, resorcinol, mannitol, or powdered silica causes an increase in the duration (Abstr., 1901, ii, 384).  
M. A. W.

**Rate of Growth and Solution of Crystals.** IWAN ANDRÉEFF (*Zeitsch. Kryst. Min.*, 1907, 43, 39—42).—The rates of growth of crystals were determined by weighing. The difference in the rates of

solution and of growth on different faces was demonstrated by covering the remaining surfaces of the crystal with platinum foil before immersing it in the liquid.

L. J. S.

**Formation of Crystals under Peculiar Conditions.** RAPHAEL E. LIESEGANG (*Zeitsch. physikal. Chem.*, 1907, 58, 541—542).—A glass plate was covered thinly with a solution of 30 grams of gelatin in 400 c.c. of water containing 5 grams potassium dichromate. When the gelatin had dried, it was found to be clear and free from crystals. A drop of water was put on the gelatin layer, and about half a minute thereafter a ring of fine crystals appeared round the drop and moved gradually further off from the drop. Instead of a drop of water, drops of 1% sodium chloride solution and 5% potassium dichromate solution were used with similar effect. No satisfactory explanation of the phenomenon has been found.

J. C. P.

**A Tetracomponent System with Two Liquid Phases** FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 607—612).—The possibilities of the system: water, ethyl alcohol, lithium sulphate, and ammonium sulphate are discussed in detail, the equilibria occurring in this quaternary system at 6.5°, 30°, and 50° being represented graphically.

W. H. G.

**Substances with Several Solid and Several Liquid Phases.** DANIEL VORLÄNDER (*Ber.*, 1907, 40, 1415—1432. Compare Abstr., 1906, i, 316).—There is a close connexion between the chemical constitution of a substance and the appearance of a crystalline liquid phase, but the problem is more complicated when there are two solid modifications; the conditions which hold good for several liquid phases are not those required when different solid forms exist.

*p*-Nitrodiphenyl, azoxydiphenyl, and anisylideneaminodiphenyl form crystalline liquids, the substituent phenyl in the para-position giving rise to the crystalline liquid condition. The unstable modification of *p*-nitrosodimethylaniline forms plates which pass into the more prismatic and darker coloured form by heat. With *p*-nitrosodiethylaniline, only one solid phase was observed. Ethyl *p*-azoxyphenoxyacetate, prepared by the reduction of ethyl *p*-nitrophenoxyacetate with zinc dust, exists in plates or prisms, the prismatic form melting at the higher temperature. The two solid phases can also be observed in *p*-azoxyacetophenone, ethyl *p*-azoxybenzenesulphonate, *p*-aminoazobenzene, *p*-dimethylaminoazobenzene, *p*-methoxydimethylaminoazobenzene, ethyl *p*-acetylaminocinnamate, anisylidene-*p*-chloroaniline, anisylidenequinoline, the product from 1 mol. isatin and 1 mol. *p*-anisidine - H<sub>2</sub>O, anisylidenephénylhydroxylamine, benzylidene-anisylhydroxylamine, the product from 1 mol. methoxytolualdehyde (Me : OMe : CHO = 1 : 2 : 5) and 1 mol. *p*-aminoacetophenone, quinoldiacetate (the corresponding diethyl ether, dibenzoate, and diethyl carbonate exist in one form only), *p*-dimethoxybenzophenone, *p*-dihydroxybenzophenone dibenzoate (probably), *p*-hydroxyacetophenone benzoate, and *p*-hydroxybenzylidene-*p*-hydroxyacetophenone dibenzoate.  $\beta$ -Ethoxynaphthalene- $\alpha$ -aldazine exists in two forms, whereas the  $\alpha$ -ethoxy-derivative has only one form.

The method of examination consists in supercooling the amorphous liquid melt and allowing crystallisation to occur. For the more sensitive substances, Lehmann's crystallisation microscope is indispensable.

The substances which can exist in two solid crystalline phases, one crystalline liquid phase and one amorphous liquid phase, include anisylidene-*p*-aminobenzoic acid (this vol., ii, 70), *p*-azoxyanisole, of which the new solid unstable modification is almost colourless, the ordinary form being yellow (*p*-azoxyphenetole apparently only exists in one solid form), *p*-anisylidene-anisylhydroxylamine, *p*-anisylidene-phenethylhydroxylamine, *p*-nitrobenzylidene-*p*-phenetidine, *p*-azophenyl benzoate, and ethyl *p*-azophenol carbonate.

The ethyl cinnamate nucleus, in combination with other unsaturated groups like  $\text{N:N}, \text{O} < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$  or  $\text{C:N}$ , leads to three crystalline solid phases, one crystalline liquid and one amorphous liquid phase. The condensation product obtained from methoxytolualdehyde ( $\text{Me}:\text{OMe}:\text{CHO} = 1:2:5$ ) and ethyl *p*-aminocinnamate has three solid modifications.

Ethyl *p*-azocinnamate exists in at least three liquid and three solid phases. On heating the solid, it changes first into another solid phase, then it melts to a crystalline liquid, II; on further heating, it begins to change into another crystalline liquid, I, and, finally, into the amorphous liquid. On cooling the amorphous liquid, a crystalline solid, I, can be obtained from crystalline liquid I in dark coloured fibres; this solid, by repeated melting and crystallising, is converted back into the pseudo-isotropic crystalline liquid II, which does not yield solid I on supercooling, but a new crystalline solid II, crystallising in plates and lighter in colour than I. This solid II passes by heat into prismatic form III. The m. p. of solid III is probably between those of I and II.

The paper concludes with a summary of the results hitherto obtained and their connexion with the chemical constitution. W. R.

**Catalysis by Chromic Acid and its Salts.** EUGEN SPITALSKY (*Zeitsch. anorg. Chem.*, 1907, 53, 184—199).—The velocity of decomposition of hydrogen peroxide by the chromates of potassium at 25° has been investigated by measuring the rate of evolution of oxygen by means of the arrangement described by Walton (Abstr., 1904, ii, 319).

The reaction is in all cases purely catalytic. With potassium dichromate it is unimolecular, and the reaction velocity is also approximately proportional to the dichromate concentration, being, however, relatively rather more rapid in dilute solution. With normal potassium chromate the velocity is much smaller. The catalytic action of mixtures of chromate and dichromate in varying proportions has also been measured, but no simple relation between the composition of the solution and the velocity has been found; the rate is at first diminished, and then increased, by successive additions of small amounts of normal chromate to dichromate solutions.

To elucidate the mechanism of the reaction, a knowledge of the equilibrium relations in dichromate solutions is necessary, but there is a difference of opinion on this question. Whilst Ostwald considers



that dichromate solutions contain chiefly  $\text{Cr}_2\text{O}_7^{''}$  ions, Abegg and Cox (Abstr., 1904, ii, 662) contend that this ion is very weak, splitting up almost completely into  $\text{CrO}_4^{''}$  ions and undissociated  $\text{CrO}_3$  in solutions of moderate strength. The results of the kinetic experiments described above are incompatible with the views of Abegg and Cox, and the equilibrium relations in solutions of chromic acid and its salts are therefore being further investigated. [Compare also Sand and Kaestle, this vol., ii, 178.] G. S.

**New Gas-generating Apparatus.** E. STEIGER (*Chem. Zentr.*, 1907, i, 521; from *Zeitsch. Chem. Appar.*, 1, 752—753).—The apparatus consists of a two-necked Woulff's bottle, in each neck of which is fixed the drawn-out end of a cylinder. One cylinder, the taller of the two, serves with the bottle as the reservoir for the acid; in the shorter cylinder, which is fitted at the top with a cork through which passes a delivery tube with stopcock, the zinc or iron sulphide is placed on a perforated hard rubber plate resting on the bottom of the cylinder. The sulphuric acid contained in the Woulff's bottle and reservoir enters the short cylinder when the cock is opened. The heavy salt solution, which is formed by the action, is forced to the top of the liquid by the rising bubbles of gas, and passes thence to the bottom of the lower vessel by means of a long funnel tube which is supported by a rubber ring or by an ebonite plate. Owing to the better circulation thus obtained, the acid is more economically used than in the case of the ordinary Kipp's apparatus.

E. W. W.

**New Gas-generating Apparatus.** ALFRED BURGER and MARTIN W. NEUFELD (*Chem. Zentr.*, 1907, i, 521—522; from *Zeitsch. Chem. Appar.*, 1, 777).—The apparatus has been devised in order to have a ready means of obtaining the exact quantity of a gas which is required, a matter which is of importance, for example, in the case of a poisonous gas like selenium hydride. The solid is placed in a glass tube which resembles a test-tube in shape and size, but has a perforated bottom. The tube is fitted in a preparation glass or bottle which contains the acid, by means of a bung which has a side channel. By moving the tube up or down the solid is brought into contact or removed from the acid and the gas escapes through a delivery tube which is fitted to the inner tube by means of a cork. The escape of gas into the outer vessel is prevented by means of a glass tube 4—5 cm. long and about 2 cm. wide, which is sealed on to the tube containing the solid above the perforations so as to form a lower bell-shaped vessel with an open end.

The stream of gas may be regulated to a nicety by means of a cock which is formed by the cork which closes the inner tube and the bent delivery tube which passes through it. The latter is closed at the lower end, but has a small hole in the middle of the portion which is in the cork; a short distance above and below this hole the tube is slightly expanded so as to form two rings about 12 mm. apart which serve as guides when the tube is revolved about a vertical axis. The cork is bored radially so as to form a passage of about 2 mm.

diameter, the inner end of which is exactly opposite the hole in the glass tube, whilst the other end communicates with a vertical channel through which the gas passes from the generating tube. E. W. W.

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## Inorganic Chemistry.

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**Molecular Weight of Iodine and the Ebullioscopic Method in the Case of Comparatively Volatile Substances.** ERNST BECKMANN [with WERNER GABEL, F. KIRCHHOFF, OTTO LIESCHE, GEORG LOCKEMANN, and EREMIE POPA] (*Zeitsch. physikal. Chem.*, 1907, 58, 543—559. Compare Beckmann and Stock, *Abstr.*, 1895, ii, 382).—Cryoscopic measurements with benzophenone, benzil, and thymol show that the molecular condition of iodine in these solvents is to be represented as  $I_2$ .

The usual formula for the calculation of molecular weight by the boiling point method is  $M = Kg/\Delta$ , but where the solute volatilises along with the solvent, this formula must be replaced by  $M = (1 - a)Kg/\Delta$ , where  $a$  is the ratio of the concentrations of the volatile solute in the vapour and in the solution. The effect of iodine in raising the boiling point of various solvents has been determined in a specially constructed apparatus, by which it was possible to find the concentration of the iodine in the condensed vapour. The results obtained are summarised in the following table, in which the column "uncorr." gives the values of the molecular weight of iodine calculated by the ordinary formula, and the column "corr." gives those calculated by the formula  $M = (1 - a)Kg/\Delta$ .

Solvent.	B. p.	K.	$a$ .	Molecular weight.		Colour of the solution.
				Uncorr.	Corr.	
Tetrachloromethane ...	78·5°	48·8	0·318	369	252	reddish-violet
Chloroform.....	61·2	38·8	0·152	315	267	reddish-violet
Benzene .....	80·3	25·7	0·144	294	252	red
Ethyl acetate.....	75·5	27·9	0·121	279	245	brown
Methylal.....	41·0	20·4	0·014	257	253	brown

In the case of tetrachloromethane and chloroform, which dissolve iodine to a small extent, the values of  $a$  fall off somewhat as the concentration increases; this is not so in the case of the other three solvents.  
J. C. P.

**Thermal Relationships between Ozone, Nitric Oxide, and Hydrogen Peroxide.** III. FRANZ FISCHER and HANS MARX (*Ber.*, 1907, 40, 1111—1119. Compare this vol., ii, 163; *Abstr.*, 1906, ii, 845; Fischer and Braehmar, 1906, ii, 224).—The yield of ozone from a glowing Nernst filament immersed in liquid oxygen depends on the duration of the experiment; the highest % obtained after ten hours was 3·91. No conclusion as to equilibrium can be drawn from this

experiment. The paper contains sketches and description of the improved apparatus employed.

By blowing a stream of highly ozonised air over a glowing Nernst filament, the concentration of the ozone is diminished, but as only a small portion of the ozone actually reaches the temperature of the filament, the same percentage composition is not obtained when ozonised air is used as with ordinary air. The equilibrium at  $2000^{\circ}$  must be higher than 0.13% and lower than 0.40% ozone, calculating the ozone on the oxygen in the air. The assumption is made that the equilibrium is attained instantaneously.

W. R.

**Igniting Point of Sulphur.** J. RUTHERFORD HILL (*Pharm. J.*, 1907, [iv], 24, 358—359).—In an earlier paper (Abstr., 1890, 849) the author described an experiment which led to the conclusion that sulphur ignites in the air at  $248^{\circ}$  under the ordinary pressure. Blount (Abstr., 1890, 849) by means of a slightly modified apparatus found the ignition point to be  $261^{\circ}$ . Moissan, however, by an entirely different method (Abstr., 1904, ii, 25) obtained results indicating that the ignition point is  $282^{\circ}$  in oxygen and  $363^{\circ}$  in air. The author, who regards the latter results as untrustworthy owing to the abnormal conditions of the experiments, has now repeated his experiment and confirmed his previous result.

E. G.

**The Gases Contained in Sulphur.** HENRI MOISSAN (*Ann. Chim. Phys.*, 1907, [viii], 10, 433—436).—Malus has shown (Abstr., 1902, ii, 131) that sulphur fused at  $120^{\circ}$  contains bubbles of sulphur dioxide which can be removed by shaking and by reducing the pressure to 2—3 cm. of mercury; if, however, the sulphur is allowed to solidify under reduced pressure and again fused at  $120^{\circ}$ , a further quantity of gas is evolved, and similar results were obtained after eighty successive fusions.

In the present paper the author confirms the above results, and shows that the sulphur prepared according to Malus's instructions contains traces of iron (compare Biltz and Preuner, Abstr., 1902, ii, 132; von Hasslinger, Abstr., 1904, ii, 39), and that the gases evolved when the sulphur is fused consist of sulphur dioxide and hydrogen sulphide caused by the combined action of the sulphur and traces of water vapour on the glass vessel, for if the sulphur is carefully dried in a vacuum, sealed in a glass tube, and heated at  $160^{\circ}$  for thirty-six hours, no trace of solid sulphur dioxide is formed when the drawn-out end of the tube is cooled in liquid air (Abstr., 1904, ii, 25). If, however, the experiment is repeated on the same sulphur after exposure to the air for twenty-four hours, a small deposit of solid sulphur dioxide is obtained; if the sulphur contains a larger quantity of water and is heated at  $170^{\circ}$  for seventy-two hours, hydrogen sulphide is found in addition to the sulphur dioxide.

M. A. W.

**Difference of Selenium from Sulphur in the Stability of its Compounds.** A. VON BARTAL (*Chem. Zeit.*, 1907, 31, 347—348).—The marked difference between the stability of several sulphur compounds and that of the corresponding selenium derivatives is attributed by the

author to the preference which selenium exhibits for existing as a quadrivalent element, whereas sulphur exists rather as a bi- or sexa-valent element; selenium should therefore not be classed with sulphur, but rather with tellurium which it more closely resembles. W. H. G.

**Synthesis of Ammonia from its Elements by the Action of the Electric Spark. Influence of Pressure.** E. BRINER and E. METTLER (*Compt. rend.*, 1907, 144, 694—697).—The mixture of nitrogen and hydrogen was prepared by passing dry ammonia gas over an electrically heated spiral of nickel, platinum, or iron, and was freed from traces of ammonia by passage through sulphuric acid. When the mixture is sparked at the ordinary temperature, not more than 3 or 4% of ammonia is produced, but at the temperature of liquid air almost complete combination can be effected. The influence of pressures, ranging from 20 to 800 mm. of mercury, on the yield of gas was investigated and it was found that the maximum production occurred at a pressure of about 100 mm., when 0.17 gram of ammonia was produced per kilowatt hour. It is uncertain to what cause the occurrence of a maximum at this point is due, and it may be the result of equilibrium established between (1) the increase in the rate of production due to the increase of pressure, and (2) the decrease of electric conductivity with increase of pressure. It is conceivable, however, that as the result of change of pressure the energy expended between the electrodes does not always bear the same quantitative relation to the energy measured at the primary, and as the latter alone was taken into consideration in these experiments this factor may have some influence on the existence of a maximum. T. A. H.

**A [Probable] Case of Formation of Nitrogen Chloride.** FERNAND REPITON (*Ann. Chim. anal.*, 1907, 12, 96—97).—An organic copper compound had been ignited in an earthenware cupel in a muffle. The mixed carbon and copper oxide was treated with hydrochloric acid, and a little ammonia was afterwards introduced into the cupel to see if any copper could be extracted. When drained and replaced in the muffle a violent explosion soon took place and shattered the cupel into fragments. The author attributes this to the formation of a minute quantity of nitrogen chloride in the porous mass. L. DE K.

**Oxidation of Nitrogen by the Action of the Silent Discharge on Atmospheric Air.** EMIL WARBURG and G. LEITHÄUSER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 229—234).—In 1881 Hautefeuille and Chappuis observed the formation of a gas possessing a characteristic absorption spectrum when the silent discharge occurs in air. The same substance is formed when ozone and nitrogen pentoxide vapour react at 0—18°. The substance disappears after some time, and seems to be capable of existence only in presence of ozone. Rise of temperature accelerates its destruction and also increases temporarily the intensity of the absorption spectrum. At -79° the residual gas is free from the substance, but the white snow deposited, when evaporated, also yields none of it. The substance is absorbed by sulphuric acid, phosphoric oxide, or water, and partially

by very concentrated nitric acid. The absorption in the infra red of nitrogen pentoxide was measured and then ozone added to it until the spectrum of the new substance was plainly visible; the absorption in the infra red remained almost unchanged, showing that very little nitrogen pentoxide had combined with the ozone.

Nitrogen pentoxide is formed when the silent discharge acts on atmospheric air in relatively considerable quantities together with traces of the new compound; it is therefore impossible to say whether the new compound has the formula  $N_2O_6$  or not.

T. E.

**Catalytic Reactions Connected with the Transformation of Yellow Phosphorus into the Red Modification.** JACOB BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 613—620).—Aluminium chloride brings about the transformation of yellow phosphorus into the red modification in vacuum tubes below  $100^\circ$ . The action proceeds more regularly if benzene (or still better phosphorus trichloride) is added as a solvent, the transformation at the boiling point of the solvent being complete in a few hours (or minutes respectively), the product produced being similar to that obtained by Schenck (*Abstr.*, 1902, ii, 205), but much contaminated with benzene and condensation products. The author does not agree with the conclusions arrived at by Schenck and Buck (*Abstr.*, 1904, ii, 117), but considers that the transformation of yellow phosphorus into the red modification is preceded by a decomposition of the  $P_4$  molecule into more simple particles ( $P_2$  or  $P$ ), which at once condense to the red modification. The reaction may be represented thus: (1)  $P_4$  (yellow)  $\rightarrow 2P_2$ , (2)  $nP_2 \rightarrow P_{2n}$ , in which the reaction velocity of (2) is considerably greater than that of (1). The action of the catalyst on the yellow phosphorus is to accelerate the dissociation of the  $P_4$  molecule, and, in general, the author considers that the formation of intermediate products can never lead to an explanation of the catalytic phenomena, but that catalysts act by accelerating dissociation in some as yet unknown manner.

W. H. G.

**Preparation of Colloidal Silicic Acid.** B. KEMPE (*Chem. Zentr.*, 1907, i, 392; from *Zeitsch. Chem. Ind. Kolloide*, 1, 43—44).—The preparation of colloidal silicic acid from the ethyl ester is not to be recommended, owing to the slowness of the hydrolysis; the reaction was not complete when 3 grams of the ester were treated with 400 c.c. of water for twelve to fifteen hours. When the ester is heated with water at  $120^\circ$ , silica separates in coarse grains and only a small portion remains in solution. Kühn's method is simplified by rapidly pressing the silica which has been precipitated by hydrochloric acid or carbon dioxide from very dilute solutions on a perforated porcelain funnel, washing, and then dialysing. If the hydrochloric acid is not added slowly and the solution vigorously agitated the precipitate contains silicate. Platinum vessels should be used and the distilled water should be distilled a second time. Solutions containing 0.5—1.2% of silica may be obtained by boiling commercial samples of silica preparations with water. The solutions of silica are neutral.

E. W. W.

**Colloidal Silicic Acid.** EDUARD JORDIS [with W. LUDEWIG] (*Chem. Zentr.*, 1907, i, 392—393; from *Zeitsch. Chem. Ind. Kolloide*, 1, 97—101. Compare preceding abstract).—The theories of the constitution of colloidal silicic acid are discussed in the original paper, and the opinion reiterated (*Abstr.*, 1903, ii, 475; 1905, ii, 317) that silica in the form of hydrogel or hydrosol always contains a certain quantity of foreign material. This conclusion is also confirmed by the following experiments. After systematically washing freshly precipitated silica hydrogel with 2 litres of distilled water until the ignition residue from 1 litre remained constant at 0.1848 gram, it still contained considerable quantities of sodium and chlorine, which could only be detected after digesting with acidified water for ten hours; the sodium and chlorine are not supposed to exist in the form of sodium chloride in the silica. Pure solid amorphous silica may be prepared by washing the hydrogel ten times with cold water, drying, and again washing in a platinum dish with hot water. Kempe's statement (compare preceding abstract), that 1.1% solutions of silica may be prepared, is disputed and the use of very impure preparations suggested. From well washed hydrogel, which was, however, still impure, solutions containing more than 3 grams per litre could not be obtained, and Kahlbaum's hydrate containing 18.51% of water yielded solutions in which only 0.88 gram per litre was present.

E. W. W.

**Preparation of Argon from Air by Means of Calcium Carbide.** FRANZ FISCHER (*Zeitsch. Elektrochem.*, 1907, 13, 107—108).—A mixture of powdered calcium carbide with 10% of calcium chloride is heated at 800° in a vacuum iron tube and then dry air is admitted; oxygen and nitrogen are rapidly absorbed, leaving argon.

T. E.

**Soil Electrolysis with Formation of a Liquid Sodium-Potassium Alloy.** HENRY BASSETT (*J. Soc. Chem. Ind.*, 1907, 26, 180—182).—The author has examined some pieces of a material surrounding a leak in an electric cable; when first taken this was still very hot although the current had been switched off for an hour and a half. On analysis it showed: potassium hydroxide, 33.37; sodium hydroxide, 32.26; potassium, liquid alloy, 1; sodium, liquid alloy, 0.8; soluble silica, 4.80; sand and earthy matter, 26.36; bitumen and water, 1.41%.

The liquid alloy was therefore composed of 55.6% of potassium and 44.4% of sodium. According to Kurnakoff such an alloy is liquid at temperatures above 7°.

L. DE K.

**Structure of Optically Active Cubic Sodium Chlorate.** H. COPAUX (*Compt. rend.*, 1907, 144, 508—510).—Apart from the ordinary cubic form of sodium chlorate, three other modifications may be distinguished: (1) orthorhombic and isomorphous with potassium nitrate; (2) monoclinic and isomorphous with potassium chlorate; (3) orthorhombic and pseudo-cubic with low birefringence. The first two are very unstable and are formed when a drop of an alcoholic solution of the salt evaporates. The third, less soluble form, is obtained by crystallising the salt in the presence of sodium sulphate

and sodium perchlorate. The rotary polarisation of the cubic crystals is explained by twin-aggregations of the pseudo-cubic modification.

L. J. S.

**Electrolysis of Fused Sodium Nitrate.** CHARLES COUCHET and G. NÉMIROWSKY (*Zeitsch. Elektrochem.*, 1907, 13, 115—117. Compare Abstr., 1906, ii, 749).—Using graphite electrodes as before it is found that at the melting point of the salt, with a high current density, metallic sodium may be formed. This reacts with the fused sodium nitrate thus,  $5\text{Na} + \text{NaNO}_3 = 3\text{Na}_2\text{O} + \text{N}$ ; at higher temperatures the reaction is  $2\text{Na} + \text{NaNO}_3 = \text{Na}_2\text{O} + \text{NaNO}_2$ . The attack of the electrodes yields some finely-divided graphite which increases the yield of nitrite especially in presence of sodium oxide. The authors explain this by supposing that the reaction  $\text{Na}_2\text{O} + \text{NaNO}_3 = \text{Na}_2\text{O}_2 + \text{NaNO}_2$  takes place.

T. E.

**Cæsium and Rubidium Mercurides.** NICOLAI S. KURNAKOFF and GREGOR U. SCHUKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1216—1229).—The melting points of the various amalgams were determined mostly by the authors' apparatus for that purpose (Abstr., 1905, ii, 10). The concentration-temperature curves for cæsium and mercury has eight branches indicating eight solid phases, and is, in general, similar to the curves obtained for sodium and potassium amalgams, but it has three maxima corresponding with the existence of three distinct *mercurides*,  $\text{CsHg}_2$ , m. p.  $208.2^\circ$ ;  $\text{CsHg}_4$ , m. p.  $163.5^\circ$ ;  $\text{CsHg}_6$ , m. p.  $157.7^\circ$ . Possibly there exists another mercuride,  $\text{Cs}(\text{Hg})_n$ , where  $n$  lies between 4 and 6, but owing to the readiness with which it is transformed into  $\text{CsHg}_6$ , its exact constitution has not yet been determined. The hexamercuride,  $\text{CsHg}_6$ , forms solid solutions of considerable concentration, and is analogous to the cadmium compound of sodium,  $\text{NaCd}_6$ . The only definite mercuride of rubidium is the *hexamercuride*,  $\text{RbHg}_6$ , m. p.  $136.5^\circ$ , and possibly one  $\text{Rb}(\text{Hg})_n$ , similar to the corresponding cæsium compound.

Z. K.

**Rubidium Arsenites and Arsenates.** A. BOUCHONNET (*Compt. rend.*, 1907, 144, 641—642).—*Rubidium meta-arsensite*,  $\text{RbAsO}_2$ , prepared by the action of arsenious oxide on rubidium carbonate in aqueous solution, is an anhydrous, white amorphous powder. It is converted into arsenate in aqueous solution and by the action of heat. It is alkaline towards litmus, methyl-orange, and phenolphthalein. *Rubidium dihydrogen arsenate*,  $\text{RbH}_2\text{AsO}_4$ , when prepared by melting together equal parts of arsenious oxide and rubidium nitrate, forms tabular crystals, or when prepared by neutralising rubidium carbonate solution with arsenic acid, using methyl-orange as indicator, forms silky needles. Both forms are anhydrous, and the aqueous solution is acid to litmus, neutral to methyl-orange and phenolphthalein. The arsenate, when heated at a dull-red heat, loses water and forms the *meta-arsenate*,  $\text{RbAsO}_3$ , a milky-white, crystalline mass which decomposes at a bright red heat. *Dirubidium hydrogen arsenate*,  $\text{Rb}_2\text{HASO}_4$ , prepared by mixing aqueous solutions of rubidium hydroxide and the monobasic arsenate in molecular proportions, forms white, very



hygroscopic lamellæ containing  $1\text{H}_2\text{O}$ . The latter is lost on heating, and above  $150^\circ$  the substance is converted into the *pyroarsenate*,  $\text{Rb}_4\text{As}_2\text{O}_7$ . At a dull-red heat, the latter decomposes forming the meta-arsenate. Dirubidium hydrogen arsenate absorbs carbon dioxide slowly from the air, more rapidly in aqueous solution. It is neutral towards litmus and methyl-orange, alkaline to phenolphthalein. *Tri-rubidium arsenate*,  $\text{Rb}_3\text{AsO}_4$ , prepared by neutralising rubidium hydroxide solution with arsenic acid using *C.L.B.*-blue (sic.) as an indicator, forms white, very hygroscopic lamellæ containing  $2\text{H}_2\text{O}$  which is lost at  $100^\circ$ . It absorbs carbon dioxide from the air, and is alkaline to litmus, methyl-orange, and phenolphthalein. E. H.

**Existence of Ammonium Hydroxide.** PHILIP BLACKMAN (*Chem. News*, 1907, 95, 133—134).—The proportion of ammonia existing as ammonium hydroxide in aqueous solution may be obtained by comparison of the experimental molecular conductivities of solutions of ammonia with the theoretical values obtained by aid of the formula  $\mu_v\text{NH}_4\text{OH} - \mu_v\text{MOH} = \mu_v\text{NH}_4\text{X} - \mu_v\text{MX}$ , assuming the whole of the ammonia to be present as hydroxide. In this way, it is found that at  $18^\circ$ , solutions of concentration  $v=1000, 500, 100, 20, 10, 2$ , and  $1$  contain respectively 12.2, 9.0, 4.3, 2.1, 1.5, 0.7, and 0.5% of ammonium hydroxide. W. H. G.

**Alloys of Silver with the Metals of the Iron Group (Iron, Cobalt, and Nickel).** G. J. PETRENKO (*Zeitsch. anorg. Chem.*, 1907, 53, 212—215).—The alloys in question are only partially miscible in the fused state, and no chemical compounds are formed.

Silver is soluble in nickel to the extent of 4% by weight, the melting point of the latter being thereby lowered by  $20^\circ$ ; on solidification, homogeneous mixed crystals separate. Above 4% of silver the metals form two layers. The melting point of silver is not affected by nickel, so that nickel is insoluble in silver at the melting point of the latter. The transition temperature of nickel at  $300^\circ$  is not affected by the presence of silver.

Up to  $1600^\circ$ , iron and cobalt are completely insoluble in fused silver. G. S.

**Alloys of Silver with Lead and Tin.** G. J. PETRENKO (*Zeitsch. anorg. Chem.*, 1907, 53, 200—211).—From an investigation of the binary systems, silver-lead and silver-tin, by Tamman's method of thermal analysis, controlled by microscopic observations, the conclusion is drawn that only one compound,  $\text{Ag}_3\text{Sn}$ , exists.

The freezing point curve of silver-lead alloys consists of two branches, meeting in an eutectic point at  $303^\circ$ , as previously found by Heycock and Neville (*Abstr.*, 1897, ii, 245), and by Friedrich (*Abstr.*, 1906, ii, 541); no mixed crystals are formed. The observation of Heycock and Neville that alloys containing 90—96% of lead separate into two layers was not confirmed.

The freezing point curve of silver-tin alloys also consists of two branches; the eutectic point is at  $220^\circ$ , the mixture containing 4% of silver. Further changes, however, take place in the solidified mass, the saturated mixed crystals with 25% of tin decomposing on cooling

with formation of the compound  $\text{Ag}_3\text{Sn}$  and saturated mixed crystals containing 19% of tin. The compound  $\text{Ag}_3\text{Sn}$  is dimorphous, the transition point being in the neighbourhood of  $232^\circ$ .

The paper is illustrated by microphotographs.

G. S.

**Thiosulphates.** JULIUS MEYER and H. EGGELING (*Ber.*, 1907, 40, 1351—1363).—The authors have prepared a number of double salts of thiosulphuric acid. Just as the possibility of the existence of isomerides of the types  $\text{KS}\cdot\text{SO}_2\cdot\text{ONa}$  and  $\text{NaS}\cdot\text{SO}_2\cdot\text{OK}$  has been indicated, so with double thiosulphates of the heavy metals there is also a similar possibility.

The examination of ammoniacal silver alkali thiosulphates showed that yellow salts occur as well as white ones; these were possibly isomerides.

Lithium thiosulphate,  $\text{Li}_2\text{S}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ , obtained from barium thiosulphate and lithium carbonate, is very hygroscopic. Lithium tetrathionate could not be isolated owing to its instability.

The salt,  $\text{Ag}_2\text{S}_2\text{O}_3\cdot\text{Li}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}$ , obtained by dissolving freshly-precipitated silver chloride in lithium thiosulphate, crystallises in plates. Its aqueous solution is readily decomposed by light with deposition of silver sulphide. It is hygroscopic, and is decomposed when boiled with water or acted on by acids.

The salt,  $\text{PbS}_2\text{O}_3\cdot\text{Li}_2\text{S}_2\text{O}_3$ , obtained by the addition of a slight excess of lead thiosulphate to a concentrated solution of lithium thiosulphate, separates in radiating crystals. When moist, it readily decomposes with the formation of lead sulphide.

*Rubidium thiosulphate*,  $\text{Rb}_2\text{S}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ , obtained from rubidium carbonate and barium thiosulphate, is easily soluble in water; it may be titrated quantitatively by iodine solution. It is more hygroscopic than the lithium salt. When acted on by iodine it forms *rubidium tetrathionate*,  $\text{Rb}_2\text{S}_4\text{O}_6$ , which separates in pyramids which are not hygroscopic and are comparatively stable. Rubidium thiosulphate forms unstable double salts with copper, which are obtained by the addition of copper sulphate solution to rubidium thiosulphate solution; the composition of the salt, which separates, varies according to the proportions of the constituents used. The following salts were prepared,  $\text{Rb}_2\text{S}_2\text{O}_3\cdot\text{Cu}_2\text{S}_2\text{O}_3\cdot 2\text{H}_2\text{O}$  (yellow);  $2\text{Rb}_2\text{S}_2\text{O}_3\cdot\text{Cu}_2\text{S}_2\text{O}_3\cdot 2\text{H}_2\text{O}$  (yellow);  $3\text{Rb}_2\text{S}_2\text{O}_3\cdot\text{Cu}_2\text{S}_2\text{O}_3\cdot 2\text{H}_2\text{O}$  (white).

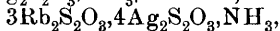
When silver chloride is dissolved in rubidium thiosulphate solution, the double salt,  $2\text{Rb}_2\text{S}_2\text{O}_3\cdot\text{Ag}_2\text{S}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ , is formed; it is not hygroscopic and is relatively stable towards light and air.

The salt,  $2\text{Rb}_2\text{S}_2\text{O}_3\cdot\text{Pb}_2\text{S}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ , crystallises in felted needles.

The salt,  $\text{Rb}_2\text{S}_2\text{O}_3\cdot\text{MgS}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ , crystallises in transparent pyramids.

The salt,  $5\text{K}_2\text{S}_2\text{O}_3\cdot 3\text{Ag}_2\text{S}_2\text{O}_3\cdot\text{NH}_3$ , obtained by the addition of ammoniacal silver nitrate to an aqueous solution of potassium thiosulphate, crystallises in glistening needles. In other cases, Schwicker's salt,  $\text{K}_2\text{S}_2\text{O}_3\cdot\text{Ag}_2\text{S}_2\text{O}_3\cdot\text{NH}_3$ , was obtained in glistening scales.

The salt,  $\text{Rb}_2\text{S}_2\text{O}_3\cdot\text{Ag}_2\text{S}_2\text{O}_3\cdot\text{NH}_3$ , is white, whereas the salt,



is yellow.

*Cæsium thiosulphate*,  $\text{Cs}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , obtained by the addition of calcium carbonate to barium thiosulphate, forms indefinite crystals; it is very hygroscopic. *Cæsium tetrathionate*,  $\text{Cs}_2\text{S}_4\text{O}_8$ , was obtained by the action of iodine on the thiosulphate.

The salt,  $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , is yellow; its aqueous solution is unstable.

The salt,  $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{PbS}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , obtained by the addition of lead thiosulphate to an aqueous solution of cæsium thiosulphate, crystallises in needles, is not hygroscopic, and is stable towards light and air; from the mother liquor the salt,  $2\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{PbS}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , separates in definite crystals.

The salt,  $2\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , forms glistening, silky needles; it is not hygroscopic, is stable towards light and air, and is decomposed when warmed with water.

The salt,  $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , was also prepared. A. McK.

**Employment of Calcium and Allied Metals in the Production of High Vacua.** FREDERICK SODDY (D.R.-P. 179526).—Under suitable conditions of temperature, calcium absorbs not only oxygen and nitrogen, but also hydrogen, carbon dioxide, carbon monoxide, water vapour, acetylene, ammonia, sulphur dioxide, and coal-gas; it has, however, no action on argon and its congeners. This property is showed by strontium and barium, and the three metals may also be alloyed with magnesium. An apparatus has been devised for exhausting vessels with the aid of the foregoing metals, in which the receptacle holding the calcium can be heated electrically.

When the air has been removed by the pump as far as possible, the metal is heated to the temperatures required for the absorption of the gases eliminated from the walls of the exhausted vessel (compare this vol., ii, 251). G. T. M.

**Changes Undergone by Certain Acid Phosphates in Consequence of Compression or Mechanical Deformation.** WALTHER SPRING (*Arch. Sci. phys. nat.*, 1907, [iv], 23, 229—246. Compare Abstr., 1904, ii, 472).—Further experiments on the changes produced by the application of high pressures to substances are described, the compression apparatus being arranged so as to permit of the escape of any liquid phase from the solid phases. Primary calcium phosphate is decomposed according to the equation  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} = \text{CaHPO}_4 + \text{H}_3\text{PO}_4 + \text{H}_2\text{O}$ . The secondary phosphate,  $\text{CaHPO}_4 \cdot 3\text{H}_2\text{O}$ , is not decomposed in the same way, but simply gives up 1 molecule of water. When the primary phosphate is mixed with gypsum in the proportion  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$ , the decomposition can be effected by pounding the mixture in a mortar. This great difference in the reactivity of the primary phosphate in the two cases is supposed to be due to the formation of a molecular compound or a solid solution of the phosphate and sulphate. In support of this view, it is found that the mixture has a very considerable vapour pressure compared with the vapour pressures of the two components. It is pointed out that this observation is of some importance in connexion with the superphosphate industry, the mixture used in these experiments cor-

responding with an average sample of superphosphate. Decomposition of primary calcium phosphate is similarly facilitated by admixture with sodium sulphate,  $(\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O})$ . Sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4, \text{H}_2\text{O}$ , and lithium dihydrogen phosphate,  $\text{LiH}_2\text{PO}_4$ , are also decomposed under pressure, and according to experiments made with these phosphates in admixture with the corresponding sulphates, molecular compounds appear to be formed as in the case of the calcium salts.

H. M. D.

**Barium Percarbonate.** EMANUEL MERCK (D.R.-P. 178019).—*Barium percarbonate*,  $\text{BaCO}_4$ , is prepared by passing carbon dioxide into water containing suspended barium peroxide, the mixture is stirred, and the introduction of the gas is stopped when there is still a slight excess of the peroxide; the temperature throughout the operation should be maintained below  $30^\circ$ . This percarbonate is insoluble in water; in the dried condition it slowly changes into barium carbonate.

G. T. M.

**Experimental Determination of the Conditions for the Quantitative Equimolecular Interaction of Barium Chloride and Sodium Nitrite and the Preparation of Barium Nitrite.** J. MATUSCHEK (*Ber.*, 1907, 40, 990—996. Compare *Chem. Ind.*, 1902, 25, 207; Witt and Ludwig, *Abstr.*, 1904, ii, 124, 171; Meyerhoffer, *ibid.*, 170).—The relation of the solubilities in water of sodium chloride, barium chloride, and barium nitrite to the formation of barium nitrite by the action of sodium nitrite on barium chloride in aqueous solution is discussed. In a series of experiments it is shown that barium chloride ( $+\text{H}_2\text{O}$ ) and sodium nitrite interact when pounded together, and that these salts react in molecular proportion in aqueous solution at  $100^\circ$  if only a limited amount of water is present. The yield of barium nitrite approaches the theoretical when the amount of water added as solvent is one-third of the weight of the nitrite which would be formed if the reaction were quantitative.

G. Y.

**Theory of the Precipitation of Metals by Hydrogen Sulphide.** LUDWIK BRUNER (*Bull. Acad. Sci. Cracow*, 1906, 603—611. Compare Biuni and Padoa, *Abstr.*, 1906, ii, 157).—By applying the law of mass action to the equations  $\text{MeS} \rightleftharpoons \text{M}^{++} + \text{S}^{--}$  and  $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{--}$ , the author deduces that the concentration of the metal ions left in solution after precipitation with hydrogen sulphide is proportional to the square of the concentration of the  $\text{H}^+$  ions, inversely proportional to the concentration of the hydrogen sulphide, and proportional to the solubility product of the precipitated sulphide. This is in harmony with known facts in connexion with the precipitation of the metals of the second and fourth analytical groups.

Experiments on the precipitation of zinc by hydrogen sulphide in acid solution indicate that the process is not a reversible one, and that acid zinc solutions from which zinc is not precipitated when the solutions are saturated with hydrogen sulphide at atmospheric pressure represent systems in a condition of false equilibrium. The non-

reversibility of the process is due to the existence of two modifications of zinc sulphide.

The time required for the appearance of a precipitate in zinc sulphate solutions acidified with sulphuric acid, when saturated with hydrogen sulphide at 25°, has been measured and found to increase with the acidity of the solution. This interval is regarded as a period of induction. When precipitation has begun, it proceeds with a velocity which depends on the acidity of the solution, the velocity diminishing as the acidity increases.

The precipitation appears to be catalysed by zinc sulphide; the effect is probably a surface phenomenon, because the acceleration is approximately proportional to the amount of zinc sulphide added. Cadmium sulphide and precipitated silicic acid exert a similar action.

The precipitation of cobalt and nickel by hydrogen sulphide is analogous to that of zinc. The induction period for these metals is, however, much longer than in the case of zinc. H. M. D.

**Metallic Substitution. IV.** ALBERT J. J. VANDEVELDE (*Bull. Acad. roy. Belg.*, 1907, 35—75. Compare Abstr., 1903, ii, 200; 1904, ii, 549; 1906, ii, 167).—When metallic zinc is added to an aqueous solution of cupric chloride the rate of substitution of copper by zinc is about the same as when the latter metal is added to a solution containing cupric sulphate and sodium chloride (Abstr., 1906, ii, 168). The precipitate formed contains at first a considerable amount of zinc chloride, but in the later stages of the reaction this is replaced by a basic salt having approximately the composition  $\text{ZnO}, 10\text{ZnCl}_2$ . The rate of replacement of copper by zinc in solutions containing cupric chloride and hydrochloric acid is proportional to the concentration of the acid, and does not reach a maximum and then diminish; in this respect it differs from the case of cupric sulphate and sulphuric acid (*loc. cit.*).

The precipitate formed when zinc is added to neutral solutions of cupric nitrate contains basic zinc nitrate, but the composition of the salt precipitated varies with the progress of the reaction. When free nitric acid is present, the rate of substitution is at first proportional to the concentration of the acid, but as in the case of cupric sulphate and sulphuric acid, a maximum is reached eventually which does not correspond with the maximum concentration of acid. The rate of substitution in solutions of cupric nitrate, neutral or containing free nitric acid, is less than in solutions of cupric sulphate or chloride.

The initial "period of induction" observed by Spring and van Aubel (Abstr., 1887, 1074) in the action of sulphuric acid on zinc also occurs when this metal is dissolved in hydrochloric acid, and in the latter case it lasts longer than with sulphuric acid, so that the rate of solution of zinc in hydrochloric acid, even after the action has been in progress for some time, is not so great as in solutions of sulphuric acid of the same strength. Nitric acid acts on zinc much less energetically than sulphuric acid, except in the early stages and in dilute solutions, the period of induction in these circumstances being much reduced. A similar period of induction occurs in the action of aqueous solutions of copper salts on zinc, and the principal effect of the addition

of acid to such solutions is to reduce the length of this period. The efficiencies of the three acids studied, in this respect, are in the order, hydrochloric, sulphuric, and nitric, and this order does not correspond with that of the electrical conductivities of the acids (compare Spring and van Aubel, *loc. cit.*). The formation of basic salts in these reactions has no doubt some influence on the reactional velocity, since this leads to a variable diminution in the concentration of acid ions in the solutions.

Equimolecular solutions of the mixed salts, (1) cupric sulphate and sodium chloride and (2) sodium sulphate and cupric chloride, react at the same rate with zinc, and this is intermediate between the rates of solution of zinc by (a) a solution of cupric sulphate and (b) a solution of cupric chloride, all four solutions containing equivalent amounts of copper. Similarly, the two mixed salt solutions have the same density, but their constituents do not diffuse into gelatin or agar-agar at the same rate, so that, at present, identity of constitution for such mixed salt solutions cannot be assumed.

T. A. H.

**Dehydration of Colloidal Copper Hydroxide by Electro-osmosis.** ERICH MÜLLER and FRITZ SPITZER (*Chem. Zentr.*, 1907, i, 397; from *Zeitsch. Chem. Ind. Kolloide*, 1, 44—47. Compare Abstr., 1907, ii, 174).—In order to explain the variation in the quantity of water contained in the oxides which are formed at the anodes in the electrolysis of many metallic salts, it is supposed that the metallic ions which are first formed are converted into negatively charged colloidal hydroxide by the action of the hydroxyl ions, and that these are deposited at the anode and lose water by a process of electro-osmosis.

The black layer formed on a platinum or iron anode by the electrolysis of a strongly ammoniacal solution of a copper salt in alkali hydroxide (Abstr., 1905, ii, 242; 1906, ii, 158) contains about 0.2 mol. of water, and consists of cupric oxide together with a trace of peroxide. A similar substance is obtained by passing a current of 2 amperes per 100 sq. cm. anode surface through a solution of sodium hydroxide in which freshly-precipitated copper hydroxide is suspended. The dehydration of the so-called crystalline, blue copper hydroxide by the electric current requires three times as long. The original chemical hydrate forms an intermediate absorption compound or an unstable peroxide.

E. W. W.

**Colour of Aqueous Solutions of Cupric Chloride in Relation to the Electrolytic Dissociation.** M. NOZARI (*Atti R. Accad. Sci. Torino*, 1907, 42, 321—327).—The author has measured the degree of dissociation of cupric chloride in solutions of various concentrations at temperature-intervals of 10° from 20° to 90°.

The results show that the degree of dissociation diminishes as the temperature rises. The increase of the conductivity accompanying the rise of temperature must, in this case, be attributed to an increased mobility of the ions.

The same change in the colour of an aqueous cupric chloride solution may be produced either by raising its temperature or by concentrating

it, although the degree of dissociation of the salt will be greater with the heated solution than with the concentrated one. Ostwald's explanation of the variation in colour of cupric chloride solutions on heating is hence inadmissible.

T. H. P.

**Silicides of Copper.** E. RUDOLFI (*Zeitsch. anorg. Chem.*, 1907, 53, 216—227. Compare Vigouroux, Abstr., 1896, ii, 362; de Chalmot, Abstr., 1896, ii, 362; Lebeau, Abstr., 1906, ii, 29).—From an investigation of silicon-copper alloys by Tammann's method of thermal analysis, controlled by microscopic observations, the author considers that two compounds,  $\text{Cu}_3\text{Si}$  and  $\text{Cu}_{19}\text{Si}_4$ , exist, the last-named resulting by secondary changes in the solidified alloy.

The freezing point curve shows a maximum about  $855^\circ$  and 13% by weight of silicon, corresponding with the compound  $\text{Cu}_3\text{Si}$ , two eutectic points at  $825^\circ$  and 9.8% and  $800^\circ$  and 18.3% by weight of silicon, and a break at  $849^\circ$  and 7.8% of the same element. From 0—4.5% of silicon, mixed crystals separate; a second series of mixed crystals from 7.34—8.3% of silicon are only stable within narrow limits of temperature. Two reactions take place during the cooling of the crystallised alloy: the mixed crystals saturated at 7.34% of silicon decompose at  $815\text{--}780^\circ$  into two other series of mixed crystals, one of which splits up at  $710^\circ$  into the compound  $\text{Cu}_{19}\text{Si}_4$  and the mixed crystals first mentioned.

Alloys containing 1—5% of silicon can be drawn into wire, but those containing a higher proportion are very brittle. From 5—10% of silicon the hardness of the alloys increases very rapidly, and beyond the latter point very gradually; those containing 60—100% of silicon have about the same degree of hardness as that element.

It is pointed out that the compounds of these elements described by Vigouroux and by Lebeau (*loc. cit.*) are really eutectic mixtures.

G. S.

**Atomic Weight of Indium.** FRANK CURRY MATHERS (*Ber.*, 1907, 40, 1220—1234. Compare Dennis and Geer, Abstr., 1904, ii, 342; Thiel, *ibid.*, 177, 410, 618).—This paper contains a *résumé* of the methods which have been employed for the determination of the atomic weight of indium, and an account of a fresh determination.

The purification and electrolytic deposition of indium are described. The atomic weight was determined by measurement of four ratios. The values obtained from the ratio,  $\text{In} : \text{InSO}_4$ , 113.03—113.08, are also discarded because of the hygroscopic nature of indium sulphate, and those from the ratio,  $\text{InCl}_2 : 2\text{AgCl}$ , 111.99—113.2, as the wide variation points to incomplete removal of hydrogen chloride or partial formation of indium trichloride. The ratios,  $\text{InCl}_3 : 3\text{AgCl}$  and  $\text{InBr}_3 : 3\text{AgBr}$ , give the mean values 114.88 and 114.86 respectively (five experiments in each case); in view of the errors inherent in the precipitation and weighing of silver chloride, the bromide method is considered to give the more trustworthy results. The value 114.9 may be taken for the atomic weight of indium ( $\text{Cl} = 35.47$ ;  $\text{Br} = 79.955$ ;  $\text{Ag} = 107.92$ ).

G. Y.

**Magnetochemical Investigations. I. Ferromagnetic Compounds of Manganese with Boron, Antimony, and Phosphorus.** EDGAR WEDEKIND (*Ber.*, 1907, 40, 1259—1269. Compare Abstr., 1905, ii, 322; this vol., ii, 175; Heusler, *Zeitsch. angew. Chem.*, 1904, 17, 260; Binet du Jassonneix, this vol., ii, 30).—A résumé is given of the previously known ferromagnetic compounds, that is, compounds which can be strongly magnetised.

[With K. FETZER.]—The strong magnetic properties of crude manganese boride must be ascribed to the boride  $MnB$ , since the boride  $MnB_2$  is only feebly magnetic (Binet du Jassonneix, Abstr., 1906, ii, 520). The boride  $MnB$  may be formed by heating its elements together at the temperature of the electric arc or to a white heat by means of the oxy-hydrogen blowpipe. Its magnetic properties are about one-sixth those of steel.

*Manganese antimonide*,  $MnSb$ , formed by the thermite method, is obtained after removal of the excess of manganese by treatment with dilute hydrochloric acid, and of the excess of antimony by careful heating in a current of chlorine, as a black, crystalline powder, D<sup>17</sup> 5·6, which is dissolved slowly by hot *aqua regia*; when pure and compact, it has stronger magnetic properties than the boride, but the magnetism is diminished to a marked extent by the presence of impurities.

[With THEO VEIT.]—A *manganese phosphide*,  $Mn_3P_2$ , is formed in small amount by heating manganese chloride and phosphorus to a red heat in a current of hydrogen; it is obtained as a dark grey, crystalline powder, is stable towards hydrochloric acid or boiling water, but dissolves readily in hot nitric acid, and has moderately strong magnetic properties.

A *manganese phosphide*,  $Mn_3P_2$ , is obtained when manganese is heated with red phosphorus in a current of hydrogen, finally over the oxy-hydrogen blowpipe; it forms glistening, metallic needles, D<sup>18</sup> 5·12, dissolves in hot concentrated nitric acid, is stable towards dilute acids, inflames when heated gently in chlorine, and is oxidised slowly by oxygen at a red heat, forming a brown powder. It has moderately strong magnetic properties, and when compact is a good conductor of electricity.

The crystalline product obtained from manganese and red phosphorus by the thermite method is a mixture; it is readily attacked by water or dilute acids and has only feeble magnetic properties. G. Y.

**Purification of Potable Waters from Manganese by Aluminate-silicates.** R. GANS (*Chem. Zeit.*, 1907, 31, 355—356).—The author finds that it is only possible in the case of those natural or artificial zeolites containing aluminium as an aluminate readily to replace the alkali metal or alkaline earth by other metals. This fact is made use of to prepare a calcium aluminate-silicate for the purpose of freeing natural waters from manganese. W. H. G.

**Formation of Colloidal Ferric Hydroxide.** WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1907, 34—35).—A solution prepared by adding salicylic acid to ferric acetate was found after some months



to contain colloidal ferric hydroxide and to exhibit properties similar to those of dialysed iron.

T. A. H.

**Cobaltous Potassium Cobaltite.** ITALO BELLUCCI and F. DOMINICI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 315—324).—The authors show that the shining, black plates obtained by Becquerel (*Ann. Chim. Phys.*, 1832, [ii], 51, 101) by fusing cobaltous oxide or carbonate with excess of potassium hydroxide in presence of air, consist of a *cobaltous potassium cobaltite*,  $K_2Co_4O_8$  or  $3CoO_2 \cdot CoO \cdot K_2O$ . The erroneous formulæ attributed to this compound by Schwarzenberg (*Annalen*, 1856, 97, 211), Pébal (*ibid.*, 1856, 100, 257), and Meyer (*ibid.*, 1857, 101, 266) were due both to the silver crucibles used being attacked by the potassium hydroxide and to hydrolysis of the compound by treating it with water.

The best method of preparing the cobaltous potassium cobaltite in a pure state is to fill a nickel crucible with alternate layers of potassium hydroxide and of either cobaltous carbonate or any oxide of cobalt, and to fuse the mass by gently heating it, afterwards heating more strongly with a bunsen flame for three hours. After cooling in a dry vacuum, the mass is introduced into 12% potassium hydroxide solution well cooled with ice. The alkali is renewed several times, the crystals being filtered off by means of a pump, washed repeatedly with alcohol, and dried.

As thus prepared, the compound is obtained in slender, hexagonal plates having a steel-grey lustre. It is rapidly hydrolysed by water, giving an alkaline solution, and dissolves in concentrated hydrochloric acid, yielding chlorine and cobalt and potassium chlorides.

The cobaltous cobaltite prepared by Hofmann and Hiendlmaier (*Abstr.*, 1906, ii, 747) is doubtless a product of hydrolysis of cobaltous potassium cobaltite, which is evidently yielded by the action of cobaltous oxide on fused potassium peroxide.

T. H. P.

**Alloys of Nickel and Tin.** ÉMILE VIGOUROUX (*Compt. rend.*, 1907, 144, 639—641).—By heating nickel with tin, the authors have obtained alloys containing 13.64%, 83.65%, and 92.71% of tin respectively. The two former are hard, brittle, and grey, the third is bluish-white and malleable. All three are non-magnetic, and only the first is sonorous. They are completely dissolved by hydrochloric and sulphuric acids, but nitric acid has only a disintegrating action, metastannic acid and nickel being the products of the action. From the third alloy only, nitric acid dissolves a small quantity of nickel.

E. H.

**Nature of the Substance obtained from Certain Alloys Rich in Nickel and Tin.** ÉMILE VIGOUROUX (*Compt. rend.*, 1907, 144, 712—714).—The alloys previously described (preceding abstract), when treated alternately with warm nitric acid and fused potassium hydroxide, leave a *substance* which has approximately the composition  $NiSn$ . This is a silver-white, crystalline powder, the particles of which show well-marked brilliant facets under the microscope. It is non-magnetic, and has  $D_4^{20} 8.44$  (calc. 7.93). The compound is attacked by

chlorine at a red heat with the production of the two metallic chlorides, and burns with incandescence in oxygen. Sulphur vapour converts it into the two sulphides; hydrochloric or sulphuric acid or *aqua regia* dissolves it completely, but nitric acid has little effect even after long boiling, and, similarly, fused alkali hydroxides, carbonates, and nitrates attack it very slowly, although potassium chlorate oxidises it rapidly even below its melting point.

Since this material is isolated from alloys containing 73.6—91.7% tin, it is probable that it is the richest in tin of the nickel-tin compounds obtainable. Gautier's compound (Abstr., 1896, ii, 602)  $\text{Ni}_3\text{Sn}_2$  was obtained from alloys containing less tin than those now dealt with. The compound  $\text{NiSn}$  may possibly be a solid solution of the two metals, a eutectic alloy, or a mixture of isomorphous forms, but it appears certain that the two metals do not occur in the free state, since a mixture of their powders in the same proportion behaves differently when warmed.

T. A. H.

**The Hydrogel of  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ .** P. A. MEERBURG (*Chem. Weekblad*, 1907, 4, 169—177. Compare Manchot and Kraus, Abstr., 1906, ii, 859; Van Bemmelen, Abstr., 1897, ii, 137; 1899, ii, 12, 84, 487, 599; 1900, ii, 466; 1902, ii, 70; 1904, ii, 18; 1906, ii, 430).—The author finds that the product of the interaction of chromic anhydride and potassium iodide in aqueous solution is an absorption compound of the oxide,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , and water, and that it has all the properties characteristic of amorphous, and especially colloidal, substances. Exsiccation at different vapour tensions did not lead to an equilibrium, the compound becoming slowly modified with decrease in absorptive power. The amount of water absorbed over concentrated sulphuric acid (vapour tension = 0.0 mm.) at the ordinary temperature is greater than that absorbed at 100°. Rise of temperature above 100° increases the loss of water and diminishes the absorptive power. The author considers that his compound is probably identical with Manchot and Kraus's product,  $\text{CrO}_2$ .

A. J. W.

**Green Chromic Chloride Decahydrate.** J. OLIE, jun. (*Zeitsch. anorg. Chem.*, 1907, 53, 268—280).—In his previous investigations on the solubility of chromic chloride hexahydrate (Abstr., 1906, ii, 859) the author assumed that the decahydrate melts at 7° and did not come into consideration in his experiments, which were carried out at 25°. As Werner and Gubser (Abstr., 1906, ii, 452) have shown that the decahydrate remains unaltered for a long time at the room temperature, the solubility determinations have been repeated in the light of this observation.

The decahydrate can be prepared by rubbing the hexahydrate with the calculated amount of water; it occurs in triclinic crystals which are strongly dichroic. The heat of solution appears to be negative. The crystals appear to melt at 32°, but this is not a true melting point, but a transition point, as partial change to the violet modification, accompanied by liquefaction, gradually takes place even at considerably lower temperatures.

Solubility determinations, starting with the decahydrate, have been

made at 25°, 29°, 32°, and 35°; at the former temperature the breaks in the curves which may be supposed to indicate the change from deca- to hexa-hydrate is scarcely noticeable. The transition point has been approximately determined at 29° by microscopic examination of the solid substance in contact with the solution; the latter contained 32% of the violet and 68% of the green salt. If a solution saturated at a temperature lower than 32° is cooled, only the decahydrate separates; if saturated above 32°, both deca- and hexa-hydrate separate on cooling.  
G. S.

**Ionisation of Chromic Sulphates.** ALBERT COLSON (*Compt. rend.*, 1907, 144, 637—639).—Ionisation of the solutions of chromic sulphates is without appreciable effect on the depression of their freezing points. Aqueous solutions containing the molecule  $\text{Cr}_2(\text{SO}_4)_3$  in the different states already described (this vol., ii, 177) which are ionised to very different degrees, all have the same molecular cryoscopic depression  $\Delta = 4.2^\circ$ . The green sulphate obtained from the violet sulphate at 90° is not ionised in solution, yet the conductivity of the latter is greater than that of the solutions of the isomerides. Thus, the conductivity at 0° of a  $N/10$  solution of the green sulphate prepared at 90° is 0.0113 and of a  $N/5$  solution 0.0198; corresponding numbers for a fresh sample of the sulphate with two acid radicles masked are 0.0081 and 0.0133, and for an old sample 0.0088 and 0.0142; the conductivity of a  $N/10$  solution of the violet sulphate is 0.0078. Although these values differ widely, the molecular cryoscopic constant is the same for all, and the actual depression is doubled when the dilution is doubled. Moreover, the conductivity of a  $N/10$  solution of the green sulphate prepared at 90° increases from 0.0100 immediately after dissolution to 0.0113 in an old solution, the corresponding increase for the green sulphate prepared by evaporation in a vacuum is from 0.00708 to 0.0080. Thus it appears that depolymerisation acts on the conductivity like dilution.

The conclusion is drawn that cryoscopic variations are in proportion to the number of chemical molecules in the solution and not to its conductivity.  
E. H.

**Equilibrium in the System: Potassium Oxide, Chromic Acid, and Water.** IWAN KOPPEL and R. BLUMENTHAL (*Zeitsch. anorg. Chem.*, 1907, 53, 228—267. Compare Schreinemakers, *Abstr.*, 1906, ii, 287).—The equilibrium relations in the system  $\text{K}_2\text{O} - \text{CrO}_3 - \text{H}_2\text{O}$  have been determined over a wide range of temperature and the results are illustrated by numerous curves and summarised on a projected space diagram. It is pointed out that the four potassium chromates already known,  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{Cr}_3\text{O}_{10}$ , and  $\text{K}_2\text{Cr}_4\text{O}_{13}$ , exist in equilibrium with solution within certain limits of concentration at all the temperatures at which measurements have been made, and no evidence of the existence of other chromates than those mentioned has been obtained.

The complete isothermals have been determined for 0°, 30°, and 60° by solubility determinations in the usual way, and some observations have also been made at 20°. The most remarkable feature of these

curves is that when sufficient solid chromic acid has been added to convert the solid potassium chromate into dichromate, on further addition of acid the amount of chromic acid in the solution diminishes until the point is reached at which solid potassium dichromate is in equilibrium with its saturated solution. This diminution of solubility is considerable at  $0^{\circ}$ , but much less distinct at  $60^{\circ}$ . Beyond the point at which the solution is saturated with potassium dichromate alone, the addition of more chromic acid only slightly diminishes the amount of potassium hydroxide in the solution. The trichromate,  $K_2Cr_3O_{10}$ , only exists within comparatively narrow limits of concentration.

Owing to experimental difficulties, it has not been possible to determine completely the cryohydric and boiling point "surfaces."

G. S.

**Perchromic Acid and its Salts.** ERNST H. RIESENFELD and WOHLERS (*Chem. Zentr.*, 1907, i, 219; from *Sonderab. Ber. Naturforsch. Ges. Freiburg*, 1906, 17, 1—60).—A solution of 16.6 grams of chromic acid in 100 c.c. of a 30% solution of sulphuric acid has been electrolysed, using platinum electrodes and a porous cathode cell. The solution was cooled by means of ether and carbon dioxide and the oxygen formed by the electrolysis of the solution and that liberated in a voltameter were measured; the oxygen absorbed by the solution was estimated volumetrically. The latter is always the same during the first minute, it then gradually decreases to nil, and after this stage more oxygen is liberated in the cell than in the voltameter. A higher oxidation product of chromium, which can be detected by precipitation with ammonia, is probably formed, but decomposes as the concentration increases until the velocity of formation becomes equal to that of decomposition. Since chromic oxide,  $Cr_2O_3$ , is formed by the decomposition and not chromic acid, the quantity of oxygen lost is greater than that produced by the electrolysis.

E. W. W.

**Uranyl Silver Chromate.** BÉLA SZILÁRD (*Chem. Zentr.*, 1907, i, 223; from *Zeitsch. Wiss. Photograph. Photophys. Photochem.*, 1906, 4, 350—351).—The author has repeated Formánek's experiments on uranyl silver chromate (*Abstr.*, 1890, 852), but has been unable to detect any decomposition of the double compound caused by the action of the light even after several days' exposure.

E. W. W.

**Binary and Ternary Alloys of Tin, Lead, Bismuth, and Cadmium.** A. STOFFEL (*Zeitsch. anorg. Chem.*, 1907, 53, 137—183).—The author discusses the six binary systems formed with tin, lead, bismuth, and cadmium, all of which have already been investigated by Kapp (*Inaug. Diss. Königsberg*, 1901), Charpy, Heycock and Neville, and others. In one or two instances, further experiments have been made to complete our knowledge of these alloys. In none of these alloys do definite chemical compounds separate from the fused mass, but the solidified tin-cadmium alloy has a transition point at  $125^{\circ}$ , which appears to indicate the formation of a compound,  $CdSn_4$ . All the systems, with the exception of cadmium-bismuth, appear to form mixed crystals within certain limits.

The freezing point curves of the two ternary systems, tin-cadmium-lead and tin-cadmium-bismuth, have been fully investigated, and the results are illustrated by numerous diagrams. The ternary eutectic point of the former alloy is at  $145^{\circ}$ , the mixture containing 57 atom % tin, 21% lead, and 22% cadmium. The transition temperature of the binary cadmium-tin alloys appears also in the ternary mixture, but is slightly lowered by the presence of lead.

Tin-cadmium-bismuth alloys also have a definite ternary eutectic point, which occurs at  $103^{\circ}$ , the mixture containing 33.2 atom % tin, 39.3% bismuth, and 27.5% cadmium. It was expected that the ternary eutectic point would be affected by the fact that it lies below the transition temperature of the cadmium-tin alloy. It was found that the transition point was lowered by bismuth, and in some alloys rich in the latter metal the transition point was not observed. To explain the lowering, it is suggested that the compound arising at the transition point forms mixed crystals with bismuth.

The majority of the alloys show another transition point at  $78-68^{\circ}$ , but the nature of the changes giving rise to this phenomenon have not been elucidated.

G. S.

**White Colloidal Tin Oxysulphide.** FRIEDRICH W. SCHMIDT (*Chem. Zentr.*, 1907, i, 397—398; from *Zeitsch. Chem. Ind. Kolloide*, 1, 129—135).—In attempting to remove traces of arsenic from freshly-precipitated and well washed tin sulphide by boiling with a solution of ammonium carbonate, it was observed that sulphuric acid throws down a very voluminous, white precipitate from the carbonate solution. The precipitate is readily soluble in ammonia or ammonium sulphide, and after washing is also soluble in water. When a solution of the yellow sulphide,  $\text{SnS}_2$ , in ammonia is acidified, an almost white precipitate is formed which on drying in the air becomes greenish-yellow; in the latter condition only half of the substance, which is still, however, completely soluble in ammonia, is dissolved by ammonium carbonate, the residue being brownish-red. By dissolving in ammonium carbonate and precipitating with sulphuric acid, a white substance is obtained which becomes amber-yellow on drying. The solubility of the substance in ammonia is not affected by keeping for a long time. It is assumed, therefore, that the decrease of solubility in ammonium carbonate solution is not due to polymerisation, but to loss of water and to a gradual change from a voluminous colloidal condition to an amorphous state in which the composition varies from  $\text{Sn}_2\text{S}_3\text{O}, 11\frac{1}{2}\text{H}_2\text{O}$  to  $\text{Sn}_2\text{S}_3\text{O}, 5\text{H}_2\text{O}$ , according to the time of drying.

The composition of yellow sulphide of tin, prepared from Banca tin and purified with the greatest care, has been found to be represented by the formula  $\text{SnS}_2$ . When dried in the air it loses a small quantity of hydrogen sulphide and becomes dark brown, hard, and brittle. It dissolves in ammonia, forming an orange-red solution which behaves like a colloidal solution of tin disulphide; the sulphide,  $\text{SnS}_2$ , is precipitated by acids from freshly-prepared solutions. The solution loses its colour on exposure to air for four to five days, ammonium sulphide being first formed and then ammonium thiosulphate; the oxysulphide and sulphur are precipitated by acids, but neither hydrogen sulphide

nor sulphur dioxide is formed. The oxysulphide may be purified and any tin sulphide removed by dissolving in ammonium carbonate. The oxysulphide is not precipitated from very dilute solutions in ammonium carbonate until carbon dioxide has been liberated, and it then separates as a very fine, flocculent, white mass which has a blue tinge; the precipitate after washing three or four times with water forms colloidal solutions which have an acid reaction and from which the colloid is precipitated by neutral salts, but not by acids. These solutions are assumed to contain the acid,  $\text{S}(\text{SnS}\cdot\text{OH})_2$ , whilst the composition of the oxysulphide, which is soluble in ammonium carbonate, is regarded as  $\text{S}:\text{Sn} < \begin{smallmatrix} \text{S} \\ \text{O} \end{smallmatrix} > \text{Sn}:\text{S}$ , and that of the original precipitate as  $\text{HO}\cdot\text{SnS}\cdot\text{S}\cdot\text{SnS}\cdot\text{ONH}_4$ .

E. W. W.

**An Intermediate Product of Thorium.** OTTO HAHN (*Ber.*, 1907, 40, 1462—1469. Compare *Jahrbuch Rad. Elec.*, 3, 330; Blanc, *Abstr.*, 1906, ii, 644; Elster and Geitel, *ibid.*, ii, 643; Boltwood, *ibid.*, ii, 415).—Numerous commercial thorium preparations of varying grades of purity have been examined in order to determine whether a diminution of activity occurs during the process of purification. The results were entirely negative. Boltwood's view that a portion of the radiothorium is removed during the preparation and purification of thorium nitrate is therefore not substantiated.

The suggestion is made that thorium is not directly transformed into radiothorium, but into an intermediate product, "*Mesothorium*," which then yields radiothorium. This view is confirmed by the fact that thorium preparations of different ages have different activities, the activity tending to diminish as the age increases. Fresh specimens of thorium nitrate exhibit an activity of the same order as the corresponding quantity of thorianite (the activities of uranium and radium present being taken into account). For several years the activity diminishes, and after three years attains a value which remains practically constant for some time, after which it again increases. These facts are in harmony with the view that in the preparation of thorium nitrate an intermediate product which does not yield  $\alpha$ -particles is removed, whereas the radiothorium remains with the thorium. The activity of the fresh preparation thus possesses the activity which would be expected. The time required for the breaking up and therefore for the formation of the intermediate product is longer (some seven years) than that of the radiothorium, hence the decrease in the activity. The conclusions, as regards the intermediate product, have been confirmed by obtaining preparations free from thorium, which after a lapse of time showed activity due to radiothorium.

J. J. S.

**Crystallography of Octahydrated Thorium Selenate.** ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 220—223).—Octahydrated thorium selenate crystallises in the monoclinic system [ $a:b:c = 0.6037:1:0.6712$ ;  $\beta = 81^\circ 40'$ ]. These ratios differ considerably from those given by Wyruboff (*Bull. Soc. franç. Min.*, 1901, 24) for the corresponding sulphate.

T. H. P.

**Bismuth Iodide.** LOTHAR BIRCKENBACH (*Ber.*, 1907, 40, 1404—1405).—The product obtained by Heintz's method of preparing bismuth iodide by fusing bismuth and iodine, always contains bismuth which causes catalytic dissociation of the iodide on sublimation (compare Muir, *Trans.*, 1881, 33; Schneider, *Abstr.*, 1895, ii, 114). That obtained by Rammelsberg's wet method, on the other hand, contains oxyiodide, but when a solution of bismuth chloride is added to a saturated solution of iodine and hydrochloric acid in stannous chloride, pure bismuth iodide separates in rhombohedral crystals. To purify the iodide further, the dry product is heated in an evacuated glass tube to expel impurities, and then sublimed in an atmosphere of carbon dioxide and hydrogen. W. R.

**A Property of Platinum Amalgam.** HENRI MOISSAN (*Compt. rend.*, 1907, 144, 593—594).—Platinum amalgam, when shaken with water for fifteen seconds or less, forms an emulsion of a buttery consistency and having five times the volume of the original amalgam. The product is stable and is not affected by being heated to 100° or cooled to -80°. Microscopical examination of a section made at the latter temperature reveals small drops of water disseminated throughout the amalgam, giving the latter a cellular appearance. When exposed in a vacuum, it diminishes in volume, a little water and a small quantity of gas separating. The emulsion is also produced by shaking 2 c.c. of pure mercury with 12 c.c. of water to which some drops of a 10% platinic chloride solution have been added, and when platinum amalgam is shaken with water similarly treated, the increase in volume is greater than with pure water. Copper, silver, and gold amalgams do not form emulsions.

Platinum amalgam emulsifies similarly when shaken with sulphuric acid, aqueous ammonia, aqueous or ammoniacal ammonium chloride solution, sodium chloride solution, glycerol, acetone, anhydrous alcohol, ether, oil of turpentine, carbon tetrachloride, or chloroform, and forms stable emulsions. Benzene is inactive.

Platinum amalgam, to which sodium has been added, also increases in volume and emulsifies when shaken with water. E. H.

**Colloidal Metals of the Platinum Group.** III. CARL PAAL and CONRAD AMBERGER (*Ber.*, 1907, 40, 1392—1404. Compare *Abstr.*, 1904, ii, 180; 1905, ii, 397).—Colloidal osmium preparations were obtained as follows. A mixture of sodium protalbate or lysalbate with an alkali osmate was reduced with hydrazine hydrate or aluminium. Sodium amalgam is, in this case, not suitable as a reducing agent. Colloidal solutions of osmium oxide hydrates were nearly always obtained, those liquid hydrosol mixtures having been purified by dialysis and having been converted into the solid form by careful evaporation. When the products obtained in this manner were powdered and warmed at 30—40° in a current of hydrogen, they were completely reduced to elementary, colloidal osmium, which is easily soluble in water. The liquid osmium hydrosol is as stable towards acids, bases, and normal salts as were the corresponding hydrosols of the other metals of the platinum group studied previously.

Colloidal osmium differs from the latter in the ease with which it undergoes oxidation in air. When solid colloidal osmium remains for some time in a desiccator, the characteristic odour of the tetroxide soon becomes evident and the solid steadily loses in weight.

Solid osmium hydrosols may be precipitated from the liquid hydrosols.

By the reduction of a mixture of sodium protalbate (or lysalbate) and alkali osmate with aluminium, colloidal osmium solutions were obtained containing alkali aluminate, which could not be separated by dialysis. When strong acid is added to such solutions, the greater part of the aluminium remains in solution, whilst the solid osmium hydrosol, in addition to adsorbed lysalbic or protalbic acid and some aluminium (in the form of adsorbed hydroxide or salt), is precipitated in dark flakes, which are again soluble in alkali. When the liquid, purified by dialysis, is dried, a colloidal product results, soluble in water and containing the three hydrosols, osmium oxide hydrate, some aluminate, and the sodium salt of the corresponding protein decomposition product.

A. McK.

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These results lead to the formula  $\text{Fe}_{11}\text{S}_{12}$  for specimens (I), (III), and (IV) and to  $\text{FeS}$  for specimen (II). It will be seen that the density of pyrrhotite is increased by the presence of nickel, lead, copper, or antimony.

T. H. P.

**Chalcopyrite from Japan: Crystalline Structure of Chalcopyrite.** JACOB BECKENKAMP (*Zeitsch. Kryst. Min.*, 1907, 43, 43—60. Compare this vol., ii, 101).—A more complete description is given of the curiously developed crystals of chalcopyrite from Arakawa, Japan, and the structure and twinning of chalcopyrite in general is discussed.

L. J. S.

**Regular Growth of Rutile and Hämatite.** HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1907, 43, 61—67. Compare Abstr., 1906, ii, 456).—Further determinations as to the crystallographic relations between the two minerals.

L. J. S.

**Brucite from Caucasus.** ADAM KARPINSKY (*Zeitsch. Kryst. Min.*, 1907, 43, 70; from *Verh. Russ. Min. Ges.*, 1905, 42, Prot., 21—23).—An asbestiform mineral, occurring as veins in schistose serpentine near the village of Lyssogorsk in govt. Elisabethpol, is shown by the following analysis, by Susanoff, to be brucite; the fibres are, however, optically biaxial and positive.

MgO.	FeO.	H <sub>2</sub> O.	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	SiO <sub>2</sub> .	Total.
63.0	6.3	29.8	0.2	0.4	0.5	100.2

L. J. S.

**Gases in Greenland Minerals.** JULIUS THOMSEN (*Zeitsch. Kryst. Min.*, 1907, 43, 89; from *Bull. Acad. Sci. Copenhagen*, 1904, 53—57).—In 1898 the author detected the presence of helium in the reddish-brown fluorite from the cryolite deposit at Ivigtut in Greenland. The gases evolved on heating 1000 grams of the mineral consist of CO, 20; H, 66; N, 5; helium 24 = 115 c.c.; in addition to this also 715 c.c. of CO<sub>2</sub>, which is due to the enclosure of carbonates in the fluorite. Helium was formed in no other mineral. Steenstrupite, from near Julianehaab, gave per 1000 grams (after deducting CO<sub>2</sub>) 1880 c.c. of gas, consisting of H, 480; CO, 820; N, 580 c.c. Eudialyte gave per 1000 grams 940 c.c. of gas, consisting of CO<sub>2</sub>, 100; H, 750; CO, 30; N, 60.

Green fluorite from England gave, when heated, a strong blue light and evolved per 1000 grams only 74 c.c. of gas, consisting of CO<sub>2</sub>, 53; H, 17; N, 4 c.c.

L. J. S.

**Analyses of Yttrocerite and Topaz from Colorado.** G. P. TSCHERNIK (*Zeitsch. Kryst. Min.*, 1907, 43, 69; from *Verh. Russ. Min. Ges.*, 1905, 42, 51—67).—The yttrocerite was present on a specimen, from Colorado, showing wine-yellow topaz, flesh-red orthoclase, greenish-white oligoclase, and quartz. The violet-blue, rounded crystals of yttrocerite somewhat resemble fluorite in appearance; they have a conchoidal fracture, with a vitreous to rather greasy lustre; hardness

4—5 ; D 4.307. From the following analysis the formula is deduced as  $\text{Ce}_2\text{F}_6, 2\text{Y}_2\text{F}_6, 9\text{CaF}_2, 2\text{H}_2\text{O}$ .

$\text{Ce}_2\text{O}_3$	$\text{Y}_2\text{O}_3$	$\text{CaO}$	$\text{H}_2\text{O}$	F.	$\text{Al}_2\text{O}_3, \text{SiO}_2$	Total (less O for F).
18.19	29.36	27.61	1.96	37.69	traces	99.03

The perfectly transparent, wine-yellow crystals of topaz gave on analysis :

$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{SiO}_2$	$\text{TiO}_2$	F.	Total (less O for F).
55.36	0.08	32.69	0.13	20.43	100.14

L. J. S.

**Thermoluminescent Limestone from Visima Utka.** N. T. BELJAEFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1240—1243).—The appearance of the limestone indicates that it is not a homogeneous substance. It consists chiefly of calcium carbonate with small quantities of iron and manganese carbonates, some specimens also containing traces of hydrogen sulphide and silicic acid. The mineral is analogous with Wiedemann's artificial preparation, forming probably a solid, crystalline solution. It commences to be luminous at 160—180°, the critical temperature being 300°. Neither cooling it with liquid air, nor exposing it to radium has any effect on its luminescence. When heated at 180°/20—30 mm. carbon dioxide is evolved.

Z. K.

**Formation of Oceanic Salt Deposits. L. Franklandite, and a New Compound Related to Boronatrocalcite.** JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Berlin*, 1907, 301—305. Compare Abstr., 1906, ii, 619, 863).—The author has examined the mineral designated by Reynolds as franklandite and finds that the analytical data correspond with an impure boronatrocalcite. Attempts to prepare a substance of the composition ascribed by Reynolds to franklandite were unsuccessful. When a mixture of boronatrocalcite, ( $\text{NaCaB}_5\text{O}_9, 8\text{H}_2\text{O}$ ), and borax is heated, the latter is transformed at 60° into the octahedral pentahydrate,  $\text{Na}_2\text{B}_4\text{O}_7, 5\text{H}_2\text{O}$ , and at 63° the boronatrocalcite loses water with the formation of a sodium calcium borate of the composition  $\text{NaCaB}_5\text{O}_9, 4\text{H}_2\text{O}$ . The formation of colemanite from boronatrocalcite at about 65° according to the equation :  $2\text{NaCaB}_5\text{O}_9, 8\text{H}_2\text{O} = \text{Na}_2\text{B}_4\text{O}_7, 5\text{H}_2\text{O} + \text{Ca}_2\text{B}_6\text{O}_{11}, 5\text{H}_2\text{O} + 6\text{H}_2\text{O}$  is therefore only possible when superheating of the boronatrocalcite takes place. This result implies that the upper temperature limit for the existence of boronatrocalcite is lower than that previously recorded, and dilatometer experiments indicate that this limit is below 60°. In presence of sodium chloride, borax, potassium chloride and glaserite, decomposition of boronatrocalcite was found to take place at 51°.

H. M. D.

**Analyses of Monazite and Xenotime.** G. P. TSCHERNIK (*Zeitsch. Kryst. Min.*, 1907, **43**, 68 ; from *Verh. Russ. Min. Ges.*, 1905, **42**, 9—30).—The following analyses are of crystals isolated from a flesh-red rock, probably from Idaho ; zircon is also present. I, Wine-

yellow crystals ; II, reddish-brown, transparent crystals ; III, reddish-brown, translucent crystals ; IV, yellowish-green, transparent crystals ; V, yellowish-green, translucent crystals ; VI, yellowish-green, opaque crystals.

	P <sub>2</sub> O <sub>5</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	ThO <sub>2</sub> .	SiO <sub>2</sub> .	SO <sub>3</sub> .	ZrO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	28.18	65.29	2.52	2.52	1.18	—	—	trace	—	—	0.18	99.87	5.165
II.	27.60	64.16	3.47	1.65	1.16	—	—	1.00	—	0.36	0.23	99.63	5.125
III.	27.72	64.48	3.48	1.67	0.96	—	—	0.71	—	0.20	0.37	99.59	5.010
IV.	30.85	58.60	—	—	1.21	1.71	2.62	1.76	1.07	1.20	0.19	99.29	4.685
V.*	32.02	57.86	—	—	1.35	1.35	2.72	1.70	1.12	0.95	0.19	99.26	4.165
VI.†	31.28	59.70	—	—	1.33	0.81	2.70	1.64	1.13	0.56	0.18	99.33	4.545

\* Trace of SnO<sub>2</sub>.

† Traces of SnO<sub>2</sub> and MnO.

I—III are therefore monazite and IV—VI are xenotime ; all except I, are more or less altered by weathering.

L. J. S.

**Anapaite and other Minerals from South Russia.** P. TSCHIRWINSKY (*Zeitsch. Kryst. Min.*, 1907, 43, 77 ; from *Ann. Géol. Min. Russ.*, 1904, 7, 28—34).—Various minerals from the deposits of brown iron-ore in the Kerch and Taman peninsulas are described. Anapaite (Abstr., 1902, ii, 268) is held to be a double salt of vivianite, Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.8H<sub>2</sub>O, and ornithite, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O. Fluid cavities in large crystals of anapaite were found to contain traces of chlorine. Attempts to prepare anapaite artificially were unsuccessful. In addition to vivianite, the following iron phosphate, which is perhaps a new mineral, also occurs in this region ; hyacinth-brown crystals up to 3 cm. across are found in the cavities of a ferruginous limestone ; analyses gave : Fe<sub>2</sub>O<sub>3</sub>, 47.71 ; P<sub>2</sub>O<sub>5</sub>, 38.87 ; H<sub>2</sub>O, 13.42 (to 14.07) ; total, 100.00 ; corresponding with the formula 100[Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, 2½H<sub>2</sub>O] + 18[Fe(OH)<sub>3</sub>.3H<sub>2</sub>O]. There are cleavages in three directions nearly at right angles to one another ; the optical characters suggest orthorhombic symmetry, and the double refraction is lower than that of vivianite.

L. J. S.

**Striiverite, a New Mineral.** FERRUCCIO ZAMBONINI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1907, [iii], 13, 35—51).—This mineral is found in detrital masses of pegmatite near Craveggia, N. Piedmont. It is black and opaque, and is crystallographically similar to rutile, tapiolite, mossite, and ilmeno-rutile ; [a : c = 1 : 0.64561] ; D<sup>16</sup> 5.54. Some of the crystals are elongated along the pyramidal edge, and are most probably twins similar to those of rutile, ilmeno-rutile, tapiolite, &c.

[With GEORGE T. PRIOR.]—Analysis of the mineral gives the composition (TaCb)<sub>2</sub>O<sub>5</sub>.9TiO<sub>2</sub>.4ZrO<sub>2</sub>.3FeO, which may be represented as a mixture of Fe(TaCb)<sub>2</sub>O<sub>6</sub>, FeZr<sub>2</sub>O<sub>5</sub>, and TiTi<sub>2</sub>O<sub>6</sub> in the proportions 1 : 2 : 3.

T. H. P.

**Celsian and other Baryta-Felspars.** JOHAN EDVARD STRANDMARK (*Zeitsch. Kryst. Min.*, 1907, 43, 89—92 ; from *Geol. För. Förh. Stockholm*, 1903, 25, 289—319 ; 1904, 26, 97—133).—Celsian (Abstr., 1897, ii, 411) is found in a manganese mine at Jakobsberg, Sweden, embedded, with schefferite, brown garnet, and manganophyllite, in a dolomite-rock at its contact with a dyke of igneous rock : it is there-

fore a mineral of contact origin. Examination of crystals, which are, however, somewhat unevenly developed, proves the mineral to be monoclinic and not anorthic as previously described; [ $a:b:c=0.657:1:0.554$ ;  $\beta=64^{\circ}58'$ ]; the optical constants are also given. The material is rendered impure by enclosures of the minerals mentioned above; analysis gave the results under I.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	BaO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total	Sp. gr.
I.	32.23	27.40	0.32	0.24	36.45	0.39	0.13	0.22	0.77	1.02	99.29*	3.384
II.	63.00	18.84	—	—	1.84	0.15	0.08	13.44	1.69	0.47	99.51	2.593
III.	[57.0]	20.9	—	—	12.4	0.2	trace	9.9	1.5	0.5	102.4	2.756

\* Including F 0.12 per cent.

The baryta-potash-feldspars probably form a complete series of mixed crystals from adularia (Or) to celsian (Cel), of which, however, only those with less than 16.4% BaO (= Or<sub>2</sub>Cel<sub>1</sub>) are known. It is proposed to apply the name hyalophane to those members of the series with the composition Or<sub>6</sub>Cel<sub>1</sub> to Or<sub>2</sub>Cel<sub>1</sub>, and to refer to those with less barium as barytiferous potash-feldspars. Crystals of the latter variety from the Binnenthal gave II as the mean of two analyses. Crystals of hyalophane, also from the Binnenthal, were found to have a zonal structure and to vary in sp. gr. from 2.660 to 2.818, the central portion of the crystals being denser; the optical constants show corresponding variations. Analysis III of a crystal of hyalophane corresponds with Or<sub>61</sub>Ab<sub>14</sub>Cel<sub>24</sub>An<sub>1</sub>. The isomorphous relations of the baryta-potash-feldspars are discussed in detail.

L. J. S.

**Glaucinite from Near Grodno, Russia.** W. SMIRNOFF (*Zeitsch. Kryst. Min.*, 1907, 43, 77; from *Ann. Géol. Min. Russ.*, 1905, 7, 246—247).—Analysis of glaucinite isolated from the Lower Oligocene sandstone of Galowitsche, near Grodno gave, after deducting 6.50% of admixed quartz:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total
48.70	12.87	16.08	2.25	1.12	1.85	5.28	2.40	9.90	100.45

L. J. S.

**Garnet and Magnetite from Caucasus.** L. JACZEWSKI (*Zeitsch. Kryst. Min.*, 1907, 43, 69; from *Verh. Russ. Min. Ges.*, 1905, 42, 75—84).—On the surface of a garnet-rock are well-developed crystals of garnet and magnetite. The three following analysis of the garnet crystals taken from the same specimen show variations in composition which indicate isomorphous mixing of different garnet types:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	Total
I.	36.83		27.98		1.39	33.76	99.96
II.	36.43	9.84	18.25	2.27	1.71	31.51	100.01
III.	37.11	9.46	17.82	1.80	1.82	32.01	100.02

Also TiO<sub>2</sub>, 0.03—0.06%; D 3.744. The magnetite is normal in composition.

L. J. S.

**Chemical Analysis of Vesuvian Ashes of April, 1906.** GIUSEPPE KERNOT (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 449—462).—The author has made analyses of ashes from Vesuvius which fell in

Naples (1) April 4-5th; (2) April 6-7th; (3) April 11th, and (4) April 13th, 1906. The main constituents are silica, potassium, calcium, iron, and alumina. Ashes collected on the crater of the volcano itself were not completely analysed, but were found to contain selenium and a relatively large proportion of arsenic.

The ashes which fell in Naples are only feebly radio-active, those which were collected from the Vesuvian cone exhibiting much more marked radio-activity, exceeding, indeed, that of the lava which flowed over Boscotrecase. Assuming all the radio-active material to be radium, the quantity of the latter would be of the order of a few hundredths of a mg. per cubic metre. In general, the radio-activity of these ashes is less than that of the ashes thrown out of the volcano during the eruptions of 1904-1905.

The rare metals present in the ashes are to be investigated later.

T. H. P.

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## Physiological Chemistry.

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**Expiration of Free Nitrogen by Animals.** AUGUST KROGH (*Chem. Zentr.*, 1907, i, 488—489; from *Skand. Archiv Physiol.*, 18, 364—420).—No evidence of the expiration of free nitrogen in animals was found. The experiments were made on pupæ, eggs, and mice.

W. D. H.

**Respiratory Metabolism after Fatiguing Work.** OTTO PORGES and ERNST PRIBRAM (*Biochem. Zeitsch.*, 1907, 3, 453—482).—In the period of rest after fatiguing bodily work the exchange is never smaller than in the non-fatigued condition. Usually it is increased immediately after work, and sinks to the normal after a variable time. The respiratory quotient is usually at first abnormally low, a part of the carbon dioxide formed being retained. Periods of work or rest lasting several days have no noteworthy effect, and fatigue does not influence the metabolic side of digestion.

W. D. H.

**Gaseous Metabolism of Mammalian Heart.** JOSEPH BARCROFT and WALTER E. DIXON (*J. Physiol.*, 1907, 35, 182—204).—A circulation of blood was maintained through the excised hearts of dogs and cats by perfusion from a living animal, clotting being prevented by the administration of hirudin. The amount of oxygen taken up varies with the heart's activity; the output of carbon dioxide varies in the same way, but lags somewhat behind it. Rate, amplitude, and tonus of the heart must be taken into account. Barium salts augment the tonus and the gaseous exchange; chloroform and potassium salts lessen both. Pilocarpine and vagus inhibition diminish, and adrenaline, atropine (after pilocarpine), and the after effect of vagus stimulation increase the rhythm. The output of carbon dioxide varies with the

rate of flow through the coronary vessels, and the vaso-motor changes in these are believed to be controlled by the metabolic products of which carbon dioxide is the chief. Calculations of the energy transformed in the heart agree with those of Tigerstedt, Stewart, and Stolnikoff. The heart is of lower metabolic value, weight for weight, than the kidney pancreas or salivary glands. In the resting organs, the pancreas uses 0.03—0.05 c.c. of oxygen per gram per minute, the submaxillary 0.03, of the kidney, 0.03. The figures for the feebly-acting heart are about one-third of these. When fully active, the figures all rise, but the heart varies least. The highest figure obtained for the dog's heart was 0.083 c.c.

W. D. H.

**Relation between Oxyhæmoglobin and the Blood Gases.** M. PIETTRE and ANTONY VILA (*Compt. rend.*, 1907, 144, 503—506).—Some experiments are recorded with some pure specimens of oxyhæmoglobin crystals in comparison with others on washed red corpuscles. The amount of oxygen yielded varied with different conditions, among which special attention is directed to the deterioration (vieillessement) oxyhæmoglobin undergoes with time. The corpuscles yield appreciable amounts of carbon dioxide.

W. D. H.

**The Effect of Certain Drugs and Toxins on Blood-coagulation.** C. J. COLEMAN (*Bio-Chem., J.*, 1907, 2, 184—205).—Small differences in coagulation time may occur in the same animal, due to food, drink, and other accidents. The administration of citric acid lengthens the time by forming sodium citrate. Calcium chloride given by the mouth is slowly absorbed and has but little effect; if given subcutaneously, the coagulation time is shortened. Milk given either way has no effect. Pathological conditions or drugs which produce leucocytosis lengthen the coagulation time. Subcutaneous injections of normal saline solution diminish the coagulability of the blood markedly.  $\beta$ -Naphthylamine, given hypodermically, increases the coagulation time; this seems to be due to the pyrexia produced. Diphtheria toxin increases the time.

W. D. H.

**Condition of Sugar in the Blood.** EDUARD PFLÜGER (*Pflüger's Archiv*, 1907, 117, 217—222).—Polemical; the grounds on which Asher and Rosenfeld base their statement (this vol., ii, 279) that the sugar of the blood is in a free state are criticised.

W. D. H.

**The Formula for the Precipitin Reaction According to Hamburger and Arrhenius.** PAUL FLEISCHMANN and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1907, 3, 425—430).—A speculative discussion, the outcome of which is that the precipitate is not of constant composition, and that there is no definite quantity of precipitin, which is, in all circumstances, equivalent to a given amount of precipitable substance. The cause of this is the colloidal nature of the substances in question, and the size of the particles is a changing factor.

W. D. H.

**Chemistry of Digestion. VIII. Experimental Methods.** E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 51, 241—243).—Further



details in the manner of making the fistulæ, &c., are given (compare this vol., ii, 107).  
W. D. H.

**Excretion of Gastric Juice.** BERNT LÖNNQVIST (*Chem. Zentr.*, 1907, i, 359; from *Skand. Arch. Physiol.*, 18, 194—262).—The observations were made on dogs with a Pawloff's fistula. The secretion of gastric juice can be elicited by psychical stimuli, and by the application of certain substances to the mucous membrane of the stomach and intestine. Fat inhibits the secretion by reflex action from the intestine. Water, alcohol, the protein-cleavage products, and meat-extract produce an abundant secretion. Hydrochloric acid (0.1—0.5%) and the natural juice act but feebly; lactic and butyric acids (0.5%) are stronger stimuli. As physiological saline solution, sodium chloride has little effect, but the effect increases with the concentration above and below this limit. Weak solutions of sodium hydrogen carbonate (0.25—0.5%) have about the same action as water, but stronger solutions act more powerfully. Saliva and bile act like water. Water and alcohol are absorbed in the stomach. Neither water nor sodium chloride have any action if applied to the duodenum, but soda solutions like fluid fat inhibit the secretion.  
W. D. H.

**Artificial Digestion Experiments with Vegetable Foods.** W. ROTHE (*Zeitsch. physiol. Chem.*, 1907, 51, 185—200).—Various vegetable foods, mainly those of agricultural interest, were subjected to artificial gastric digestion. The results obtained with various degrees of acidity are stated in tabular form, and the amount digested is seen to vary a good deal. The figures are only of value from the comparative point of view.  
W. D. H.

**Protein Digestion.** W. GRIMMER (*Biochem. Zeitsch.*, 1907, 3, 389—402. Compare this vol., ii, 107).—The experiments were made on dogs taking vegetable food. The stomach has no power of sorting out the constituents of food; it does not, for instance, push the carbohydrate into the duodenum more quickly than the protein. About three hours after a meal, about half the stomach contents have entered the intestine. The amount of absorption in the stomach is very small. The amount of protein in solution is lessened by overfilling the stomach. The relative amount of peptone, however, is not influenced by this factor, but the relative and absolute amount is even in early stages of digestion very large. The dry substances of the contents of the small intestine varies between 19% and 33%, and is dependent on the quantity of the digestive juices. The quantity of protein cleavage products in the small intestines show no regularity; the sum of the peptone and products which cannot be salted out is in most cases between 50% and 60%.  
W. D. H.

**Effect of Hydrocyanic Acid on Protein Katabolism.** I. ADOLF LOEWY (*Biochem. Zeitsch.*, 1907, 3, 439).—The importance of ferment action in the metabolism of protein as of carbohydrate material is insisted on. In poisoning of dogs by hydrocyanic acid, the examination of the urine showed an increase in protein katabolism, and a rise in

the caloric quotient of the secretion. As is the case also in poisoning by carbon monoxide, there are present in the urine intermediate products of katabolism.

W. D. H.

**The Value of Protein Cleavage Products in the Dog's Organism.** EMIL ABDERHALDEN and BERTHOLD OPPLER (*Zeitsch. physiol. Chem.*, 1907, 51, 226—240).—The paper is very largely a discussion of the results of previous workers. The question at issue is how far the results of extreme protein cleavage can replace protein in a diet. If the proteins are normally broken down to peptides and amino-acids there is no *a priori* reason why the cleavage products themselves should not be equally as nutritious as their parent substances. Distaste of the animals for the diet, and the onset of such symptoms as diarrhoea, increase the difficulties of the work. Some have stated that the products of pancreatic cleavage can maintain equilibrium, whilst those of acid hydrolysis can not. This opens up the question of the relative value of the different "Bausteine." In the present research, caseinogen was split to an extreme degree by a combination of digestive juices, and the products were found to be efficacious in maintaining the nitrogenous equilibrium of dogs. Further work in this direction is promised.

W. D. H.

**Activation of Pancreatic Juice by Calcium Salts.** C. DELEZENNE (*Compt. rend.*, 1907, 144, 388—390, 506—508. Compare Abstr., 1906, ii, 99, 100).—After calcium salts have activated pancreatic juice, they can be removed without affecting the activity of the juice, and so are not essential for the digestive action of trypsin. After the addition of the calcium salts, a certain latent period occurs, and then the activation occurs quite suddenly. The activation is thus similar to that which occurs in the part played by calcium salts in the activation of fibrin-ferment.

The change is believed to be a physical one, and the analogy to fibrin-ferment formation is accentuated by the fact that calcium salts do not activate the juice if it is contained within a well-paraffined vessel, or only after a long delay. The delay is prolonged if the juice has been previously dialysed.

W. D. H.

**Glycolysis.** G. W. HALL (*Amer. J. Physiol.*, 1907, 18, 283—294).—Pancreas alone cannot destroy dextrose; muscle alone destroys small quantities; but muscle juice *plus* a small amount of the expressed juice of the pancreas destroys considerable quantities. This confirms O. Cohnheim's statement; the alcoholic extract of boiled pancreas is a still more energetic co-operator. The active substance is completely precipitated by phosphotungstic acid. Under the same circumstances neither lactose, arabinose, nor lævulose is subject to the same destruction. The mixtures were sterile. Trypsin or some other constituent of the pancreas acts harmfully on the active muscle substance, and so causes inhibition in some experiments. In these experiments the use of a mixture of mono- and disodium phosphates to preserve neutrality is advantageous.

W. D. H.

**Nitrogenous Metabolism in Man after Removal of the Spleen.** LAFAYETTE B. MENDEL and ROBERT BANKS GIBSON (*Amer. J. Physiol.*, 1907, 18, 201—212).—The precise functions of the spleen are still debatable in spite of numerous experiments on animals, and a few observations on man. The present research deals with the course of metabolism in a young man in whom disease had rendered necessary the operation of removal of the spleen. The diet was poor in purine. The result of the study may be summarised by stating that aside from incidental details attributed to other factors (such as a lessening of chlorides during a febrile attack), no striking variations from the normal distribution of the urinary components were discoverable.

W. D. H.

**Equilibrium in Metabolism.** ROBERT EHRSTRÖM (*Chem. Zentr.*, 1907, i, 360—361; from *Skand. Arch. Physiol.*, 18, 281—297).—After the administration of different substances (compounds containing nitrogen, sulphur, bromine, iodine, fluorine, chlorine, phosphorus, sodium, and potassium) a temporary retention was observed previous to excretion.

W. D. H.

**Glycogen Metabolism of the Fœtus.** JAMES LOCHHEAD and WILHELM CRAMER (*Proc. Physiol. Soc.*, 1907, xi—xii; *J. Physiol.*, 35).—In pregnant rabbits glycogen was estimated by Pflüger's method in the maternal placenta, the fœtal placenta, the fœtal liver, and the remainder of the fœtus. At early dates, the maternal placenta possesses a large store of glycogen, and is comparable with the normal liver; this remains constant until the twenty-fourth day, and a progressive decrease then sets in, although some is still left there at the end of pregnancy. This corresponds with a steady increase of glycogen of the fœtal liver; it is on the twenty-fifth day that it here rises for the first time above that in the rest of the fœtal body. Feeding on carbohydrates does not affect the placental store of glycogen or that of the fœtal liver. In badly nourished fœtuses, the fœtal glycogen is less than normal, although the placental glycogen is unchanged.

W. D. H.

**Superiority of the Dispensation of Energy in Assimilation of Protein Nutriment.** AUGUSTE CHAUVEAU (*Compt. rend.*, 1907, 144, 237—243, 604—610).—The paper is mainly theoretical. A distinction is drawn between the immediate and ultimate destination of food material. So far as protein is a reserve material, it is regarded as being transformed into fat, but the amount of energy expended for the formation of such a reserve is much greater than in the simple storage of fat from fat food, or of the transformation of carbohydrate into fat. The principle of isodynamic substitution of one food for another is therefore incorrect; the nutritive values of foods cannot be calculated from their heats of combustion.

The second paper continues the argument from the pathological standpoint, especially that of the diabetic conditions in depancreatised animals. Here the transformation of the protein into sugar instead of fat occurs. The importance of the part played by oxygen is insisted on.

W. D. H.

**Effect of Partial Inanition followed by Return to Normal Diet on the Growth of White Rats.** SHINKISHI HATAI (*Amer. J. Physiol.*, 1907, 18, 309—320).—So far as body weight and weight of central nervous system are concerned, the effect of a twenty-one day period of partial inanition on albino rats thirty days old is eventually completely compensated. The brain and spinal cord are, however, richer in water and poorer in ether-alcohol extractives than in control animals.

W. D. H.

**Neutrality of Protoplasm.** LAWRENCE J. HENDERSON and OTIS F. BLACK (*Amer. J. Physiol.*, 1907, 18, 250—255).—In the presence of both free and combined carbon dioxide at 20°, mono- and disodium phosphates can exist only in molecular proportions varying between 1:9 and 5:5. All such solutions are neutral, and the hydrogen or hydroxyl ionisation cannot vary more than about  $5 \times 10^{-7}$ . Accordingly by the presence of phosphates and carbonates in considerable amount protoplasm is extraordinarily safeguarded from variations in hydrogen or hydroxyl ionisation, which can hardly amount to more than 5 parts in 10 billion parts of protoplasm. The occurrence of alkalinity is absolutely prevented by the presence of free carbon dioxide, and the system can neutralise relatively enormous quantities of acid without losing its precise neutrality.

W. D. H.

**Normal Occurrence of Arsenic in the Human Organism.** GUILLAUME SCHEFER (*Ann. Chim. anal.*, 1907, 12, 52—58, 97—101).—Arsenic has been detected in thyroids, the hair, skin, liver, kidneys, and the brain; negative results were obtained with mammary glands, the spleen, heart, lungs, and stomach. The exact particulars as to quantity are recorded in a table.

For a full description of all the precautions to be taken to guard against errors and for details of the apparatus used, the original paper should be consulted. The chief improvement in the apparatus is the use of two hydrogen generators, one for expelling the air and the other for generating the arsenic hydride. The hydrogen is dried over cotton-wool desiccated at 120°.

L. DE K.

**Genesis of Fat from Albuminous Substances (Lipogenetic Enzymes).** RAFFAELE PALADINO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 520—525).—The author has made experiments on three purulent liquids, either exuded or transuded, obtained from patients of the Hospital for Incurables at Naples. After their fat content had been determined, the liquids were mixed with chloroform, and kept in a state of continual agitation in closed vessels at 40°. In the course of two or three months, considerable increases occurred in all three cases in the amount of substance extracted by ether. These changes are assumed to be due to lipogenetic enzymes, which effect the transformation of albuminous substances into fat.

T. H. P.

**Occurrence of Caprylic (*n*-Octoic) Acid in the Butyric Fermentation; the Constitution of the Hexoic Acid in Butter Fat.** HENRY S. RAPER (*Proc. physiol. Soc.*, 1907, xxiv—xxvi; *J. Physiol.*, 35).—Nencki suggested that in the butyric fermentation

of lactic acid, the latter splits into formic acid and acetaldehyde, two molecules of the latter then uniting to form butyric acid. Leathes has suggested that by a further union of aldehyde molecules and ensuing reduction higher fatty acids can be formed. The butyric fermentation would thus represent the first stage of a reaction which goes to a completion in the formation of fats in the body. The fact that *n*-hexoic (caproic) acid is a regular product of the butyric fermentation supports this view, and in the present research *n*-octoic (caprylic) acid was also discovered.

The hexoic acid in butter-fat is not anomalous in having a branched chain, as some have stated, but is normal hexoic acid. W. D. H.

**Fibrinolysis.** STANISLAW N. PINKUS (*Proc. physiol. Soc.*, 1907, xiii—xiv; *J. Physiol.*, 35).—Fibrin left in contact with the blood dissolves to a considerable degree, and dissolves also in concentrated saline solutions. If left in contact with chloroform water under conditions of sterility, it dissolves after a period of latency (from three to twenty-two days) which varies for each species of animal. If placed in chloroform, fibrinolysis occurs, but a thick curd appears, due to the coagulating effect of the chloroform. Fibrinolysis does not occur in all cases; fibrin from castrated animals usually remains quite insoluble; cat's fibrin was insoluble in seven cases out of nine. The effects of temperature are described, but altogether the process is very capricious; even in one and the same animal the variations are extreme.

W. D. H.

**Transformation of Formic Acid and Formates in the Organism.** C. FLEIG (*Compt. rend.*, 1907, 144, 386—388).—Formic acid according to some is eliminated in the urine as carbonates, according to others, it is excreted in greatest measure as such. The present research shows that the amount of carbonates in the urine increases so as to account for 56% of the acid if given by the mouth, or 64% if given intravenously. Possibly some is excreted by other channels, especially as carbon dioxide by the lungs. The transformation can be effected as Battelli showed by liver extracts in the presence of hydrogen peroxide, but extracts of other tissues (spleen, kidney, lungs, intestinal mucous membrane) will do so also, and the addition of hydrogen peroxide is unnecessary. The same change occurs as the result of bacterial action in the intestines.

W. D. H.

**General Physiology of Muscle. I. Influence of Sodium Salts on Frog's Muscle.** CARL SCHWARZ (*Pflüger's Archiv*, 1907, 117, 161—217).—The experiments were made on the frog's sartorius. After this is immersed in a sucrose solution it loses its salts (exosmosis) and its irritability in the course of a few hours. When it is then placed in a solution of a sodium salt, irritability returns. A large number of sodium salts were employed in equal molecular concentrations. The time of return of irritability and the onset of fatigue on subsequent excitation differ in the different salts. Full details of each are given, and also a discussion of the cause of the differences noted.

The general view taken is that the difference is due to action of the anions, and that the latter act in some way on the membranes.

W. D. H.

**Cause of the Treppe (Staircase Phenomenon).** FREDERIC S. LEE (*Amer. J. Physiol.*, 1907, 18, 267—282).—A full account of experiments of which preliminary notice has already appeared (this vol., ii, 187).

W. D. H.

**Lactic Acid in Amphibian Muscle.** W. M. FLETCHER and F. GOWLAND HOPKINS (*J. Physiol.*, 1907, 35, 247—309).—Estimations of the lactic acid yielded by frog's muscles under various conditions are given. Manipulative treatment of irritable muscle increases the amount, so special precautions to avoid this error were necessary. The estimations were made by weighing the acid as zinc sarcolactate in the anhydrous state. Fresh resting muscle yields very small amounts, and possibly most of this is due to unavoidable manipulation. A large increase follows mechanical injury, heating, chemical irritation, and the destruction due to immersion in alcohol. It is spontaneously developed under anaërobic conditions in excised muscles, equal increments arising in equal times. After complete loss of irritability the yield remains stationary. Fatigue due to contractions of excised muscles leads to an increase of lactic acid, and the amount attainable is not more than about half that reached by destructive agencies, such as full heat-rigor. In an atmosphere of oxygen there is no survival development of the acid for long periods after excision. The acid formed in an excised fatigued muscle disappears when it is placed in oxygen. This disappearance proceeds rapidly at first, then more slowly, and usually ultimately reaches to about one-half that originally present. This does not occur at temperatures over 30°, or when the muscle has been mechanically injured; the normal architecture of the muscle must be maintained for this oxygen effect to be manifested. The amount of acid produced in full heat rigor at 40—45° is constant for similar muscles, and is not affected by a previous appearance of the acid due to fatigue, or by a previous disappearance due to the action of oxygen, or by alternate appearances and disappearances several times repeated.

The following new colour test for lactic acid is recommended. Five c.c. of sulphuric acid, a drop of saturated solution of copper sulphate, and a few drops of the suspected solution are placed in a test tube in a water-bath at 100° for two minutes. The tube is cooled, and 2 or 3 drops of a dilute alcoholic solution of thiophen (10 to 50 drops in 100 c.c.) added. The tube is replaced in the boiling water, when, if lactic acid is present, the fluid assumes a light cherry-red colour. This is due to an aldehyde reaction with thiophen.

W. D. H.

**Adrenal Gland of Rat.** CHALMERS WATSON (*J. Physiol.*, 1907, 35, 230—232).—Statistics are given which show that the adrenal glands of wild rats are considerably larger than those of tame rats. In tame rats the proportionate weight of adrenal tissue diminishes with age and growth of the animal. There is not such a marked

diminution in the case of the wild animals. It is suggested that these facts are related to the greater muscular activity of the latter class.

W. D. H.

**First Products of Decomposition of the Testicular Pulp of the Ram by Means of Cold Dilute Sodium Hydroxide Solution.** MICHELE BARBERIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1907, [iii], 13, 14—28).—When the finely-divided testicular pulp of the ram is treated in the cold with 1, 2, or 3% sodium hydroxide solution, ammonia is evolved and the following compounds formed: (1) products soluble in water, consisting of proto- and hetero-albumoses and albumoses A and B; deutero-albumoses and peptones were not detected; (2) products insoluble in water, consisting of an alkali-albumose corresponding with that of Maas (Abstr., 1900, i, 708), and an acid, *orcoproteinic acid*, which must be regarded as a mixture of de-aminated proteins having the formula  $C_{113}H_{180}O_{36}N_{26}S$ .

T. H. P.

**Analysis of a Rhinolith.** DURIU (*Chem. Zentr.*, 1907, i, 367, from *Bull. Sci. pharmacol.*, 13, 327).—A stone from the nasal cavity of a man weighed 7.75 grams, and contained water, 2%; protein, 30%; calcium phosphate, 44%; calcium carbonate, 21%; magnesium phosphate, 3%, and traces of iron, ammonia, and sodium chloride. No foreign body was found to form the nucleus of the concretion.

W. D. H.

**Analysis of a Rhinolith.** MAURICE JAVILLIER (*Chem. Zentr.*, 1907, i, 367; from *Bull. Sci. pharmacol.*, 13, 454).—The stone weighed nearly a gram, and contained water, 3%; organic substances, 19.5%; calcium phosphate, 50.5%; calcium carbonate, 18%; magnesium phosphate, 7%, with traces of iron, &c.

W. D. H.

**The Catalase of Human Milk.** R. VON DER VELDEN (*Biochem. Zeitsch.*, 1907, 3, 403—412).—The presence of catalase in human milk distinguishes it from cow's milk. In the present research, human milk was examined within an hour of its removal by the breast pump, mixed with hydrogen peroxide, agitated by a small turbine at constant speed, and the amount of oxygen liberated read off from minute to minute. The chief part is liberated within the first six or seven minutes. Marked ("bizarre") irregularities were noted. The more bacteria present, the less oxygen as a rule. The more cells in the milk, the more oxygen. But these two factors do not explain the great variations. There is no parallelism between the amount of fat present and the amount of oxygen obtained.

W. D. H.

**Existence of a Kinase in Cow's Milk.** A. HOUARDY (*Bull. Acad. roy. Belg.*, 1906, 888—900. Compare Frouin, 1901, ii, 561; Hamburger and Hekma, Abstr., 1902, ii, 515; Delezenne and Mouton, Abstr., 1903, ii, 229, 448; Hekma, Abstr., 1903, ii, 559; Pawloff and Parastschuk, Abstr., 1904, ii, 748).—It is shown that cow's milk contains a kinase, which it is proposed to call *lactokinase*, resembling the enterokinase which occurs in the intestines of animals,

in rendering pancreatic juice active. The results of the experiments described in the original show that the addition of the pancreatic juice of the dog promotes autodigestion of unboiled cow's milk, but this action is much enfeebled in the case of milk which has been heated during twenty minutes at 75° or beyond that temperature. The pancreatic digestion of milk is hastened by the addition of enterokinase. By the maceration of coagulated albumin in milk it acquires the property of being digested by pancreatic juice due to the absorption of lactokinase, and if the impregnated albumin be heated during thirty minutes at 73°, it is no longer digested by pancreatic juice.

T. A. H.

**Excretion of Sodium Chloride and Nitrogen by the Skin.** SCHWENKENBECHER and SPITTA (*Arch. exp. Path. Pharm.*, 1907, 56, 284—300).—The amounts of sodium chloride and nitrogen excreted by the skin of healthy men in bed are about equal, and amount to 0.3 gram per diem. In diseases such as Basedow's disease, articular rheumatism, and the crisis of pneumonia when sweating is excessive, the amount of chloride excreted may reach nearly 1 gram a day. The "insensible perspiration" has only a very small sodium chloride concentration (about 0.06%); on increase of the activity of the sweat glands, the percentage may reach 0.3. In profuse secretion produced by warmth, pilocarpine, or the pathological states mentioned, it falls to 0.05%. The patients investigated had no kidney trouble.

W. D. H.

**Elimination of Thiocyanates.** D. H. DE SOUZA (*J. Physiol.*, 1907, 35, 332—345).—Thiocyanates are rarely present in the saliva, urine, pancreatic juice, and blood of the dog. If present in the blood they pass out into saliva, bile, pancreatic juice, and urine. The concentration in the urine may be less or greater than in the blood; it is diminished by sodium sulphate diuresis. It is considered that the glomeruli turn out the substance at a concentration equal to that of the blood, and that absorption by the renal cells regulates the final output. Thiocyanates in the food are readily absorbed and remain in the body a considerable time. After feeding or injection, the parotid saliva contains less than the submaxillary, and still less than the serum. After feeding with acetonitrile, thiocyanates are present in urine, saliva, and serum. The substance is regarded not as a specific secretion of the salivary glands, but merely as a waste product in the blood, from which it is turned out by various excretory channels.

W. D. H.

**Excretion of Calcium in the Urine.** W. A. BOEKELMAN and J. PH. STAAL (*Arch. exp. Path. Pharm.*, 1907, 56, 260—283).—The excretion of calcium is shown to vary with the amount in the diet. The excretion of phosphoric acid is in the main parallel to that in the diet; the excretion of calcium rises on a calcium-poor and falls on a calcium-rich diet. The observations recorded relate to four patients; in one of these there was an abnormally high calcium excretion under all circumstances, and she was never well unless the diet was rich in calcium.

W. D. H.



**The Formation of Acetone in Urine.** ALEX. MÜLLER (*Chem. Zentr.*, 1907, i, 366—367; from *Pharm. Zeit.*, 51, 1019).—Acetone was found in the urine of people who become suddenly ill after partaking of the decomposition products of fish or flesh; from this the conclusion is drawn that in diabetes the urinary acetone does not arise directly from organ-protein or fat, but from ptomaines formed from these. Such a poisonous product was extracted from the urine of persons suffering from diabetes and lung disease. W. D. H.

**Endogenous Purine Metabolism in Man.** WALTER O. SIVÉN (*Chem. Zentr.*, 1907, i, 361; from *Skand. Arch. Physiol.*, 18, 177—193).—Burian concluded that endogenous purine excretion is raised by severe muscular work. In the present research, it was found that it is smaller during sleep than in the working state. As a rule, it is greater in the forenoon than in the afternoon, but any direct relation between it and muscular work cannot be established. W. D. H.

**The H:N Quotient in Alcaptonuria.** ARCHIBALD E. GARROD and T. SHIRLEY HELE (*Proc. physiol. Soc.*, 1907, xv—xvi; *J. Physiol.* 35).—The proportion of homogentisic acid to total nitrogen is comparatively constant, although variations occur in the diet. In four previous cases the quotient varied from 46 to 55:100. A fifth case now added had the quotient 50:100. W. D. H.

**Excretion of Nitrogen, Creatinine, and Uric Acid in Fever.** JOHN B. LEATHES (*J. Physiol.*, 1907, 35, 205—214).—The work of Folin and others has shown the importance of a study of creatinine excretion as a measure of tissue metabolism, urea in health being mainly a measure of exogenous nitrogenous katabolism. In abstinence from protein food, however, the principal nitrogenous katabolite remains urea, although its amount is reduced both absolutely and relatively. In fever it has long been known that the excretion of nitrogen is high, and independent of the amount in the food; it must therefore come from the breakdown of nitrogenous materials in the tissues. The present observations made partly on patients and partly on the author's person (fever being artificially produced) confirm this statement. Accompanying the increase of total nitrogen there is also a rise of both creatinine and uric acid. But the increased output is most marked in the case of uric acid, and least in the case of creatinine. The paper is illustrated by full details of analyses with curves. W. D. H.

**The Mechanism of Experimental Glycosuria.** HUGH MCGUIGAN and CLYDE BROOKS (*Amer. J. Physiol.*, 1907, 18, 206—266).—Glycosuria may be experimentally produced in many ways, but the mechanism is in all cases believed by the present authors to be the same, and related to changes in protoplasmic activity and not to ferment action. It is believed that glycogen exists in combination with protein, and that all salts which decompose this compound cause glycosuria. Calcium chloride prevents its decomposition by the formation of a more stable combination of calcium, protein, and glycogen. W. D. H.

**Creatinine Excretion in a Case of Pseudo-hypertrophic Muscular Dystrophy.** EDMUND I. SPRIGGS (*Biochem. J.*, 1907, 2, 206—216).—In this case, the excretion of creatinine, on a diet free from meat and meat extracts, was about half the normal, and was less than normal on an ordinary diet. Since the muscular tissues had suffered much reduction, this agrees with the view that creatinine is mainly of muscular origin. On a diet of sufficient caloric value, but containing hardly any protein, nitrogen elimination sank in four days to 2 grams or 0.039 gram per kilo. Under these circumstances, the proportion of nitrogen excreted as creatinine approached that found in normal individuals on such a diet. W. D. H.

**Partial Nephrectomy in Cats.** FRANCIS A. BAINBRIDGE and ARTHUR P. BEDDARD (*Proc. physiol. Soc.*, 1907, xxi—xxii; *J. Physiol.*, 35).—Bradford found in dogs that removal of three-quarters of the total kidney weight led to an increased output of water and of nitrogen, and concluded that the kidneys exercised an influence on the nitrogenous metabolism of the body. The present experiments on cats do not confirm this view; the cats usually took little or no food after the operations, and the course of metabolism was not found to vary from that usually observed in cases of inanition. W. D. H.

**Action of Alcohol on the Circulation.** WALTER E. DIXON (*J. Physiol.*, 1907, 35, 346—366).—In moderate doses, and if well diluted, ethyl alcohol has little effect on the rate of the normal heart; in large doses it excites the medulla and slows the heart through the vagus. The failing heart is accelerated by alcohol. When taken by the mouth in concentration, even if not swallowed, alcohol reflexly quickens the beat. If it is swallowed the effect lasts longer. In moderate doses, alcohol causes dilatation of the superficial vessels and some slight constriction, which after large doses is followed by dilatation, of the internal vessels. In moderate doses, alcohol increases the activity and output of the heart. This is partly due to the fact that alcohol is a readily assimilable food-stuff. In large doses (over 0.5% in the blood) it exerts a direct toxic action depressing the heart. If given to animals which show signs of circulatory failure, moderate doses raise the arterial pressure mainly on account of its action on the heart. In normal animals and in man the systolic pressure may rise a little or remain unchanged, and the diastolic pressure tends to diminish. W. D. H.

**Action of Ethyl Alcohol on the Isolated Mammalian Heart.** E. LOUIS BACKMAN (*Chem. Zentr.*, 1907, i, 489; from *Skand. Arch. Physiol.*, 18, 323—363).—Experiments on the hearts of rabbits show that alcohol has neither a stimulating nor nutritive action. Small doses (0.05—0.1%) added to the perfusing fluid lessen the contractions and produce arrhythmia; this is more marked with larger doses; smaller doses have no effect at all. W. D. H.

**Action of Alcohol on the Body-temperature of Men.** GEORG VON WENDT (*Chem. Zentr.*, 1907, 650—651; from *Skand. Arch. Physiol.*, 19, 171—181).—Alcohol produces a fall of body-temperature if at the

time this is much above the lower limit of the normal temperature. It never sinks below this limit. The drug produces no noteworthy change in the loss of heat, but there is a transitory fall in the production of carbon dioxide, which is attributed to lessened oxidation processes.

W. D. H.

**Action of Glyoxylic Acid on the Animal Body.** OSCAR ADLER (*Arch. exp. Path. Pharm.*, 1907, 56, 207—235).—Glyoxylic acid has been assigned a place in the intermediary metabolism of plant life, and more recently in animals. Pohl found that administration of the sodium salt to animals did not lead to the passage of the acid into the urine, but to a slight increase of oxalic acid there. Eppinger discovered the acid in the urine after the administration of numerous substances, but his indole test for the acid has been shown to be untrustworthy. Eppinger also noted the increase of allantoin after feeding with potassium glyoxylate, and it is known that *in vitro* glyoxylic acid and urea form allantoin. In the present research the estimation of glyoxylic acid in the solutions employed was carried out with phenylhydrazine, and the test used for that substance in the urine is the violet colour produced by the addition of peptone solution and sulphuric acid. Hopkins and Cole's statement that glyoxylic acid is the cause of the Adamkiewicz reaction is accepted without question. It is generally supposed that glyoxylic acid can be distilled off from urine, but it is admitted that this is not the case, and the explanation advanced is the affinity of the acid for urea. If 1.3—2.4 grams of the sodium salt are injected hypodermically in dogs, no noteworthy result occurs, but larger doses, repeated daily, lead to loss of appetite and of weight; the dogs drink a good deal and pass a large amount of urine which after a few days becomes albuminous. The symptoms culminate in death, preceded by convulsions and paresis. Given by the mouth it is less toxic. Smaller doses cause similar symptoms in rabbits. *Post mortem* the kidneys only show pathological signs, which are similar to those produced by oxalic acid, the tubules being filled with calcium oxalate crystals. Intravenous injection slows the heart and may cause an alternating action; there is a slight and temporary rise of arterial pressure; death occurs from respiratory failure. The same effects occur when the vagus is thrown out of gear by atropine; glyoxylic acid acts directly on the heart muscle. The acid rapidly disappears from the blood, but can be obtained from the liver; in no case could it be identified with certainty in the urine, nor was there any evidence of an increased formation of allantoin.

W. D. H.

**[Physiological] Action of Forgenine.** P. PICCININI (*Chem Zentr.*, 1907, i, 651; from *Boll. Chim. Farm.*, 1906, 45, 945—957).—Forgenine (tetramethylammonium formate) has an action like digitalis. The indications for its clinical use are described.

W. D. H.

**The Diuretic Action of Dimethylaminoparaxanthine and its Decomposition in the Body.** J. FORSCHBACH and S. WEBER (*Arch. exp. Path. Pharm.*, 1907, 56, 186—200).—This substance,

known in commerce as *paraxine*, is an energetic diuretic, and illustrative cases of its clinical usefulness are cited. It sometimes produces nausea and nervous symptoms. A crystalline substance separated from the urine is not paraxine, but 2:6-dioxy-8-dimethylamino-7-methylpurine, m. p. above  $319^{\circ}$ , which contains one  $\text{CH}_2$  group less. This substance has a strong diuretic action. W. D. H.

**Physiological Action of Muscle Extract.** J. G. SLADE (*J. Physiol.*, 1907, 35, 163—181).—Muscle extract was prepared from fresh muscle, or from Liebig's extract, and for most experiments was freed from salts by alcohol. Experiments on the author's own person with the ergograph showed that taken in practical amounts it had no action on the onset of fatigue or on the power of doing arithmetical work. It produces diuresis and vaso-dilation of the kidney. In strong solutions and large amounts it is liable to cause purgation. Experiments on animals showed it to have a powerful physiological effect, but the deductions as to which constituents this is due are put forward with reserve. If injected it produces fatigue and prostration. In moderate doses it increases the heart's rate and activity; this is not due to creatine, xanthine, or urates. The vessels are constricted after an initial dilatation when small doses are used. The movements of plain muscle throughout the body are increased. This is probably due to ornithine and novaine. 0.1% Solution of muscle extract has no effect on voluntary muscle; a 0.5% solution increases and a 2% solution diminishes its work. Xanthine has a similar action in increasing work, but creatine is devoid of action. Fatigue increases the extractives of muscle, and the activity of the extract rises. W. D. H.

**The Uptake of Carbon Monoxide by the Nervous System.** EDUARD HOKE (*Arch. exp. Path. Pharm.*, 1907, 56, 201—206).—In addition to the well known action carbon monoxide has on the blood, several investigators have surmised that it has a direct action on the nervous system. It is agreed that if this is so, the gas ought to be obtainable from nervous tissues in greater amount than from the blood and other parts. This argument is based on the analogy of chloroform poisoning. None was obtained from brain, and so the conclusion is drawn that any direct action of the gas on the brain is excluded, and that the symptoms are due to asphyxia. W. D. H.

**Dropsy and Glycosuria in Uranium Poisoning.** RUDOLF FLECKSEDER (*Arch. exp. Path. Pharm.*, 1907, 56, 54—67).—Uranium salts often cause dropsy of various kinds; this is not necessarily of nephritic origin, although nephritis often occurs. The primary cause of the exudation is regarded as a specific lesion of the walls of the blood vessels. There is also glycosuria and usually hyperglycæmia. Increase of sugar in the blood occurs if the kidneys have been extirpated. W. D. H.

**Diminution of Toxicity of Silver Nitrate Treated with Sodium Thiosulphate, and the Influence of Light on the Phenomenon.** LUCIANO PIGORINI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 359—362).—A specimen of *Carassius auratus* weighing

about 4 grams is killed in *N*/500 silver nitrate solution in about three hours. If an equivalent amount of sodium thiosulphate is also present, death occurs after five hours ten minutes, whilst, if the proportion of thiosulphate is doubled, the time is increased to one hundred hours, and, if trebled, to one hundred and ninety-two (or two hundred and forty) hours. If the experiments are made in light, comprising the red, orange, and yellow rays of the spectrum, these lethal periods are greatly diminished. No explanation is suggested for these results.

T. H. P.

**Pathology of Lysol and Cresol Poisoning.** WANDEL (*Arch. exp. Path. Pharm.*, 1907, 56, 161—185).—Cresol is split off from lysol in the body, and the toxicity of the latter substance is due to this circumstance. Local destruction of cells occurs at the place of application. There is destruction of blood corpuscles in the vessels where absorption occurs. Degenerative changes in the liver form a marked feature. It acts as a poison to cells and protoplasms whereon it occurs in a free state. Hæmoglobinuria and albuminuria of hepatic origin are usually present. Some tolerance is established by the formation of a compound between the cresol and some substance in the liver, and also by the fact that the bile excreted is abundant, by which channel the cresol is removed from the body. W. D. H.

**Action of Colloidal Poisons on Paramœcium.** WALTHER HAUSMANN and W. KOLMER (*Biochem. Zeitsch.*, 1907, 3, 503—507).—The natural immunity of certain unicellular organisms towards certain poisons does not depend on the colloidal nature of the poisons. Diphtheria toxin, tetanus toxin, alrin, and ricin are non-toxic to paramœcia, but the colloidal substances, tannin, saponin, and colloidal mercury are highly poisonous. Colchicin has no noteworthy effect at room temperature, but at 33° it is highly toxic. It has been previously shown that colchicine is non-toxic to bats during their winter sleep, although it is toxic at other times. W. D. H.

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### Chemistry of Vegetable Physiology and Agriculture.

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**Action of Nickel Salts on Micro-organisms.** E. MANOILOFF (*Centr. Bakt. Par.*, 1907, ii, 18, 199—211).—Nickel salts are much less poisonous than salts of copper and other metals. N. H. J. M.

**Micro-organisms Oxydising Hydrogen.** BRONISLAS NIKLEWSKI (*Bull. Acad. Sci. Cracow*, 1907, 911—932).—It was shown by de Saussure (*Mem. Soc. phys. hist. nat. Genève*, 1839, 8, 163) and by Immendorf (*Abstr.*, 1892, 374) that soil has the power of condensing a mixture of oxygen and hydrogen. An organism has now been obtained from soils which grows readily on mineral solutions

forming a skin on the surface which will condense 0.13 c.c. of oxygen-hydrogen mixture per hour per square cm. The condensing power is, however, soon lost. The production of the skin depends on the presence of hydrogen and free carbon dioxide unless organic carbon is provided. In presence of organic matter (acetates) it is formed when hydrogen is absent. Attempts to completely isolate the organism failed, a few colonies being always found which failed to oxidise hydrogen.

N. H. J. M.

**Alcoholic Fermentation of *Aspergillus Niger*.** S. KOSTYTSCHIEFF (*Ber. deut. bot. Ges.*, 1907, 25, 44—50).—The anaërobic respiration of *Aspergillus niger* is as feeble in presence of dextrose as when sugar is absent. When *Aspergillus niger* is completely immersed, the dextrose is decomposed into carbon dioxide and alcohol, a small portion being perhaps utilised for the production of oxalic acid. Mannitol gave similar results.

N. H. J. M.

**Some New Autotrophic Nitrogen Bacteria.** HERMANN KASERER (*Chem. Zentr.*, 1907, i, 652; from *Zeitsch. landw. Versuchswes. Oesterr.*, 10, 37—42).—*Bacillus nitrator* converts ammonia directly into nitrates. It is a long, medium-sized bacillus, which forms dense, white colonies, and does not liquefy gelatin. *Bacillus azotofluorescens* decomposes ammonium formate into nitrogen and formic acid, and then utilises the formic acid. It also, in absence of combined nitrogen, produces ammonium carbonate from formic acid and atmospheric nitrogen. A bacillus (*B. Hiltneri*) was obtained, which decomposes cyanides with production of nitrogen and carbon dioxide and which fixes free nitrogen in presence of sugar.

N. H. J. M.

**New Method of Staining the Tubercle Bacillus.** MICHELE BARBERIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 446—449).—This method consists in staining the bacterial preparation with a solution of magenta containing phenol and afterwards treating it with a dilute solution of nitrous acid, which does not affect the staining of the tubercle bacillus, but decolorises most bacteria, owing to the conversion of the basic magenta into a colourless diazo-compound.

The preparation is first treated, for twenty-five to thirty minutes at 40—50°, with a mixture of 2 c.c. of a cold saturated solution of magenta in 96% alcohol with 8 c.c. of a 5% aqueous phenol solution. It is then washed rapidly in water and immersed for ten to fifteen minutes in 10 c.c. of a dilute sodium nitrite solution (1:20,000) containing a drop of dilute hydrochloric acid (D 1.12). Bacteria other than the tubercle bacillus can then be stained differentially by means of methylene-blue. The preparation is finally washed in water, dried, and mounted in balsam.

T. H. P.

**Fatty Matters in, and Resistance to, Acids of the Tubercle Bacillus.** JULES AUCLAIR and LOUIS PARIS (*Compt. rend.*, 1907, 144, 278—287).—It is not possible to obtain all the fatty matters from Koch's bacillus unless it is extracted with several reagents in suc-

cession. Thus, from eight grams of the bacilli, light petroleum extracted 0.95, alcohol 0.46, ether 1.2, and chloroform 1.3 grams of fatty matter. The resistance to acids is not only a property of the fatty material, as some assume, but the protoplasm and cellulose possess it also.

W. D. H.

**Sulphurous and Acetaldehyde-sulphurous Acids and their Action in Various Organisms of Wine.** W. SEIFERT (*Chem. Zentr.*, 1907, i, 286—287; from *Zeitsch. landw. Versuchswes. Oesterr.*, 9, 1019—1059).—When wine casks are treated with burning sulphur a considerable proportion of the sulphur dioxide is rapidly absorbed by the wood even when the casks are dry. If the casks are closed the flame is extinguished when not more than one-third of the total oxygen has been used. When casks which have been very recently treated in this way are filled with water or must, about half the sulphur dioxide is absorbed by the liquid (100 mg. per litre). A wine containing 10 vols.% of alcohol absorbs about four-fifths of the sulphur dioxide (160 mg. per litre) and, in the ordinary method of filling, wine containing 10—12 vols.% of alcohol takes up on an average 8.2 mg. of sulphur dioxide per litre when 1 gram sulphur has been used per hectolitre of cask capacity.

Sulphur dioxide rapidly attacks the aldehyde of the wine, the largest quantity being absorbed in the first hour. In twenty-four hours, 12.8 mg. of the compound were formed in new wine, whilst a three year old wine was found to contain 32.7 mg. The quantity of aldehydesulphurous acid varies from 24—108 mg. per litre according to the wine, whilst the free sulphur dioxide is practically the same (2—4 mg. per litre) in all cases, and this quantity was also detected in a wine which had been fermented in the laboratory. It cannot be assumed therefore that the so-called free sulphur dioxide is present in a dissociated condition or in fact that free sulphur dioxide is contained in the wine at all. The presence of 1—4 mg. of free sulphur dioxide, determined by titration with iodine, cannot therefore have any practical signification. It has been observed that certain components of wine extract, which are probably nitrogen compounds, take up a considerable quantity of iodine and that the dissociation of aldehydesulphurous acid is delayed by the presence of these substances.

The quantity of sulphur dioxide which affects fermentation varies with the kind of yeast. When 1% of must which is being actively fermented by a pure yeast is added to a sulphurised must, the fermentation is not perceptibly decreased unless the must contains 80—100 mg. of sulphur dioxide per litre, and under similar conditions the presence of aldehydesulphurous acid equivalent to 100 mg. of sulphur dioxide per litre has no perceptible effect. The presence of 50—100 mg. of sulphur dioxide per litre delays the beginning of the fermentation for several days, but an equivalent quantity of the aldehyde compound has no effect when the usual quantity of yeast is used. *Mycoderma aceti* offers great resistance to the action of aldehydesulphurous acid and is comparatively little affected by free sulphur dioxide. *Bacterium aceti* is much more sensitive, but, whilst the presence of 100 mg. of the aldehyde compound per litre does not



prevent the growth of the bacterium, it is killed by 50 mg. of free sulphur dioxide.  
E. W. W.

**Influence of Manganese Salts on Alcoholic Fermentation.** E. KAYSER and H. MARCHAND (*Compt. rend.*, 1907, 144, 714—716. Compare this vol., ii, 288).—Wine, cider and beer yeast which have been grown through several generations in musts to which manganese sulphate has been added, retain their acquired property of initiating fermentation more rapidly and producing more alcohol when they are sown in musts free from manganese sulphate, but the amounts of "fixed" and volatile acids and of glycerol produced are below the normal. Further, the addition of manganese sulphate to the must produces a greater effect in the cases of yeasts which have been accustomed to this salt than with yeasts not previously grown in a medium containing it. The amount of manganese sulphate to which yeast can be accustomed varies with the different species.

T. A. H.

**Conditions of the Formation of Fusel Oil and Their Connexion with the Formation of Proteins in Yeast.** FELIX EHRLICH (*Ber.*, 1906, 40, 1027—1047).—It is assumed by the author that the occurrence of fusel oil during alcoholic fermentation is due to the hydrolysis of *l*-leucine and *d*-isoleucine by means of an enzyme, thus,  $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} = \text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} + \text{CO}_2 + \text{NH}_3$  and  $\text{CHMeEt}\cdot\text{CH}(\text{NH}_2)\text{CO}_2\text{H} + \text{H}_2\text{O} = \text{CHMeEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} + \text{CO}_2 + \text{NH}_3$ . The liberated ammonia is immediately used up for the formation of proteins.

Yeast, containing as little nitrogen as possible, was added in excess to a sugar solution containing leucine; the percentage of nitrogen in the yeast was increased at the expense of the leucine, whilst amyl alcohol was formed simultaneously. Within one to three days a comparatively large amount of fusel oil may be obtained from leucine. The yeast used was a pure culture of top yeast obtained from the Berlin "Institut für Gährungsgewerbe." When this yeast was added to a 5—10% sugar solution, containing leucine, the fermentation began after a few minutes and was finished in a comparatively short time, the presence of the leucine having the effect of accelerating the fermentation. The amyl alcohol obtained was optically inactive; when isoleucine was employed in place of leucine the resulting amyl alcohol was lævorotatory. In the preliminary experiments the sugar solutions were first sterilised before the yeast was added, but this was subsequently found to be unnecessary. The amount of amyl alcohol produced in each fermentation was estimated according to the Röse-Herzfeld method, which, however, is not free from objection.

The amount of fusel oil formed during alcoholic fermentation may be increased to from seven to eight times the customary amount by the addition of leucine. The best yield of fusel oil in the crude spirit was obtained when an excess of leucine was used with a relatively small amount of yeast and with much sugar; in the fermentation of a little sugar with much yeast the spirit contained a less percentage of fusel oil. The percentage of nitrogen in the yeast used considerably affects

the yield of fusel oil; when the yeast is poor in nitrogen the yield of fusel oil is good.

In the fermentation experiments quoted, in addition to estimating the ethyl alcohol and fusel oil formed, the author also estimated the amount of leucine which survived the fermentation. When *r*-leucine was added at the start, the residual leucine was dextrorotatory. The amount of leucine which disappeared during the fermentation corresponded with the amount of amyl alcohol obtained. Experiments showed that an amount of nitrogen, corresponding with the leucine used and the amyl alcohol formed, is removed from the fermenting liquid and assimilated by the yeast.

If equal amounts of leucine and asparagine are added to a sugar solution which is then fermented by yeast, only about half as much of fusel oil is obtained as when the asparagine is absent. Even less fusel oil is obtained when, in place of the asparagine, ammonium carbonate is added with the same nitrogen content as the asparagine in the preceding experiment. Experiments are quoted which show that, when other substances besides leucine are present as a source for supplying nitrogen to the yeast, the latter preferably takes its nitrogen from them; the leucine is accordingly less attacked than it would be if those substances were absent, and the yield of amyl alcohol is accordingly less.

The effect of leucine in increasing the yield of amyl alcohol was also shown when, in place of the fermentation of sugar, the fermentation of molasses was studied.

The proportion of *isoleucine* to leucine in unfermented molasses is greater than in plant materials used as a source of alcohol; this is in agreement with the fact that the crude fusel oil obtained from molasses is much more levorotatory than that obtained from other sources, such as grain or potatoes (Marckwald, *Abstr.*, 1902, i, 418).

The author has also converted tyrosine by means of sugar and yeast into *p*-hydroxyphenylethyl alcohol, m. p. 92.5°. Similarly, phenylethyl alcohol was obtained from phenylalanine and benzyl alcohol from phenylaminoacetic acid.

A. McK.

**Assimilation of Nitrogen Compounds by Fungi.** M. RACIBORSKI (*Bull. Acad. Sci. Cracow*, 1906, 733—770).—Nitrites are assimilated by various fungi in neutral solutions, but are poisonous in presence of acid. Nitrates behave similarly. The growth of fungi supplied with nitrates or with ammonium salts is affected in different ways by different oxidising or reducing substances.

Hydroxylamine and hydrazine salts are not invariably poisonous; they are assimilated by several fungi. The nitrogen of amino-acids is indirectly utilised by fungi, being first converted into ammonia.

N. H. J. M.

**Chemical Studies on the Cell and its Medium. II. Chemicobiological Relations in Liquid Culture Media.** AMOS W. PETERS (*Amer. J. Physiol.*, 1907, 18, 321—346. Compare this vol., ii, 121).—A medium consisting of water, salts, gases of organic matter from hay was studied as a type. After seeding with various plants and

animal organisms, its changes (acidity, alkalinity, conductivity, &c.) were determined daily. Different organisms produce different effects. The concentration of acid, due to bacterial metabolism, is one of the chief factors determining the biological content and history of a culture. Four periods may be recognised; the first is characterised by maximum acidity and the abundant development of certain bacteria; the second has lower, and the third (a prolonged stage) still lower acidity; other organisms then flourish better. In the fourth period the organic matter is in an exhausted condition, but the saline constituents are favourable to the growth of green algæ. When an organism has a pronounced optimum position in the history of the culture, it is not possible to reverse the position of its optimum by seeding it into the culture at a different time than that of its optimum. W. D. H.

**Excretion of Hydrogen by Seed-bearing Plants.** S. KOSTYTSCHIEFF (*Chem. Zentr.*, 1907, i, 283—284; from *Ber. deut. bot. Ges.*, 1906, 24, 436—441).—Müntz and de Luca state that in absence of oxygen, fungi and seed-bearing plants which yield mannitol excrete hydrogen. The present experiments on the leaves and twigs of mannitol-yielding seed-plants placed in air show that hydrogen is formed during respiration; but when oxygen is excluded, no formation of hydrogen occurs. W. D. H.

**Anaërobic Respiration of Seed Plants without Alcohol Production.** WLADIMIR PALLADIN and S. KOSTYTSCHIEFF (*Ber. deut. bot. Ges.*, 1907, 25, 51—56. Compare Abstr., 1906, ii., 696).—Seed plants only produce alcohol in presence of carbohydrates. It is suggested that the liberation of carbon dioxide in absence of carbohydrates may be due to decomposition of proteins. Palladin showed (*Ibid.*, 1888, 6, 205 and 296) that proteins break down in absence of oxygen without acid amides being formed. N. H. J. M.

**Decomposition of Phosphorus Compounds in Ripening Seeds.** W. ZALESKI (*Ber. deut. bot. Ges.*, 1907, 25, 58—66. Compare Abstr., 1906, ii, 881).—Seeds which were cut in half and kept for three days showed an increase of protein phosphorus and a corresponding decrease of phosphoric acid; the amounts of phosphatides remained practically unchanged. When, however, unripe seeds undergo autodigestion the protein phosphorus diminishes, as in the case of germinating seeds.

It remains to be ascertained whether these changes are brought about by the same or different enzymes. It is, however, suggested that enzymatic reactions may be reversible. N. H. J. M.

**Ferment Reactions in the Expressed Juice of Seedlings Rich in Fat.** ASTRID EULER and HANS EULER (*Zeitsch. physiol. Chem.*, 1907, 51, 244—258).—In certain fat-containing seeds, fats are split. In the expressed juice, protein-hydrolysis, increase of reducing carbohydrates, and carbon dioxide respiration also occur. W. D. H.

**Physiological Rôle of Phosphoric Acid in the Nutrition of Plants.** MME. GABRIELLE BALICA-IWANOWSKA (*Bull. Acad. Sci. Cracow.*, 1906, 616—642).—In plants germinating in a liquid free from phosphoric acid, an increase of mineral phosphorus takes place at the expense of organic phosphorus compounds. The phosphorus thus separated from organic compounds is not utilised for the reproduction of organic phosphorus compounds when no further amount of phosphates is supplied. When plants are deprived of phosphoric acid manures a portion of the organic phosphorus compounds formed previously in the plant is decomposed after a time, as in the case of germinating seeds.

Under normal conditions, barley plants transform relatively small amounts of phosphates into organic compounds up to the time of flowering, the change being chiefly during the production of seed. At this period the nucleo-proteins migrate towards the grain; during the ripening, a portion of the phytine separates from the protein compounds.

N. H. J. M.

**The Quantity of Sucrose in the Seeds of some of the Loganiaceæ.** JULES LAURENT (*J. Pharm. Chim.*, 1907, 25, 225—228).—By subjecting the aqueous extract of seeds of members of the *Loganiaceæ* to the action of invertase, the following percentages of sucrose were found: *Strychnos nux vomica*, 1·34; *S. Ignatii*, 8·60; *S. potatorum*, 1·22; *S. spinosa*, 1·70, and *S. Bakanko*, 1·70, after taking into account the small quantities of reducing sugars present naturally in the seeds.

W. P. S.

**Occurrence of Calcium Oxalate in Radix Columbo.** TUNMANN (*Chem. Zentr.*, 1907, i, 643; from *Pharm. Centr.-h.*, 1906, 47, 1069).—The whole of the wood of *Radix Columbo* has been found to contain crystals of calcium oxalate, and the statement commonly found in text-books that this substance is only present in the stone cells of the external bark is therefore incorrect.

E. W. W.

**Poisons in Tephrosia Vogelii.** MAURICE HANRIOT (*Compt. rend.*, 1907, 144, 498—500, 651—653).—The active substances separated from this leguminous plant are three in number. *Tephrosal*,  $C_{10}H_{16}O$ , is a liquid, which begins to distil at 60° in a vacuum, but shows no fixed boiling point; it has a strong odour. *Tephrosin*,  $C_{31}H_{26}O_{10}$ , forms lustrous prisms, m. p. 187°, and can be distilled in a vacuum. A neutral substance, which is not a glucoside, unites with bromine. Tephrosin is the most toxic, tephrosal less so, and the neutral substance still less so. Tephrosin is specially toxic to fish; when placed in water containing one part of it to fifty million parts of water they die in less than two hours. Some fish are more readily killed than others, but all are more easily affected than other animals. Tephrosin acts specifically on the gills, but there are general effects (convulsions and paralysis) as well. In dogs, convulsions and paralysis also occur; death is due to stoppage of respiration, the heart still continuing to beat.

W. D. H.

**Medicinal and Useful Plants** Brazil. THEODOR PECKOLT (*Chem. Zentr.*, 1907, i, 647—648; from *deutsch. Pharm. Ges.*, 1906, 16, 443—452. Compare Abstr., 1906, ii, 484, 701).—The composition of the useful parts of *Bernardinia fluminensis*, *Rourea glabra*, *Connarus cymosus*, and *Connarus Uleanus* is described in the abstract.

E. W. W.

**Influence of Some Manures on the Composition of Rye Grain.** SANTE DE GRAZIA and S. CALDIERI (*Chem. Zentr.*, 1907, i, 656; from *Staz. sper. agrar. ital.*, 39, 514—528).—The amount of protein is increased by ammonium sulphate, and especially by sodium nitrate; potassium salts also increase the protein, but their action is much less marked. The same manures, but especially potassium chloride, increase the amount of starch, whilst they diminish the cellulose. The amounts of total ash, fat, sugar, and dextrin were not very appreciably altered by the various manures.

N. H. J. M.

**Consumption of Nutrients by Parent Beets and Seedlings.** II. KARL ANDRLÍK, JOSEF URBAN, and VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1907, 31, 339—350. Compare Abstr., 1906, ii, 300).—The authors have determined the amounts of nutrient materials absorbed from the soil by sugar-beets during the various stages of the second year of their growth. The beets were examined at the following five stages of their development: (1) when stalk began to form; (2) when the formation of stalk was complete; (3) when the flowers appeared; (4) when seeds were formed, and (5) when the seeds were ripe and the beets were harvested; these stages spread over periods of 62, 17, 21, 24, and 16 days respectively. The root, leaves, and stalk were analysed completely, the results being given in tables and in curves.

The growth of the beet during its second year varies considerably, as also does the rate at which food materials are absorbed from the soil. The periods during which the least amount of dry matter is formed in the beet and the extraction of nutrients from the soil is slowest, are the first two months after planting and the last fortnight, when the seed is ripening. The growth and formation of dry matter and the absorption of soil-constituents are most rapid from the time the stalk appears until it becomes completely developed just before flowering occurs; these actions are less rapid during the flowering and much slower still during the development of the seed.

When the second season of growth is completed, the nutrient materials extracted from the soil are present in the beet in the proportions of 1 part  $P_2O_5$  to 2.84 parts N, and 3.29 parts  $K_2O$ . It is hence in these proportions that they should be replaced by manures.

T. H. P.

**Formation of Solanine in Potatoes as the Product of Bacterial Action.** RICHARD WEIL (*Arch. Pharm.*, 1907, 245, 70—77).—A reply to Wintgen (Abstr., 1906, ii, 701), explaining why the latter failed to confirm the author's observations. C. F. B.

**Origin of Aldehydes in Cheeses.** AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1907, 144, 495—498).—The production of aldehydes in cheese is due to the fermentation of lactose. One of the causes of bitterness in cheese is the prolonged exposure of curds when being drained to an atmosphere rich in all kinds of germs.

N. H. J. M.

**Action of Calcium Fluoride on Vesuvian Soil.** GASPARE AMPOLA and SANTE DE GRAZIA (*Chem. Zentr.*, 1907, i, 496; from *Staz. sper. agrar. ital.*, 1906, 39, 590—592. Compare Abstr., 1904, ii, 767).—Further experiments have shown that the addition of calcium fluoride to Vesuvian soil always increases the yield and the quantity of assimilable potassium.

E. W. W.

**Treatment of Soils with Carbon Disulphide.** BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1907, ii, 18, 246—264. Compare this vol., ii, 295).—Treatment of almost air-dry soils with carbon disulphide considerably increased the amounts of soluble potassium, magnesium, and calcium compounds. In the case of fresh soil the treatment resulted in a great increase of sulphuric acid.

The results of pot experiments with mustard showed that treatment with carbon disulphide just before sowing the seed diminished the yield except when nitrogen, in the form of ammonium salts or nitrates, was also supplied. The injurious action of carbon disulphide is therefore indirect, and is due to its retarding effect on nitrification.

N. H. J. M.

**Gas from Spring Water.** WILLEM P. JORISSEN (*Chem. Zentr.*, 1907, i, 295—296; from *Chem. Weekblad*, 1906, 3, 764—767).—A gas containing 2.8%  $\text{CO}_2$  (with  $\text{H}_2\text{S}$ ), 0.4 O, 77.1  $\text{CH}_4$ , and 19.7 N has been collected from a boring in the neighbourhood of Helder. Heavy hydrocarbons, carbon monoxide, and hydrogen did not appear to be present. The observations agree with Söhngen's theory (*Diss. Delft*, 1906) that hydrogen is always produced by fermentation in waters containing carbohydrates and proteins, whilst methane is formed in the mud of the sea, rivers, moors, and ditches, and not in the water itself. The water of the spring yielded 984 mg. of dry residue per litre, 254.4 mg. Cl, 3.8 mg.  $\text{NH}_3$ , 0.24 mg. albumenoid ammonia, 1.0 mg.  $\text{HNO}_3$ , and 0.02 mg.  $\text{HNO}_2$ , and required 20.3 mg.  $\text{KMnO}_4$ . The presence of oxides of iron could not be detected, and the hardness was 10.4 German degrees.

E. W. W.

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### Analytical Chemistry.

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**Indicators.** NICOLAAS SCHOORL (*Chem. Zentr.*, 1907, i, 300—301, 502—503, 585; from *Chem. Weekblad*, 1906, 3, 719—739, 771—780, 807—815).—A study of the indicators generally used (phenolphthalein,

tropæolin 000, curcumin, rosolic acid, litmus, *p*-nitrophenol, lacmoid, Congo-red, and methyl-orange) and their behaviour towards cold and hot water. They may be classified as: (1) indicators sensitive to acids, namely, those which exhibit their intermediate colours in aqueous solutions containing free hydroxyl ions: *phenolphthalein*, *tropæolin* 000, *curcumin*; (2) indicators sensitive to alkalis, those exhibiting their intermediate colours in aqueous solutions containing free hydrogen ions: *p*-nitrophenol, *lacmoid*, *Congo-red*, *methyl-orange*, and (3) neutral indicators, those which exhibit their intermediate colours in solutions which contain both ions to the same small extent as they occur in pure water: *rosolic acid*, *litmus*. In titrating a weak acid it is advisable to use a strong base and an indicator sensitive to acids.

In titrations, different results are sometimes obtained when the acid is added to the alkali or reversedly. This may be prevented by titrating in either case to the same final colour, for instance, a clear rose colour with phenolphthalein. Another difficulty is that different results are obtained when, for instance, methyl-orange is used instead of phenolphthalein; this may be remedied by titrating until the indicator exhibits the same colour as it does in pure water. When titrating weak bases in a very dilute condition the use of dimethylaniline is recommended, this being very sensitive to alkalis.

L. DE K.

**Acidimetric and Alkalimetric Indicators.** EDUARD SALM and HANS FRIEDENTHAL (*Zeitsch. Elektrochem.*, 1907, 13, 125—130. Compare Abstr., 1904, ii, 536, and 1906, ii, 218).—The cause of the change of colour of an indicator is discussed and reasons are given for believing that, in most cases, the change is due to intra-molecular change rather than to ionisation.

The concentration of the hydrogen ions in a solution of a salt of a weak acid or base can be determined readily by means of the colorimetric method previously described (Abstr., 1906, ii, 218). Such a weak acid or base may be titrated accurately by using an indicator which changes colour in a solution of the same acidity as that yielded by the salt.

T. E.

**Alizarin-Red IWS as Indicator in Volumetric Analysis.** GEORGE E. KNOWLES (*J. Soc. Dyers*, 1907, 23, 120).—Alizarin-red IWS (alizarinmonosulphonic acid) is recommended in alkalimetry instead of methyl-orange. Addition of an alkali hydroxide causes the yellow solution to turn violet, which colour is then again changed to yellow on addition of acids. If an alkali carbonate is added, the liquid turns also violet, but, on adding acid gradually, the liquid changes through the various hues from violet to orange and then suddenly to yellow. The chief advantage of this indicator over methyl-orange is that it can be used with artificial (incandescent gas) light, and that a slight excess does not vitiate the result.

Alizarin-red may be used advantageously in the estimation of total alkali in hot soap solutions, where methyl-orange is useless, in ammonia determinations, and in water analysis. Borates, however, interfere with its use.

L. DE K.



**Standardisation of Acids by Metallic Magnesium.** ALBERT VESTERBERG (*Zeitsch. anal. Chem.*, 1907, 46, 81—93).—The approximately correct acid is heated on the water-bath in a Jena flask with an accurately weighed quantity of pure magnesium ribbon sufficient to neutralise about nine-tenths of the acid. After the metal has dissolved, the liquid is boiled for a few minutes, and, when cold, the acid still remaining is titrated with carefully standardised barium hydroxide solution. L. DE K.

**Standardised Ammonia in Acidimetry.** FACUNDO J. R. CARULLA (*J. Soc. Chem. Ind.*, 1907, 26, 186—187).—A series of experiments showing that ammonia, even when of  $N/2$  strength, may be used safely as a standard solution in acidimetry. With ordinary care there is no danger from volatilisation or absorption by india-rubber and consequent weakening of the solution. L. DE K.

**Apparatus for Storing of, and Titrating with, Alkali Hydroxides.** C. J. VAN LEDDEN HULSEBOSCH (*Chem. Zentr.*, 1907, i, 370—371; from *Pharm. Weekblad*, 1906, 43, 1309—1347).—A rather complex device by which the only gas in contact with the solution is oxygen. Pressure on an attached elastic bag in which the oxygen is contained serves to force the liquid up the tube by which the burette is filled. L. DE K.

**A Self-Filling Burette.** NATHANIEL J. LANE (*J. Soc. Chem. Ind.*, 1907, 26, 136—137).—An improvement in the burette arrangement in the U.S. Appraiser's laboratory. Suction with the mouth is now dispensed with, the necessary reduction of pressure being obtained by means of a pump. For full details the figures in the original should be consulted. L. DE K.

**New Absorption Apparatus.** BALTHASAR PFYL (*Zeitsch. anal. Chem.*, 1907, 46, 150—157).—The apparatus is in the main a wash-bottle with stirrer, and so constructed that during absorptions the air is completely excluded. It may replace the simple Hempel gas-pipette and the washbottles of the Orsat apparatus, &c. For a full description the illustration in the original article must be consulted. L. DE K.

**Use of Nickel Crucibles for Quantitative Work, and the Composition of the so-called "Nickel-soot."** R. KRZÍŽAN (*Zeitsch. öffentl. Chem.*, 1907, 13, 103—110).—On account of the considerable increase in weight which nickel crucibles undergo when heated over a free flame, the author considers that they should not be employed in quantitative estimations, such as the ignition of precipitates, &c. When heated in a muffle-furnace the crucibles become coated with a uniform layer of oxide, and the subsequent increase in weight is less, but still plainly noticeable. The spongy coating formed on a nickel crucible which had been heated over a Bunsen burner was found to have the composition: carbon, 89.81%; hydrogen, 1.12%; ash, 8.04%; nickel, 6.30%; sulphur, 0.46%. W. P. S.

**System of Qualitative Analysis for the Common Elements.** ARTHUR A. NOYES and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1907, **29**, 137—205).—A lengthy article unsuitable for adequate abstraction and based largely on Noyes's previous system for all the elements (*Abstr.*, 1906, ii, 803). The present paper is divided into two parts, the preparation of the solution, and the analysis of the silver, copper, and tin groups. L. DE K.

**New Tests for Halogens in Alkali Haloids.** C. REICHARD (*Pharm. Zeit.*, 1907, **52**, 221).—A particle of red mercuric iodide placed on a porcelain slab dissolves to a colourless solution when a crystal of potassium iodide and a drop of water are added. The same result is obtained with potassium bromide, but potassium chloride has no action. On evaporating to dryness, the iodide leaves a dark yellow residue, but the bromide residue turns gradually to a permanent dark red. A small admixture of potassium iodide prevents the formation of this red colour. If sodium iodide is used, a residue is obtained which is of a dark red colour on warming, but on cooling it again becomes yellow.

With sodium bromide, a yellow residue is obtained which gradually turns dark red; the colour disappears when the mass gets moist, but reappears on heating. Ammonium bromide gives a yellow residue which gradually becomes colourless, but shows no signs of reddening. The residue from sodium bromide is as hygroscopic as calcium chloride; the ammonium bromide residue is more permanent. L. DE K.

**New Method for Estimating Halogens in Organic Substances.** G. BIANCHI (*Chem. Zentr.*, 1907, i, 664—665; from *Boll. Chim. Farm.*, 1906, **45**, 821—830).—An adverse criticism of Vaubel and Scheurer's method (*Abstr.*, 1906, ii, 250). L. DE K.

**Estimation of Chlorine in Urines.** FERNAND REPITON (*Ann. Chim. anal.*, 1907, **12**, 139).—The author considers that the best results are obtained by simply acidifying strongly with nitric acid, and then precipitating the chlorine with silver nitrate. The precipitate may be collected and weighed, or the excess of silver added may be titrated by the well known thiocyanate process. If the gravimetric process is employed, it is advisable first to remove any albumin present.

L. DE K.

**Estimation of Peroxidised Compounds by Means of Alkali Hypiodite.** ERWIN RUPP and J. MIELCK (*Arch. Pharm.*, 1907, **245**, 5—12).—Many substances which liberate iodine but slowly from hydriodic acid, react immediately and quantitatively with a solution of an alkali hypiodite, liberating oxygen gas (one  $O_2$  for each "available" O in the substance). By acidifying and titrating the iodine liberated, the excess of hypiodite can be determined. Only soluble substances can be estimated in this way, and of them, not sodium peroxide, as it loses oxygen when merely brought into contact with water; persulphates are without action on the hypiodite. The substances

examined with success were hydrogen peroxide, sodium perborate, and potassium percarbonate.

A suitable quantity of the substance to be estimated is dissolved in 20–50 c.c. of water, 10–20 c.c. of approximately *N*-potassium hydroxide solution are added, and then 25 c.c. of *N*/10 iodine solution; the mixture is shaken to promote the evolution of oxygen, and, after five minutes, 20–30 c.c. of dilute hydrochloric or sulphuric acid are added, and the iodine liberated is titrated with thiosulphate solution.

In estimating the oxidising power of perborates by means of an acidified solution of an iodide, it is necessary either to work in the absence of air or to mix the reagents in the order: iodide, acid, perborate, and titrate after fifteen minutes or thirty at most.

In estimating the oxidising power of zinc peroxide by means of acidified iodide solution, ten to fifteen minutes suffice to complete the reaction.

C. F. B.

**Use of Ammonium Tri-iodate in Iodometry and Alkalimetry.** EMANUEL RIEGLER (*Chem. Zentr.*, 1907, i, 503–504; from *Bull. Assoc. Chim. Sucr. Dist.*, 1906, 24, 528–532).—A solution of ammonium tri-iodate (3.025 grams per litre) keeps for any length of time. When required for standardising sodium thiosulphate, 10 c.c. of the solution are diluted with 40 c.c. of water, 1 gram of potassium iodide, and 1 c.c. of hydrochloric acid are added, and the liberated iodine is titrated as usual. One mol. of the salt liberates 9 mols. of iodine. The titration may also be carried out without addition of acid and potassium iodide. In that case a solution is prepared containing 54.468 or 27.234 grams per litre, and after adding starch water, the thiosulphate is added until the blue colour formed at first again disappears. In this case 3 mols. of the tri-iodate = 6 mols. of sodium thiosulphate. As thiosulphate has no action on a neutral iodate, the reagent may be used in alkalimetry by simply adding it in excess to an alkali hydroxide or carbonate, and then titrating the remaining tri-iodate either as just described, or, as ammonium tri-iodate acts like a dibasic acid, it may be titrated with alkalis as usual, using Congo-red or luteol as indicator. Advantage may also be taken of its action in acid solution on hydrazine sulphate when nitrogen is liberated.

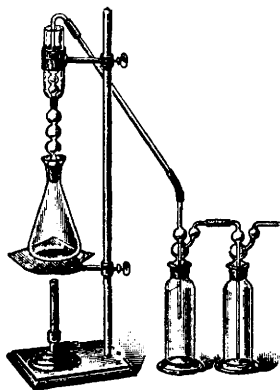
L. DE K.

**Calcination of Zinc Sulphate in the Presence of Zinc Oxide.** H. POMMERENKE (*Bull. Soc. chim. Belg.*, 1907, 21, 128–132).—In the estimation of sulphur in blends by ignition with zinc oxide, a certain proportion of insoluble basic zinc sulphate is formed, which is not extracted in the subsequent treatment with water. The author shows, however, that the extraction of the total amount of sulphate simply depends on the use of a sufficient quantity of hot water; for instance, 500 c.c. of boiling water suffice to dissolve the whole of the sulphate from a calcined mixture consisting of 4 grams of zinc oxide and 0.5 gram of zinc sulphate.

W. P. S.

**Apparatus for the Estimation of Sulphur [in Iron].** von NOSTITZ and JÄNKENDORF (*Zeitsch. anal. Chem.*, 1907, 46, 157—158).

—The apparatus will be readily understood from the figure. Five grams of the sample of steel are placed in the flask and the cylinder is filled with hydrochloric acid (1 : 1). The first receiver is intended for the condensation of acid fumes, the second one contains 50 c.c. of water and 0.5 gram of potassium hydroxide. By gently raising the delivery tube, 100 c.c. of acid are introduced into the flask and heat is applied. The hydrogen sulphide formed is then estimated by adding to the alkaline solution 50 c.c. of dilute sulphuric acid (1 : 3) and titrating with iodine solution (7.9 grams of iodine, 20 grams of potassium iodide, 1000 c.c. of water) with starch as indicator. One c.c. of iodine solution = 0.0022 gram of sulphur.



L. DE K.

**Estimation of Total Sulphur in Ichthyol Preparations by Means of Sodium Peroxide.** WILHELM HINTERSKIRCH (*Zeitsch. anal. Chem.*, 1907, 46, 241—245).—About 0.5 gram of the well-mixed substance is placed in a nickel crucible and mixed gradually with a mixture of 4 grams of sodium peroxide and 3 grams of coarse dry potassium carbonate. A little more of this mixture is then sprinkled over the mass. The action starts at once, and the covering lid is put on. After a while, the crucible is placed in a perforated asbestos board and heated with a spirit lamp, at first very gently, then more strongly. The heat generated in the reaction is now so great that the spirit lamp may be removed, and still the mass becomes quite liquid. The crucible is once more heated for one and a half to two hours over a Barthel burner. The fused mass is then dissolved in bromine water and filtered; a pinch of magnesia added ensures a clear filtrate.

The alkaline liquid is acidified with hydrochloric acid; any silica is removed by evaporation to dryness as usual, and the sulphuric acid formed in the reaction is finally precipitated and weighed as barium sulphate.

L. DE K.

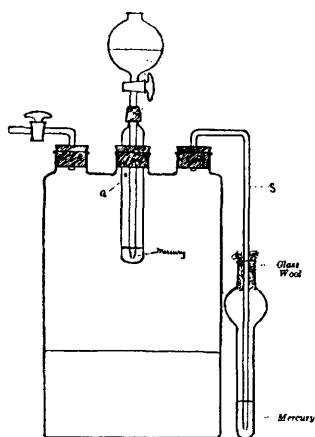
**Apparatus for Estimating Sulphur Dioxide.** E. ARGYRIADÈS (*Chem. Zentr.*, 1907, i, 500—501; from *Bull. Assoc. chim. Soc. Dist.*, 1906, 24, 511—512).—The apparatus consists of a graduated tube, the lower part of which is connected with a mercury reservoir and the top with a two-way stopcock, to which has been sealed a dish-shaped funnel. The tube having been filled with mercury, the gas to be tested is introduced through the side tube of the stopcock; a definite volume of standard iodine solution is placed in the funnel, and by raising the reservoir 100 c.c. of the gas is made to bubble slowly through the iodine solution. The excess of iodine is then estimated with thiosulphate.

L. DE K.

**Estimation of Free Acid in Superphosphates.** JOS. VAN DORMAEL (*Bull. Soc. chim. Belg.*, 1907, 21, 103—115).—The following process, consisting in extracting the sample with ether and titrating the acid extract with sodium hydroxide, is recommended as being both rapid and trustworthy. Five grams of the superphosphate, dried previously for three hours in a water-oven, are shaken in a stoppered flask with 100 c.c. of dry ether for three hours. The ethereal solution is filtered and 50 c.c. of the filtrate are evaporated; the residue is dissolved in water, the solution is filtered, if necessary, and then titrated with  $N/4$  sodium hydroxide solution, using dimethyl-orange as indicator. When the neutral point is reached, phenolphthalein is added and the titration continued until the solution is neutral to the latter indicator. Alcohol may be employed instead of ether for the extraction, but the latter is preferred, as the filtrate obtained is quite clear.

W. P. S.

**Apparatus for Supply of Carbon Dioxide in the Estimation of Nitrogen in Organic Compounds by the Absolute Method.** GEORGE YOUNG and BEN CAUDWELL (*J. Soc. Chem. Ind.*, 1907, 26, 184—185).—The Woulff's bottle (see Fig.) holds from 2 to 3



litres and is partly filled with dilute sulphuric acid (1:1). The separating funnel contains solution of potassium carbonate ( $D 1.5$ ), and when the tap is opened it runs through a into the acid; 100 c.c. generate enough gas to expel all the air. The further supply is then very easily regulated. When using the apparatus, it is necessary to take care that the pressure in the nitrometer is not reduced so far as to draw air through the safety tube.

L. DE K.

**"Nitron" as a Micro-Chemical Reagent.** H. L. VISSER (*Chem. Zentr.*, 1907, i, 302; from *Chem. Weekblad*, 1906, 3, 743—746).—Nitrates may be estimated approximately by adding a solution of nitron (diphenylendoanilodihydrotriazole) and comparing the volume of the nitrate precipitate with that obtained by using a nitrate solution of known strength.

Nitrous acid, chloric acid, perchloric acid, oxalic acid, and salicylic acid also give precipitates which are but slightly soluble and may be distinguished microscopically by their crystalline appearance. "Saccharin" also may be detected after it has been converted by a little alkali into *o*-sulphaminobenzoic acid. Sulphuric acid, hydrochloric acid, formic acid, acetic acid, boric acid, benzoic acid, tartaric acid, citric acid, and phosphoric acid yield compounds which are readily soluble. Microphotographs are given in the original.

L. DE K.

**Methods for Detecting Small Amounts of White Phosphorus in Presence of a Large Excess of Phosphorus Sesquisulphide.**

LOUIS ARONSTEIN (*Chem. Weekblad*, 1907, 4, 183—191).—A reply to C. van Eyk (*ibid.*, 1906, No. 41; compare Aronstein, *Abstr.*, 1906, ii, 705 and 899; Jungfleisch, *Abstr.*, 1905, ii, 244; Habermann and Oestereicher, *Chem. Weekblad*, 1906, 3, 407). Phosphorus sesquisulphide reacts with lead acetate in accordance with the equation  $P_4S_3 + 9H_2O = H_3PO_2 + H_3PO_3 + H_3PO_4 + PH_3 + 3H_2S$ , lead sulphide being then formed. The results of quantitative estimations have not, however, substantiated this equation. A. J. W.

**Estimation of Phosphoric Acid as Ammonium Phosphomolybdate.** HENRI PELLET (*Chem. Zentr.*, 1907, i, 505; from *Bull. Assoc. Chim. Sucr. Dist.*, 1906, 24, 525—528).—A reply to Graftiau (this vol., ii, 196), who uses, practically, the same process as that already advocated by the author. L. DE K.

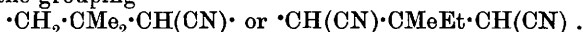
**Estimation of Phosphoric Acid in Manures.** FELIX MACH (*Landw. Versuchs.-Stat.*, 1907, 66, 1—62).—It was shown previously (*ibid.*, 63, 81) that results obtained by the method of the German Association were lower than those obtained by Wagner's method. It is now shown that the two methods yield concordant results when (in the Association's method) the heating is discontinued as soon as the residue becomes gelatinous.

The greater portion of the paper consists of a summary of the different volumetric methods of determining phosphoric acid.

N. H. J. M.

**Evolution of Combustible Gases in Elementary Analysis.**

ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1907, 42, 79—82).—The author claims priority over Haas (*Trans.*, 1906, 89, 570), since, together with Grande, he showed (*Atti R. Accad. Sci. Torino*, 1898, 33) that the evolution of difficultly combustible gases, such as methane, often gives rise to considerable errors in the estimation of nitrogen, and also in that of carbon and hydrogen. Guareschi and Grande (*Abstr.*, 1900, i, 112) stated that the evolution of methane and also of ethane occurs especially with compounds containing the grouping



The compounds investigated by Haas (*loc. cit.*) are somewhat analogous with these, since they contain two methyl groups attached to one carbon atom, which, in its turn, is united with two hydrogenated carbon atoms.

Similar observations were made, in the case of picrotoxin, by Francis prior to 1842, and, in the case of a non-nitrogenous compound, by Gerhardt (*Comptes rend. trav. chim.*, 1846, 174).

T. H. P.

**Detection of the Alkali Metals.** GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1907, 42, 250—265).—The author has studied the properties, more especially the solubilities in water and other reagents, of the 2-sodium and 2-potassium derivatives of 3:5-dicyano-

2-hydroxy-4-methyldihydro-6-pyridone and of 3:5-dicyano-2-hydroxy-4-piperonyldihydro-6 pyridone, in order to ascertain whether these compounds can be employed for the detection of sodium and potassium.

The composition of these sodium and potassium derivatives does not change with the conditions of formation. The potassium salts have solubilities less than, and molecular weights much greater than, those of the hydrogen tartrate, platinichloride, borofluoride, picrate, and perchlorate, so that the formation of these compounds is a far more sensitive reaction for potassium than that of the other salts mentioned. The fact that the sodium derivative of 3:5-dicyano-2-hydroxy-4-methyldihydro-6-pyridone is considerably more soluble in 70–80% alcohol than the corresponding potassium compound admits of it being separated from the latter. The two salts appear so different under the microscope that they can be readily distinguished. The salts can be precipitated in solutions rendered slightly acid by mineral acids.

T. H. P.

**Separation of Potassium from Sodium as Potassium Platinichloride.** JÓZEF MOROZEWICZ (*Bull. Acad. Sci. Cracow*, 1906, 796–803).—In absolute alcoholic solution, sodium platinichloride dissociates to some extent according to the equation  $\text{Na}_2\text{PtCl}_6 = 2\text{NaCl} + \text{PtCl}_4$ , and, since sodium chloride is practically insoluble in absolute alcohol, the weight of the potassium platinichloride is found to be too large. In 80% alcohol, however, the above dissociation does not take place to an appreciable extent, and correct results are found for the precipitated potassium when alcohol of this concentration is used. In order to obtain accuracy by the use of absolute alcohol, it is necessary to add excess of acid platinic chloride (about four times the theoretical amount) and thus diminish the dissociation of the sodium salt.

H. M. D.

**A Method for Estimating the True Alkalinity of Ashes.** K. FARNSTEINER (*Zeitsch. Nahr. Genussm.*, 1907, 13, 305–338).—It is well recognised that the phosphates present in ashes interfere with the direct titration of the alkalinity of the latter, owing to the influence of certain phosphates on the indicators used. To overcome this difficulty, the author proposes to dissolve the ash in hydrochloric acid, precipitate the phosphoric acid by the addition of calcium chloride and ammonia, and to titrate the phosphate-free solution. The quantities of acid and ammonia added being known, the alkalinity is calculated. The details of the process are: A weighed quantity of the ash is dissolved in from 10–20 c.c. of  $N/2$  hydrochloric acid, and the solution boiled gently in a flask for about two minutes in order to expel all carbon dioxide. The solution is then transferred to a stoppered measuring cylinder, from 5–10 c.c. of a solution containing 5% of calcium chloride and 10% of ammonium chloride are added, then 20 c.c. of  $N/2$  ammonia, and the whole is diluted to a volume of 100 c.c. with water free from carbon dioxide. The contents of the cylinder are well shaken and set aside overnight; next day 25 c.c. of the clear solution are titrated with  $N/10$  hydrochloric acid, using methyl-orange as indicator. The alkalinity is expressed by the formula  $a = S + s - n$ ,

where  $a$  is the weight of the ash,  $S$  the volume of  $N/1$  acid used for dissolving the ash,  $s$  the volume of  $N/1$  acid used in the final titration, and  $n$  the volume of  $N/1$  ammonia added. Experiments with tricalcium phosphate, disodium phosphate, phosphoric acid, and mixtures of phosphates, &c., gave results agreeing with the calculated values. Silicates count as carbonates in the above process, but, as the quantity of silicates occurring in the ash of organic substances is generally quite small, their influence may be ignored. The results obtained are usually much lower than those yielded by the direct titration method.

W. P. S.

**The Presence of Traces of Zinc in Commercial Alcohol, and its Detection.** GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1907, 25, 97—98).—Alcohol often contains traces of zinc, derived from zinc-lined vessels in which the spirit is stored. The quantity of zinc present is generally too small to be detected by the usual tests without previous evaporation of the alcohol, but the following test, applied directly to the alcohol, will detect the presence of 0.0001 gram of zinc in 100 c.c. of alcohol. To 50 c.c. of the spirit are added 3 c.c. of a chloroform solution of urobilin, then 50 c.c. of water, and a few drops of ammonia. A green fluorescence by reflected light and a red coloration by transmitted light denote the presence of zinc in the sample.

THOMAS ROMAN and G. DELLUC point out (*ibid.*, 25, 243) that they had previously observed the occurrence of zinc in alcohol, and that such alcohol gave a green fluorescence with urobilin (Abstr., 1900, ii, 700; 1901, ii, 40).

W. P. S.

**Influence of Iron and Manganese on the Estimation of Zinc by Schaffner's Process.** M. HUYBRECHTS (*Bull. Soc. chim. Bely.*, 1907, 21, 121—127).—The estimation of zinc by this process (titration with sodium sulphide solution) yields trustworthy results if the sodium sulphide solution is standardised on a zinc solution containing iron and manganese in quantities equal to the weights of these metals present in the blende solution under examination. It is almost impossible to separate zinc from iron and manganese by one precipitation with ammonia.

W. P. S.

**Estimation of Zinc as Carbonate and Silicate in Ores.** PERCY H. WALKER and HERMAN SCHREIBER (*J. Amer. Chem. Soc.*, 1907, 29, 211—214).—*Zinc as silicate.*—0.5 Gram of the ore is heated with 5 c.c. of water and 10 c.c. of hydrochloric acid and filtered at once before the silica has time to gelatinise. From the filtrate and washings the silica is then recovered as usual. One part of silica = 2.17 parts of zinc as silicate. The results are only approximately correct.

*Zinc as carbonate.*—The process is based on the fact that foreign carbonates likely to occur in zinc ores (even magnesite) withstand a temperature of 350—400°, whilst zinc carbonate loses its carbon dioxide when heated at that temperature for forty-five minutes. The results are, however, only approximately correct. One part of carbon dioxide = 1.49 parts of zinc as carbonate.

L. DE K.



**The Ferrocyanide Method for the [Titration] of Zinc.** W. H. SEAMAN (*J. Amer. Chem. Soc.*, 1907, 29, 205—211).—The following process is recommended. 0.5 Gram of the ore is covered with 7 c.c. of nitric acid and 7 c.c. of hydrochloric acid are added. The mixture is heated for fifteen minutes at a temperature not exceeding 60°, 7 grams of ammonium chloride are added, and the whole is evaporated to dryness. Five c.c. of ammonia are added, followed by 15 c.c. of bromine water or hydrogen peroxide, the liquid is boiled for three minutes, and filtered; the iron precipitate is washed with a hot ammoniacal solution of ammonium chloride. The filtrate is slightly acidified with hydrochloric acid, boiled for three minutes with a piece of aluminium foil to remove any copper, lead, and cadmium, and diluted to 150—200 c.c. It is then mixed with 5 c.c. of hydrochloric acid and titrated with ferrocyanide solution according to Low's method, using uranium acetate as indicator at a temperature of 85—90°.

When standardising the ferrocyanide, it is of great importance that the amount of metallic zinc, or zinc oxide, used should be about the same as that contained in 0.5 gram of the ore. Treatment with bromine is, of course, unnecessary, also the treatment with aluminium, but in other respects the standardisation should be conducted as if an ore was being tested. L. DE K.

**Analysis of Lithopones.** FERNAND REPITON (*Ann. Chim. anal.*, 1907, 12, 93—94).—Lithopones contain as the essential constituent zinc sulphide. This may be estimated by dissolving the sample in hydrochloric acid and passing the hydrogen sulphide evolved through an ammoniacal solution of copper sulphate of known strength and then estimating the excess of copper left in the solution.

Any zinc present as oxide may be extracted with a solution of sodium acetate containing excess of acetic acid and then determined by the usual process.

Lithopone paint must be first extracted with ether and the process applied to the dry residue. L. DE K.

**Separation of Zinc from Nickel, Cobalt, Iron, and Manganese by Means of Hydrogen Sulphide.** W. FUNK (*Zeitsch. anal. Chem.*, 1907, 46, 93—106).—A criticism of the various processes proposed from time to time. The best results are obtained by adding to the neutralised solution about two or three times as much sodium formate as there is zinc present and then passing a current of hydrogen sulphide until all the zinc has precipitated and traces of the other metallic sulphides are beginning to form. Instead of sodium formate, a few drops of dilute hydrochloric acid and a little ammonium chloride or sulphate may be added. The precipitate is then collected and to free it from any nickel, &c., it is redissolved in acid, neutralised with sodium carbonate, and, after addition of sodium formate, again treated with hydrogen sulphide. If, however, the zinc in a mixture strongly predominates, a single precipitation generally suffices. L. DE K.

**Colorimetric Estimation of Lead in Drinking Water.** CORNELIS GULDENSTEEDEN EGELING (*Pharm. Weekblad*, 1907, 44, 338—341. Compare Abstr., 1896, ii, 549).—After reviewing the

existing methods of estimating lead in drinking water, the author describes a colorimetric estimation with potassium chromate.

0.1827 Gram of lead acetate is dissolved in water, a few drops of acetic acid added, and the solution made up to 100 c.c. Dilution of 10 c.c. of this solution to 1 litre yields a solution containing 0.01 mg. of lead per litre. To 100 c.c. of the sample in a cylinder are added one drop of acetic acid and one drop of 10% potassium chromate solution. In presence of lead, a turbidity develops slowly. This turbidity is matched with the standard lead solution, the best results being obtained with samples containing 0.5—1 mg. of lead per litre, after contact with the reagent during half an hour. With samples of higher concentration, dilution is necessary, and those of lower concentration must be evaporated in presence of a few drops of acetic acid. An excess of potassium chromate must be avoided, as it hinders the formation of lead chromate. The test gives trustworthy results for 0.2 mg. of lead per litre. For solutions of less concentration it is not recommended. A. J. W.

**Use of Acetylene as a Precipitant.** HUGO ERDMANN (*Zeitsch. anal. Chem.*, 1907, 46, 125—127).—Copper (and also silver, mercury, gold, palladium, and osmium) may be precipitated by a current of acetylene. The gas is conveniently stored in a gasholder and purified by passing it over bleaching powder and through a washbottle containing lead acetate solution. For testing purposes its aqueous solution or preferably its solution in acetone, which is stronger, may be employed. L. DE K.

**Estimation and Separation of Copper by Precipitation with Acetylene.** HUGO ERDMANN and OSKAR MAKOWKA (*Zeitsch. anal. Chem.*, 1907, 46, 128—141).—Copper is completely precipitated by a current of acetylene (see preceding abstract) if the liquid has been made ammoniacal and the cupric salt reduced to the cuprous state by means of hydroxylamine hydrochloride. The precipitate has the composition  $C_2H_2OCu_2$ . The washed and still moist precipitate is then treated with nitric acid and the copper nitrate converted by ignition into oxide. Silver, if present, is removed previously with hydrochloric acid and mercury by heating with phosphorous acid. When alkaline earths or magnesium are present, the precipitation may be carried out in presence of a slight excess of acetic acid. In presence of aluminium or chromium, the precipitation of the hydroxides by ammonia may be prevented by addition of tartaric acid. Permanganates are precipitated by acetylene as peroxide, but the addition of hydroxylamine reduces them to manganous salts which are not precipitated; an addition of tartaric acid is, however, advisable to prevent subsequent precipitation of the manganese by ammonia. In presence of iron, tartaric acid should be added, or else the precipitation should take place in presence of a little free acetic acid. In presence of nickel, the precipitation of the copper is carried out in ammoniacal solution. In presence of cobalt, some tartaric acid should be added, or else the precipitation should take place in acetic acid solution. In presence of lead it is not

quite safe to use tartaric acid, but a slight excess of acetic acid should be added finally. In presence of bismuth or antimony, tartaric acid should be employed. In presence of excess of arsenic trioxide, the treatment with hydroxylamine hydrochloride is superfluous, and acetylene may be passed at once through the ammoniacal solution. In presence of tin (if this has not been removed as dioxide) the precipitation by ammonia may be also prevented by previous addition of tartaric acid.

From the filtrates the metals are then recovered as usual.

L. DE K.

**Gasometric Estimation of Copper Salts by Means of Hydrazine Sulphate.** JOSEPH DE GIRARD and ANTOINE DE SAPORTA (*Bull. Soc. chim.*, 1907, [iv], 1, 294—295. Compare Abstr., 1904, ii, 678, and Rimini, 1906, ii, 897).—Rimini's statement that the amount of nitrogen formed in this reaction is greater than the theoretical, due to a secondary action of the hydrazine on the cuprous oxide first formed, has led the authors to repeat their experiments, and their results confirm those previously obtained. They suggest that Rimini's results may be due to the different conditions under which he worked, and point out that it is important to avoid variation in temperature.

T. A. H.

**Simple Process for the Estimation of Corrosive Sublimate in Dressing Materials.** FRANZ UTZ (*Chem. Zentr.*, 1907, i, 373; from *Pharm. Post.*, 39, 785—786).—Five grams of the material are placed in an Erlenmeyer flask and covered with water. Five c.c. of 15% sodium hydroxide solution and 5 c.c. of 10% potassium iodide solution are added, and then 5 c.c. of formalin, which at once gives a precipitate of metallic mercury. After adding 5 c.c. of acetic acid and 5 c.c. of 3*N*/10 iodine solution and waiting for five minutes, the excess of iodine is titrated with starch as indicator. Each c.c. of iodine = 0.01355 gram of mercuric chloride.

L. DE K.

**Estimation of Manganese in Drinking Water.** HERMANN NOLL (*Zeitsch. angew. Chem.*, 490—492).—Two hundred and fifty to five hundred c.c. of the sample are mixed with 1—2 c.c. of hydrochloric acid, evaporated to a small bulk, and any iron is removed by the sodium acetate method. The filtrate is then mixed with slight excess of bromine and heated in a flask for a long time on the water-bath. The manganese dioxide formed is collected on a small filter which, after washing, is returned to the flask. One hundred c.c. of water, a few crystals of potassium iodide, and 3 c.c. of hydrochloric acid are added, and the liberated iodine is then titrated with *N*/100 or *N*/1000 thiosulphate, using starch as indicator. One c.c. of *N*/100 thiosulphate = 0.382 mg. of  $Mn_2O_4$ .

Titration of the precipitate with oxalic acid and potassium permanganate gave results less satisfactory.

L. DE K.

**Quantitative Separation of Iron from Titanium and Aluminium. Application of a Diaphragm to Quantitative Electrolytic Analysis.** GIUSEPPE MAGRI and G. ERCOLINI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 331—336).—The authors have devised

a method by which minerals containing titanium may be dissolved and the iron present in the solution estimated electrolytically. Iron is only deposited quantitatively in the absence of mineral acids, the usual method of satisfying this condition being by adding a large proportion of alkali tartrate or citrate. From such a solution, the iron is not deposited in a pure state, but in admixture with carbon. The authors avoid this difficulty by separating the anodic and cathodic spaces by means of a parchment diaphragm.

The mineral is fused with potassium hydrogen sulphate and the mass gently heated in the crucible with concentrated sulphuric acid and afterwards poured into water. In this way the whole of the iron, titanium, and aluminium pass into solution, together with part of the silica, the remainder of which, and also the calcium sulphate, are undissolved. The insoluble part is filtered off and washed with water and sulphuric acid, whilst the dissolved silica is precipitated from the filtrate by adding excess of sodium potassium tartrate and ammonia. The filtrate from this precipitate is placed in a platinum dish which serves as cathode. Supported over this so that the smaller end, over which parchment paper, extracted with hydrochloric acid, is tied tightly, dips below the surface of the liquid, is a glass bell-jar containing water rendered conducting by means of sodium hydroxide. In this alkaline solution is immersed a platinum anode. The electrolysis, which is carried on under a voltage of 110 and a cathode current density,  $ND_{100}$ , of 0.39 rising finally to 0.78, is slow and may occupy twenty-four hours, during which time the anodic liquid must be prevented from becoming acid by the addition of sodium hydroxide and the cathodic one from being too alkaline by addition of tartaric acid. The iron is thus obtained in an adhesive, compact layer, the completion of the deposition being determined by testing the liquid with hydrochloric acid and potassium ferrocyanide. The platinum dish is washed with water and alcohol, dried at  $90^\circ$ , and weighed. The anodic and cathodic solutions, together with the diaphragm and washings, are acidified with sulphuric acid and evaporated in a muffle until the tartaric acid and parchment are completely carbonised. The mass is heated with concentrated sulphuric acid until it all dissolves and the cooled liquid poured into water, from which the titanium and aluminium are precipitated by addition of ammonium chloride and ammonia. After washing, the precipitate is heated with a slight excess of sodium hydroxide solution ( $26^\circ$  Bé.), which dissolves the aluminium hydroxide. The insoluble titanic anhydride is washed and weighed, and the aluminium precipitated from the solution by heating with excess of ammonium chloride and ammonia. T. H. P.

**Action of Phenylhydrazine on Molybdates.** M. EMMANUEL Pozzi-Escot (*Ann. Chim. anal.*, 1907, 12, 92).—If to a solution of an alkaline molybdate is added a little phenylhydrazine acetate, a wine-coloured liquid is obtained, and also a similarly coloured precipitate.

If before adding the phenylhydrazine some tannic acid is added, the liquid turns orange, and then under the influence of the phenylhydrazine a yellow or mahogany-brown precipitate is formed according to concentration. L. DE K.

**Volumetric Estimation of Titanium.** GINO GALLO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 325—330. Compare Knecht, *Abstr.*, 1903, ii, 217; Knecht and Hibbert, *Abstr.*, 1903, ii, 509).—The method devised by the author for estimating titanium volumetrically is based on the fact that salts of titanium sesquioxide are oxidised to salts of titanium dioxide by ferric salts, which are thereby converted into ferrous salts:  $Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4$ .

Titanic and metatitanic acids are reduced to sesqui-salts by means of zinc and sulphuric acid, the latter being used in the proportion of about 10 c.c. (D 1.3) to 100 c.c. of solution. The reduction should be carried out at a temperature not exceeding  $10^\circ$  in a vessel filled with carbon dioxide and closed by a Bunsen valve, the zinc being added gradually; under these conditions the reduction occupies about five hours, but it is safer to allow about twelve hours, especially if iron is present in the solution. The liquid is filtered through glass wool inside a vessel through which carbon dioxide is kept passing, the filter being washed several times with water which has previously been boiled, cooled, and saturated with carbon dioxide. Three c.c. of saturated potassium thiocyanate solution are now added, and a solution of ferric alum of known titre and free from ferrous salt is run in from a burette until a permanent red coloration is obtained.

When, as is usually the case, the titanium is accompanied by iron, either of the two following methods of procedure may be employed: (1) after the reduction by means of zinc, the liquid is made up to a known volume and divided into two equal parts, care being taken to avoid oxidation. In one portion the titanium is estimated by titration with ferric alum, whilst the other, by titration with permanganate, gives the titanium plus the iron. Where permanganate is used, a blank experiment should be made to estimate the iron in the zinc used for the reduction. (2) The liquid is divided into two portions, in one of which, after reduction by hydrogen sulphide, the iron alone is estimated by means of permanganate, whilst the other is reduced by zinc and titrated with ferric alum to obtain the titanium.

The method can be applied to the estimation of titanium and iron in presence of substances such as aluminium, silica, and zirconium, which are not acted on by zinc. The modes of adapting the process to iron and steel, silicates and bauxite are described.

In the case of silicates and other minerals, the precipitate, yielded by ammonium hydroxide and constituted usually of the hydroxides of aluminium, iron, and zirconium, together with orthotitanic acid, is boiled with excess of potassium hydroxide solution to remove the aluminium hydroxide, which can then be reprecipitated and weighed. The insoluble residue is dissolved in hydrochloric acid, reprecipitated with ammonium hydroxide, washed, dried, and weighed; this gives  $Fe_2O_3$ ,  $TiO_2$ , and  $ZrO_2$ . This mixture is then fused with potassium hydrogen sulphate, and the iron and titanium estimated volumetrically in the liquid obtained by treating the cooled mass with sulphuric acid.

Test estimations show that the above method yields accurate results.

T. H. P.

**Critical Studies on Volumetric Estimations of Bismuth.** L. MOSER (*Zeitsch. anal. Chem.*, 1907, 46, 223—241).—The author finds most of the processes proposed from time to time for the volumetric estimation of bismuth to be quite untrustworthy, but recommends the chromate method as modified by Rupp and Schaumann. In this process, the bismuth solution is precipitated with an excess of potassium chromate, and in an aliquot part of the filtrate the chromate remaining is estimated volumetrically as usual. On account of the great concentration of the liquid, the measurements should be made with scrupulous care. The precipitation of the bismuth, as directed by Riederer, with ammonium molybdate, and estimation of the excess of molybdate by reduction with zinc and subsequent titration with permanganate, is also a trustworthy process. L. DE K.

**Detection and Colorimetric Estimation of Traces of Gold by Means of Phenylhydrazine.** M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, 12, 90—91).—The finely-powdered mineral is treated with freshly prepared chlorine water and the excess of chlorine is expelled by warming. The solution, measuring 20—25 c.c., is acidified with formic acid and a few drops of phenylhydrazine hydrochloride solution are added when the least trace of gold is shown by the bluish-violet colour (transmitted light). By comparison with a solution containing a known amount of gold, a fair idea as to the gold content of the mineral will be obtained. L. DE K.

**Hot-gilding, and Discoloration of Gilded Surfaces.** HEINRICH STRUVE (*Zeitsch. anal. Chem.*, 1907, 46, 106—124).—It is very difficult to judge from the external appearance whether a metal, copper for instance, has been gilded by means of the old gold-amalgam process or by the modern galvanic method, but when the amalgamation process has been applied, the coating always retains traces of mercury. The discoloration of the surface on exposure to the air is due to formation of copper oxide, as the amalgam always dissolves more or less copper. L. DE K.

**Behaviour of Some Noble Metals towards Acetylene.** OSKAR MAKOWKA (*Zeitsch. anal. Chem.*, 1907, 46, 145—150).—Palladium may be separated quantitatively from platinum and iridium by means of acetylene in acid solutions, as these metals are not affected. Osmium, however, is completely precipitated. Gold is also completely reduced to metal, but not in alkaline solution. After igniting the joint precipitate of gold and palladium in a current of hydrogen, the latter metal may be extracted with hot nitric acid. L. DE K.

**Separation and Estimation of Palladium by Means of Acetylene.** HUGO ERDMANN and OSKAR MAKOWKA (*Zeitsch. anal. Chem.*, 1907, 46, 141—145).—Palladium may be precipitated quantitatively by passing a current of acetylene through a solution containing about one-fifth of its bulk of free hydrochloric acid. The precipitate

is ignited, preferably with addition of ammonium nitrate, and the residual mass is then fully reduced to metal by heating in a current of hydrogen.

Any copper remaining in the filtrate may be reduced with ammonia and hydroxylamine hydrochloride, and then also precipitated by acetylene (see this vol., ii, 399).  
L. DE K.

**Osmium.** CARL PAAL and CONRAD AMBERGER (*Ber.*, 1907, 40, 1378—1391).—The authors have tested the validity of a number of the methods suggested for estimating osmium and found several of them to yield untrustworthy results.

The method by separating osmium from alkaline osmate solutions as osmyldiammine chloride by addition of ammonium chloride and hydrochloric acid, and then heating in a current of hydrogen, is inaccurate, as also is the method of Leidié and Quenessen (*Abstr.*, 1903, ii, 576). According to the latter, osmium separates when aluminium acts on an alkaline solution of sodium osmate,  $\text{Na}_2\text{OsO}_4$ ; the authors now find that the method is also inapplicable when amalgamated aluminium is substituted for aluminium, and further that the osmium precipitates do not contain osmium alone, but the dioxide or its hydrate.

Satisfactory results are obtained by precipitating with dilute sulphuric acid from solutions containing potassium or sodium osmates, such as are obtained when osmium tetroxide is dissolved in aqueous alcoholic potassium hydroxide. The method was tested as follows. Weighed amounts of osmium tetroxide were dissolved in 3 c.c. of 15% potassium hydroxide, 25 c.c. of water added, and then 5 c.c. of alcohol; the mixture was then warmed at 40—50° in order to form potassium osmate. A slight excess of dilute sulphuric acid was then added, and then 10 c.c. more of alcohol in order to prevent reoxidation. After ten to twelve hours, a bluish-black deposit settled, whilst the supernatant liquid was colourless and free from osmium. The precipitate was then filtered, washed with aqueous alcohol, and converted into metallic osmium by reduction in a current of hydrogen.

Frémy describes a method whereby osmium disulphide is precipitated from solutions of potassium osmate by means of hydrogen sulphide. The authors converted this precipitate into metallic osmium but the results obtained are generally too low.

The method of estimating osmium by reducing alkaline osmates by hydrazine hydrate and then weighing as metallic osmium does not give satisfactory results.

Osmium tetroxide, as obtained by heating osmium preparations in a current of oxygen, cannot be converted quantitatively into osmium. Satisfactory results are, however, obtained when alcoholic solutions of osmium tetroxide are reduced by a dilute aqueous solution of formaldehyde. The reduction product first forms a colloidal solution, but is gradually entirely precipitated, and is then converted into metallic osmium by heating in a current of hydrogen at 230—250°.

The reduction may also be effected by means of alcohol or hydrazine hydrate, good results having been attained in both cases.

A. McK.

**Estimation of Higher Alcohols in Spirits: the Ester Iodine Method.** CHARLES HENRY BEDFORD and ROBERT L. JENKS (*J. Soc. Chem. Ind.*, 1907, 26, 123—126).—In order to estimate not only the amyl but also the intermediate (butyl and propyl) alcohols the following procedure is recommended. The spirit freed from esters and aldehydes is reduced to 20 vol.% alcohol, and to 30 c.c. of this are added 25 grams of dry calcium chloride, and the solution is shaken twice in succession with 50 c.c. of carbon tetrachloride. The 100 c.c. thus obtained are washed twice with 30 c.c. of calcium chloride (D 1.4) and the alcohols are then converted into nitrites by adding a mixture of 1 gram of sodium nitrite and 2 grams of potassium hydrogen sulphate (Beckmann, *Abstr.*, 1905, ii, 768). The nitrite formed is then estimated by the potassium iodide method (Dunstan and Dymond, *Abstr.*, 1890, 193). The authors find that the reaction between the nitrite and the potassium iodide is much accelerated by addition of 20 c.c. of absolute alcohol.

Another portion of the sample may then be tested according to the Allen-Marquardt method (oxidation with chromic acid and titration with standard alkali). This gives the amyl alcohol only, so the butyl-propyl alcohols are found approximately by difference.

L. DE K.

**A New Mercury Solution as a Reagent for Aldehydes, Especially Formaldehyde.** E. FEDER (*Arch. Pharm.*, 1907, 245, 25—28).—Two solutions are made, one containing 20 grams of mercuric chloride, the other 100 grams of sodium sulphite and 80 grams of sodium hydroxide per litre. Just before use, a suitable volume of the alkaline sulphite solution is added rapidly to an equal volume of the mercuric solution, which is shaken during the process. Aldehydes give a grey precipitate with this mixture, whereas ammonium salts give a white precipitate. With 10 c.c. of the reagent 0.05 mg. of formaldehyde produces a distinct reaction after one to two minutes. Dextrose reacts, but the reagent cannot be used to detect it in urine, because urine free from dextrose also produces the reaction.

By allowing the grey precipitate of metallic mercury to settle thoroughly, collecting it in an Allihn filter-tube, and weighing it, an estimation of formaldehyde is possible, with an error of -1.5% of the whole:  $\text{Hg} = \text{C}_2\text{H}_2\text{O}$ .

C. F. B.

**A New Reaction for Chloral.** ERCOLE COVELLI (*Chem. Zeit.*, 1907, 31, 342).—One c.c. of castor oil is heated in a porcelain capsule on the water-bath for ten minutes, and in the centre of the oil is then placed a small lump of antimony trichloride, when an orange-yellow, resinous mass is formed. If now a trace of chloral hydrate is dropped on to this mass, a spot is gradually formed of a fine bluish-green colour. The chloral hydrate may also be dissolved in castor oil and the solution heated on the water-bath with a little antimony trichloride, when a blue ring is gradually formed around the latter. To detect chloral in aqueous solution, the liquid is agitated with ether; this is then mixed with 1 c.c. of castor oil, evaporated on the water-bath, and dried over sulphuric acid; the test is then applied. The colour is also formed by



adding sulphuric acid to a solution of chloral hydrate and castor oil in a mixture of equal parts of ether and chloroform, or by simply warming a mixture of sulphuric acid, castor oil, and chloral. The colouring matter is soluble in chloroform, but insoluble in water, and fades when boiled with alcohol or by treatment with potassium hydroxide. The reaction is characteristic for chloral. L. DE K.

**Influence of Creatinine in Modifying the Reactions of Sugar in Urine.** HUGH MACLEAN (*Biochem. J.*, 1907, 2, 156—173).—The presence of creatinine markedly interferes with Fehling's reaction. Creatine, if present, has a similar although less marked effect. It holds the reduced oxide in solution. The differences of tint from red to yellow of the precipitate when it occurs is due to admixtures of the cuprous oxide and hydroxide, and all shades may be obtained by varying the different amounts of sugar and creatinine. In the nitroprusside test for acetone, it is important not to heat the alkaline mixture of nitroprusside before adding the acetic acid, for heat alone so alters the nitroprusside that it gives a blue colour on adding the acetic acid apart from the presence of either acetone or creatinine. Creatinine when boiled with alkali of half the strength of Fehling's solution is partly converted into creatine, and partly destroyed; four to seven minutes' boiling leads to a loss of 50% of the creatinine. Creatine resists this action longer. Sugar in weak solutions can be absolutely destroyed by boiling with 2—4% sodium hydroxide for a few seconds. W. D. H.

**Wine Analysis. Estimation of Sugars, Reducing Substances, and Dextrin.** HENRI PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1907, 24, 1213—1215).—A criticism of the [French] official method. For polariscopic purposes it is recommended to destroy the red colouring matter of the wine by cautious addition of sodium hypochlorite solution followed by a few c.c. of normal lead acetate. When estimating the reducing substances before and after inversion with hydrochloric acid, it is unnecessary to submit the sample to a preliminary treatment with lead solution, &c. Dextrin is not affected by treatment with hydrochloric acid, but it is converted quantitatively into dextrose by heating the wine for two or three hours with an equal volume of 8% sulphuric acid on the water-bath. The author prefers the gravimetric estimation, as copper oxide. L. DE K.

**Influence of Basic Lead Acetate on the Rotation of Sucrose in Aqueous Solution.** FREDERICK BATES and J. C. BLAKE (*Zeitsch. Ver. deut. Zuckerind.*, 1907, 614, 314—323).—It has been stated by von Lippmann (*Chemie der Zuckerarten*, 2, 1185) that basic lead acetate in aqueous solution has no influence on the rotation of sucrose. The results of the authors' experiments show this statement to be incorrect, the rotation of sucrose being at first slightly decreased and afterwards considerably increased by the presence of increasing quantities of the basic acetate.

The sucrose employed was highly purified commercial sugar, 26.048 grams of which in 100 c.c. of solution at 20° gave a rotation of 99.9

Ventzke divisions when read in a 20-cm. tube. The basic lead acetate solution ( $D^{15}$  1.25) was prepared either by boiling aqueous lead acetate with lead oxide or by dissolving the pure basic acetate in water. All the apparatus used was calibrated at  $20^{\circ}$ , for which temperature the readings were corrected.

The presence of 1 c.c. of the lead acetate solution in 100 c.c. of the sugar solution lowers the rotation to a minimum of about 99.78 Ventzke divisions, whilst with 6 c.c. the rotation is again 99.9; with 20 c.c., 99.45, and with 63 c.c., 98.95.

This influence of basic lead acetate on the rotation of sucrose appears to be due to the formation of a soluble lead sucrate, the rotation of which differs from that of sucrose.

T. H. P.

**Estimation of Sucrose and Reducing Sugars in Liquid Sugar Products.** FERDINAND GERHARD WIECHMANN (*Zeitsch. Ver. deut. Zuckerind.*, 1907, 612, 65—75).—The author has analysed a large number of sugar syrups by various methods which have been proposed, and, as a consequence of the results obtained, proposes, on behalf of the International Commission, the adoption of the following procedure in the examination of these products. Fehling's solution is to be used in Soxhlet's modification, containing 34.639 grams of crystallised copper sulphate, 173 grams of Rochelle salt, and 50 grams of sodium hydroxide per litre, the copper sulphate and alkaline tartrate solutions being stored separately and mixed just before using.

Twenty-six grams of the syrup are dissolved in about 75 c.c. of water in a 100 c.c. flask and sufficient basic lead acetate solution (Intern. Com. Standard) added to effect complete clarification of the solution, any excess of the clearing agent being precipitated by means of a 10% sodium chloride or sulphate solution; the liquid is then made up to the 100 c.c. mark with water, shaken, and filtered. The following estimations are then made. (1) *Total sugar*.—To 50 c.c. of the filtered solution, 5 c.c. of 38% hydrochloric acid ( $D$  1.188) are added and the mixture heated on a water-bath in three minutes to  $67$ — $70^{\circ}$ . The solution is then kept well shaken and the temperature maintained as nearly as possible at  $69^{\circ}$  for five minutes, at the end of which time the liquid is rapidly cooled and 50 c.c. of it made up to 1 litre with water; 25 c.c. of the solution thus obtained, corresponding with 0.1625 gram of the syrup, are neutralised by the addition of about 25 c.c. of a sodium carbonate solution containing 1.7 grams of the crystallised salt per litre. Fifty c.c. of Fehling's solution are added and the mixture heated to boiling in about four minutes and kept boiling over a small flame for exactly three minutes, counting from the rising of bubbles of steam from the walls of the vessel and from the interior of the liquid. The liquid is then cooled immediately, mixed with 100 c.c. of boiled, cooled, distilled water, and filtered as usual through an asbestos filter, the precipitate being washed successively with hot water, alcohol, and ether, and dried for thirty minutes at  $100^{\circ}$ . After cooling over calcium chloride, the cuprous oxide is weighed and the weight multiplied by 0.888 to give the equivalent amount of copper; the sucrose corresponding with the latter is read off from the German Government Tables (Law of July 9th, 1887). (2) *Reducing sugar*.—

Four c.c. of the clarified solution are made up to 100 c.c. with water, and 50 c.c. of the solution thus prepared, corresponding with 0.52 gram of the syrup, boiled with 50 c.c. of Fehling's solution for three minutes as described above. The amount of copper thus obtained is subtracted from the corresponding amount found in the estimation of the total sugar, the remainder representing the real quantity of sucrose present. The amount of sucrose corresponding with the weight of copper obtained in the estimation of reducing sugar is read off from the tables referred to above and is then divided by 0.95 to convert it into invert sugar.

T. H. P.

**Detection of Small Quantities of Raffinose.** CARL NEUBERG and FRITZ MARX (*Zeitsch. Ver. deut. Zuckerind.*, 1907, 615, 453—456).—The hydrolysis of raffinose by emulsin, which converts it into galactose and sucrose (this vol., i, 389), may be used as a means of detecting small proportions of this sugar mixed with non-reducing sugars. Thus, the authors find that when a solution containing 0.04 gram raffinose and 10 grams sucrose per 100 c.c. is mixed with a little emulsin and a drop or two of toluene and the solution kept at 38° for forty-eight hours, the galactose formed from the raffinose can be detected by its reducing action on Fehling's solution. Although the action of the emulsin is not prohibited by the faintly alkaline reaction of commercial sucrose, it is best to use for the test a solution neutral to phenolphthalein.

The test naturally fails in presence either of reducing sugars or of other sugars hydrolysed by emulsin, such as stachyose, which is, however, of very rare occurrence. Care must be taken that no glucosides are present.

Commercial preparations of emulsin, when digested with water, in some cases yield solutions which reduce Fehling's solution. Such may be purified as follows. Ten grams of the emulsin are shaken by means of a machine for two hours with 100—200 c.c. of water and a drop of toluene, the solution being afterwards left for thirty-six hours and then filtered. The clear solution is mixed with four times its volume of absolute alcohol, the flocculent precipitate being collected, after half an hour, on a filter and washed with alcohol and ether. The emulsin so purified is active and stable.

T. H. P.

**Detection of Hydrocyanic Acid by Means of Paper Impregnated with Phthalophenone.** THIÉRY (*J. Pharm. Chim.*, 1907, 25, 51—53).—An alkaline solution of phthalophenone is prepared by dissolving 0.5 gram of phenolphthalein in 30 c.c. of absolute alcohol, sufficient water to produce a faint turbidity is added, and then 20 grams of sodium hydroxide. Aluminium powder is introduced, a little at a time, until the solution is decolorised; the solution is now diluted to a volume of 150 c.c. with boiled and cooled water, and then filtered. To apply the test, strips of paper, previously steeped in a 0.05% copper sulphate solution and dried, are moistened with a few drops of the alkaline phthalophenone solution, and immersed in the solution containing the hydrocyanic acid. The red coloration produced is permanent for twenty-four hours. Solutions containing

ammonium persulphate, sodium peroxide, or perchlorate also give a positive reaction with the test-paper, but the coloration fades slowly; hydrogen peroxide, ferric chloride, nitric acid, and ethyl nitrate do not give a reaction. The test will detect the presence of 1 part of hydrocyanic acid in 2,000,000.

W. P. S.

**Toxicological Detection of Hydrocyanic Acid.** GIOVANNI CALVI and MARIO MALACARNE (*Chem. Zentr.*, 1907, i, 676; from *Giorn. Pharm. Chim.*, 56, 5—9).—The decomposition of alkali cyanides is much accelerated by the action of the air, particularly in presence of matters in a state of decomposition containing free acid. Alcohol, which prevents putrefaction of the organs, also retards the decomposition of hydrocyanic acid, so that this poison may be detected even after one month.

L. DE K.

**Volumetric Estimation of Some Combined Organic Acids.** RENÉ DUCHEMIN and GASTON CRIQUEBEUF (*Bull. Assoc. Chim. Sucr. Dist.*, 1907, 24, 1216—1220).—Neutral acetates, propionates, and butyrates may be conveniently titrated with  $N/2$  sulphuric acid, using methyl-violet as indicator, the end reaction being noticed by the appearance of a blue colour. If the solution should be acid or alkaline, it must be neutralised first with phenolphthalein as indicator. If the sample is coloured by tarry matter, minute spots of the indicator should be placed on a porcelain slab and the "spot test" applied. Metals, such as copper, should be removed first by means of sodium hydroxide, also those metals which form insoluble sulphates. Acetates which are soluble with difficulty may be dissolved with the aid of a definite volume of standard acetic acid, which is then allowed for. It is advisable to check the determinations by a blank experiment.

Formic acid cannot be titrated in this way, as it is not without action on the indicator; still with a little practice and using a comparison liquid of known strength it is possible to get good results by the "spot test."

L. DE K.

[Detection of Lactic Acid.] W. M. FLETCHER and F. GOWLAND HOPKINS (*J. Physiol.*, 1907, 35, 247—309).—See this vol., ii, 373.

**Joulie's Process for Estimating the Acidity of Urine.** FERNAND REPITON (*Ann. Chim. anal.*, 1907, 12, 94—96).—An adverse criticism of Joulie's process (adding standardised calcium succrate solution until a precipitate of calcium triphosphate commences to form). Neutral and even ammoniacal urines show acidity by this process.

L. DE K.

**Hydrolysis of Sodium Palmitate.** ROBERT COHN (*Ber.*, 1907, 40, 1307—1309. Compare *Abstr.*, 1906, ii, 58).—In reply to Holde and Schwarz (this vol., i, 176), the author maintains that sodium hydroxide may be titrated accurately in presence of sodium palmitate, with phenolphthalein as indicator, if the end of the reaction is taken as the change from deep red to light rose. This is shown to be in agreement with Salm's view that the colour of an indicator is a function

of the concentration of the hydrogen or hydroxyl ions (Abstr., 1906, ii, 218).

Experimental results are quoted to show that the method may be used also for the estimation of sodium stearate and cerotate. G. Y.

**Reactions of Photographic Developers with Unboiled Milk.** WILLIAM MACADIE (*Pharm. J.*, 1907, 207).—Nearly all photographic developers give a more or less coloured solution with milk that has not been heated above 75°, in the presence of hydrogen peroxide. Some of the substances which are used as developers, such as *p*-phenylenediamine, have been employed previously for the detection of unheated milk, but it is now shown that ortol (methyl-*o*-aminophenol) will detect as little as 1% of raw milk in boiled milk. Amongst the other developers which give a reaction are metol (methyl-*p*-aminophenol), *p*-aminophenol, catechol, amidol (diaminophenol), glycine, hydroquinone, adurol, eikonogen, and pyrogallol. The names in parentheses denote the constituent of the developer to which the reaction is due, and not necessarily the composition of the developer. W. P. S.

**A Simple Clinical Method for Estimating Fat in Human Milk.** ARTURO PRIMAVERA (*Biochem. Zeitsch.*, 1907, 3, 508—518).—A simple and rapid clinical method giving sufficiently accurate results for most purposes is obtained by counting the number of fat globules in a small amount of milk, taking the average diameter ( $d$ ) of a certain number, and calculating the volume  $V$  of each globule by the formula  $V = 1/6\pi d^3$ . From this the total volume of the fat is easily reckoned. W. D. H.

**Analysis of Fish Oils.** GEORGES HALPHEN (*Bull. Soc. chim.*, 1907, [iv], 1, 280).—It is claimed that the use of phenol as a method of eliminating excess of bromine, and the employment of a mixture of carbon tetrachloride and absolute alcohol for the separation of the liquid and solid bromo-compounds formed, suggested by Procter and Bennett (*J. Soc. Chem. Ind.*, 1906, 25, 798), has already been indicated by the author (Abstr., 1902, ii, 293).

Further experiments have, however, shown that it is almost impossible to limit the action of the phenol to the free bromine and that the results are influenced by the amount of water present in commercial alcohol and in other ways. T. A. H.

**Estimation of Unsaponifiable Matters in Fats.** HEINRICH SCHICHT and KARL HALPERN (*Chem. Zeit.*, 1907, 31, 279—282).—Most of the processes in use for the estimation of unsaponifiable matters in fats, and more particularly in bone-fat, are attended with sources of error.

The following method gives satisfactory results. Five grams of the sample are boiled in a reflux apparatus with 25 c.c. of absolute alcohol and 3 grams of potassium hydroxide dissolved previously in a very little water. When cold, the soap solution is mixed with 25 c.c. of a 10% solution of potassium chloride and shaken four times in succession with 200 c.c. of light petroleum containing no constituents boiling

above 60°. The mixed petroleum extracts are evaporated and the residue is dissolved in 25 c.c. of absolute alcohol and rendered faintly alkaline with potassium hydroxide, using phenolphthalein as indicator. After adding 25 c.c. of 10% potassium chloride solution, the liquid is again shaken with 200 c.c. of light petroleum, which is then freed from the last traces of soap by shaking a few times in succession with 100 c.c. of 50% alcohol. The washings are each shaken with 100 c.c. of light petroleum (the same petroleum is used over again) and this is finally shaken once more with 100 c.c. of dilute alcohol. The light petroleum now quite free from soap is then distilled off and the unsaponifiable matter is weighed.

L. DE K.

**Reaction of Hydroxyquinones.** A. BRISSEMORET and R. COMBES (*J. Pharm. Chim.*, 1907, [vi], 25, 53—58. Compare Abstr., 1906, ii, 118).—When a solution of nickel acetate is added to a hydroxyquinone in alcohol, characteristic colorations are produced; thus hydroxyquinones of the benzene series, such as perezone and embelic acid, furnish a blue colour and a precipitate; those of the naphthalene series, such as juglone and the hydroxyquinone present in *Drosera intermedia*, furnish a violet coloration, and those of the anthracene series, such as chrysophanic acid and emodin, give a rose-pink colour. In each case if the coloured product obtained by evaporating the mixture to dryness is dissolved in dilute hydrochloric acid and shaken with chloroform, the nickel compound is decomposed and the hydroxyquinone dissolves in the chloroform. If filter paper is impregnated with this solution, and then dried and exposed to ammonia gas, colours similar to those produced by the addition of nickel acetate to the respective hydroxyquinones are obtained. In applying this colour reaction to a plant material, the latter is extracted with dry ether and the residue, dissolved in alcohol, is treated as already described. In this way the dry fruits of *Embelia ribes* are shown to contain a benzenoid hydroxyquinone; the leaves of *Juglans regia*, the dry bark of *J. cinerea*, *Drosera intermedia*, and *D. rotundifolia* to contain a hydroxyquinone of the naphthalene series; whilst Barbadoes aloes, *Cascara sagrada* bark, and Turkey rhubarb give the rose-pink coloration characteristic of hydroxyanthraquinones. Carmin does not give the colour reaction of a hydroxynaphthaquinone. From *Ceratostigma plumbaginoides* and *Drosophyllum*, two substances giving the colour reaction of hydroxynaphthaquinones have been isolated, and a similar substance occurs in *Plumbago europæa* (compare Bettinck, Abstr., 1888, 848). This colour reaction is not applicable to hydroxyquinones containing two hydroxyl groups in the ortho-position relatively to each other.

T. A. H.

**Detection and Estimation of  $\alpha$ -Naphthaquinone,  $\beta$ -Naphthaquinone, Phthalonic Acid, and Phthalic Acid.** MAITLAND C. BOSWELL (*J. Amer. Chem. Soc.*, 1907, 29, 230—238).—*Estimation of  $\alpha$ -Naphthaquinone.*—This is titrated in alcoholic solution with  $N/10$  stannous chloride in 2% hydrochloric acid until the colour is nearly discharged. The end reaction is then noticed by testing a drop of the liquid on a watch-glass with a drop of a mixture of equal volumes of

alcohol and phenylhydrazine, when no bright pink colour should be formed; or the alcoholic solution may be boiled with a few drops of redistilled aniline and the stannous chloride run in until the red colour is completely discharged. Two mols. of stannous chloride = 1 mol. of  $\alpha$ -naphthaquinone.

*Estimation of  $\beta$ -Naphthaquinone.*—The substance is dissolved in ether and  $N/10$  stannous chloride is added. At first the liquid turns dark green and almost black and opaque, but on carefully adding more tin solution the liquid suddenly becomes colourless and transparent, showing the complete reduction to  $\beta$ -naphthaquinol. One mol. of stannous chloride = 1 mol. of the quinone.

*Estimation of Phthalonic Acid.*—The substance is heated at  $130-180^\circ$  in a test-tube with sulphuric acid in a current of carbon dioxide, and the carbon monoxide formed is collected in a nitrometer over 30% potassium hydroxide solution and measured, or the substance may be titrated with  $N/10$  permanganate. The liquid should contain free sulphuric acid, and any excess of permanganate added may be titrated back with standard ferrous sulphate. The titration must not be carried out in hot solutions; otherwise homophthalic, phthalidecarboxylic, and even phthalic acids would be acted on.

*Separation and Estimation of Phthalic Acid.*—The mixed substances are heated in a test-tube in a current of air for half an hour at  $200-220^\circ$ , and the phthalic anhydride which sublimes is retained in a layer of absorbent cotton. When cold, the bottom of the test-tube is cut off, and the glass and the cotton soaked in volumetric solution of potassium hydroxide, the excess of which is then titrated with volumetric sulphuric acid, using dry phenolphthalein as indicator, because the least amount of alcohol vitiates the result.

*Fluorescein Reaction.*—0.1 Gram of resorcinol is mixed with its own weight (or less) of the substance to be tested, and heated with a drop of sulphuric acid at  $160^\circ$  for three minutes. When cold, the mass is shaken with 2 c.c. of 10% potassium hydroxide and poured into 500 c.c. of water. With phthalic acid a more or less red-coloured liquid with green or bluish-green fluorescence is obtained. Phthalonic acid, phthalidecarboxylic acid, homophthalic acid, naphthalene, and  $\alpha$ -naphthaquinone also give a similar reaction.  $\alpha$ - and  $\beta$ -Naphthols give a red solution with blue fluorescence, but  $\beta$ -naphthaquinone gives a dark green solution without fluorescence.

L. DE K.

**New Reactions for Abrastol.** GIOVANNI SALOMONE (*Chem. Zentr.*, 1907, i, 306; from *Giorn. Farm. Chim.*, 1906, 55, 481—485).—One to two c.c. of the abrastol solution is mixed with 2—4 drops of fuming nitric acid (D 1.98) and, if necessary, heated to  $40-50^\circ$ . Even if the quantity of abrastol does not exceed 1 in 300,000 a permanent, ruby-red coloration will be observed. After some hours, however, and immediately on adding alkali, the colour turns pale yellow. On adding to the red solution a small crystal of sodium hyposulphite the colour changes to blue, violet, dark green, and finally to yellow. On adding a crystal of sodium sulphite the red colour changes at once to yellow. On adding to the red solution stannous chloride and then a few drops of hydrogen peroxide or ammonium persulphate the liquid turns reddish-violet; a

little sulphuric acid assists the reaction. In order to detect abracistol in wine, 25—50 c.c. are shaken with a few drops of ammonia and 15—30 c.c. of amyl alcohol, and the residue from the amyl alcohol is then submitted to the test; or the residue may be fused with a little metallic sodium and the mass tested for sulphide with sodium nitroprusside. This reaction distinguishes abracistol from  $\beta$ -naphthol with which it has many reactions in common. L. DE K.

**Detection and Estimation of "Saccharin" in Cocoa-Powder.**

WILLEM P. H. VAN DEN DRIESSEN MAREEUW (*Pharm. Weekblad*, 1907, 44, 245—247).—Ten grams of cocoa-powder are boiled for an hour with 100 c.c. of 1% hydrochloric acid, the liquid made faintly alkaline with sodium carbonate, filtered, and the residue washed with water until the washings have neither a sweet nor alkaline taste. The alkaline filtrate and washings are made faintly acid with phosphoric acid, evaporated to small bulk, 5 grams of calcium sulphate added, and the mixture evaporated to dryness. The residue is extracted with ether in a Soxhlet or separating funnel. A measured volume of the ethereal solution is evaporated, and the residue tested for "saccharin" as follows. (1) Taste. (2) Add 5 c.c. of 8% sodium hydroxide to a small portion, evaporate to dryness, fuse, and test with ferric chloride for salicylic acid, and with barium chloride for sulphate. (3) Warm with resorcinol and sulphuric acid, and dissolve the mixture in water containing alkali. A green fluorescence indicates "saccharin." (4) Dissolve in alkali and add acetic, oxalic, or citric acid. In presence of a *p*-sulphaminobenzoate, a precipitate with the properties of the *o*-compound, but lacking its sweet taste, is formed.

Another portion of the ethereal solution is evaporated to dryness in a crucible, and the residue fused with a mixture of sodium carbonate (free from sulphate) and potassium nitrate. The mass is dissolved in water, the solution acidified with hydrochloric acid, and evaporated to expel nitric acid. The sulphuric acid is then estimated as barium sulphate. A. J. W.

**Detection of Oil of Wormwood.** L. CUNIASSE (*Bull. Soc. chim.*, 1907, [iv], 1, 279—280).—The presence of thujone in wormwood oil enables the latter to be detected by such reactions as the formation of thujoneoxime, the action of phenylhydrazine, the action of mercury hydrogen sulphate (Denigès's reaction), and the green coloration produced by the addition of iodine. Further, a solution of sodium nitroprusside to which sodium hydroxide and acetic acid have been added (Légal's reagent) furnishes with oils of wormwood and tansy an intense red coloration, but gives no coloration with oil of aniseed, star aniseed, fennel, hyssop, or coriander, or with acetaldehyde.

T. A. H.

[**Estimation of Hexamethylenetetramine in Urine.**] PETER BERGELL (*Chem. Zentr.*, 1907, 487—488; from *Deut. med. Woch.*, 33, 55—56). See this vol., i, 392.



**Some New Ureometers.** M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, 12, 135—138).—Garcia's ureometer and a modification of it by the author are described. The author also describes a new ureometer which bears a great resemblance to Lunge's nitrometer. It consists of a laboratory tube (*B*) holding 30 c.c. and divided to 0.1 c.c., which may be closed at the top by a tap (*A*) and at the lower end by a tap (*C*); to the top is sealed an elongated funnel (*F*). A long india-rubber tube furnished with a pinchcock (*P*) connects *C* with an elongated small mercury reservoir (*E*).

By opening *A* and *C* and raising *E* the mercury ascends a little above *A*; 5—10 c.c. of water are introduced into *F* and the mercury is lowered until the tube contains some 3—8 c.c. of water, when *A* is closed. The mercury reservoir is now lowered until the mercury in the tube falls below *C*, which is then closed. The tube now contains only water vapour at a low pressure. After closing *P* and disconnecting the reservoir and tube, the urine is introduced first through *F*, then the washings, and finally the hypobromite. After gently shaking, the tube is placed in water and the tap (*C*) is opened. The volume of the nitrogen evolved is then measured with the usual precautions.

L. DE K.

**The Herapathite Reaction.** E. HÖST MADSEN (*Chem. Zentr.*, 1907, i, 673; from *Ber. Deut. pharm. Ges.*, 10, 442).—In order to obtain the reaction without fail, the reagent should be made according to Christensen's directions. One part of iodine is dissolved in 1 part of 50% hydrogen iodide, 0.8 part of sulphuric acid, and 50 parts of 70% alcohol. On adding 1 c.c. of the reagent to the alcoholic solution of quinine, the herapathite crystals are soon deposited. The iodine solution may be kept.

L. DE K.

**Alkaloid Reactions [Narceine].** C. REICHARD (*Chem. Zentr.*, 1907, i, 379—380; from *Pharm. Centr.-h.*, 47, 1028—1031).—Narceine dissolves in sulphuric acid with a greenish-yellow colour, which on heating turns blood-red. Nitric acid gives a yellow colour, which on adding 40% aqueous potassium hydroxide turns red and then again deep yellow. A mixture of narceine, mercurous nitrate, and water turns black on adding sulphuric acid; after a time the mass turns yellowish-red. A trace of narceine added to a drop of strong solution of bismuth chloride gives a deep yellow colour; when evaporated to dryness and moistened with sulphuric acid, a colourless solution is obtained. Stannous and antimonious chloride give no coloration but the residues, when treated with sulphuric acid, turn, respectively, yellow, and yellow changing to dirty brown. A mixture of narceine and sodium arsenate, when moistened with sulphuric acid, turns yellow, and on warming becomes dark red. If to a mixture of narceine and stannous chloride are added some drops of 40% aqueous potassium hydroxide, the mass on drying and warming turns green, and finally blackish-green. A mixture of narceine and ammonium molybdate turns blue with hydrochloric or sulphuric acid, but not with acetic acid. A mixture of narceine and a strong yellow solution of sodium iodide gives a faint

blue coloration, which becomes dark blue on adding zinc chloride. A few more reactions of less importance are also given. L. DE K.

**Action of Formaldehyde on Tannins.** FERDINAND JEAN and C. FRABOT (*Ann. Chim. anal.*, 1907, 12, 49—52).—When an aqueous solution of a tannin of the catechol type (those which yield catechol when heated) is heated on the water-bath with formaldehyde and a little hydrochloric acid, the tannin is completely precipitated as a condensation product, the weight of which represents practically the original amount of tannin. Tannins of the pyrogallol type (those which yield pyrogallol when heated) are not precipitated.

In this manner it is possible to detect and even estimate the frequent adulteration of sumach with lentisk.

To the catechol type belong the tannins from cork-tree bark, oak bark, lentisk, gambier; mangrove, quebracho, mimosa, fir, larch, China galls, and hemlock; to the pyrogallol type, the tannins from sumach, bearberry, chestnut-tree, logwood, divi-divi, myrobolans, valonia, tamarisk, oak wood, and *Ailanthus globulosa*. L. DE K.

**Estimation of Indigotin in Commercial Indigo.** CYRIL BERTHEIL and RICHARD V. BRIGGS (*J. Soc. Chem. Ind.*, 1907, 26, 182—184).—An unfavourable criticism of Bloxam's process (*Abstr.*, 1906, ii, 818), it being stated that there is a considerable loss of indigotin during the salting out and filtering. L. DE K.

**Botanical Microchemistry.** M. RACIBORSKI (*Bull. Acad. Sci. Cracow*, 1906, 553—560).—*p*-Benzoquinone is recommended as a test for proteins and amino-acids, and dimethylaminobenzaldehyde (instead of vanillin) for detecting phloroglucinol derivatives. The nitrite reaction is carried out by immersing the sections successively in 10% sodium nitrite, 10% sulphuric acid, and 10—20% sodium carbonate, the treatment with acid being of short duration (not more than a minute).

In the diazo-reaction, the sections are placed on watch-glasses containing 10—20% sodium carbonate and, by means of a glass-rod, treated with some drops of a diazo-solution prepared from either nitroaniline or sulphanilic acid. N. H. J. M.

**Nessler Solution as a Test for Gelatin.** JEAN VAMVAKAS (*Ann. Chim. anal.*, 1907, 12, 58—59).—Nessler solution when added to a solution of gelatin (D 0.1032), gives an emulsion of a brilliant leaden colour, and after a while a precipitate of similar colour is formed. On boiling, the precipitate forms immediately even when tartaric acid has been added. This test fully distinguishes gelatin from gum, dextrin, sucrose, dextrose, saponin, or liquorice, and allows its detection in mixtures. L. DE K.

**Action of Quinine on the Colouring Matter of Blood and a Simple Method for the Detection of Carbon Monoxide in Blood.** STEFAN VON HOROSZKIEWICZ and HUGO MARX (*Chem. Centr.*, 1906, ii, 1878; from *Berl. klin. Woch.*, 43, 1156—1157).—Old blood-

stains may be removed by means of a 10—15% solution of quinine; a brownish-yellow solution is formed which has a characteristic band in the spectrum between *C* and *D* corresponding with 628—596 $\mu$  (compare *Arch. exp. Path. Pharm.*, 54, 460). The change takes place instantaneously when the mixture is boiled. When normal blood mixed with an 8% solution of quinine chloride in the proportion of 2 : 4, is slowly heated until it just boils and the liquid then shaken with 2—3 drops of freshly prepared ammonium sulphide, a dirty brownish-green coloration is formed, whilst blood which contains carbon monoxide gives a brilliant red coloration which persists for many weeks.

The mixture of blood and quinine contains a substance which appears to belong to Takayama's catahæmoglobins, and is also related to the hæmatins. The spectrum of the solution obtained by filtering the mixture, washing the insoluble residue with hot water and dissolving in acetone, not only contains the band between *C* and *D*, but also a faint shadow in the green, the position of which corresponds with the two bands of hæmochromogen; a strong band in the blue directly in front of the *F* line is also apparent. After the addition of ammonium sulphide the brownish-red colour of the acetone solution changes to green, and the two hæmochromogen lines appear. An alcoholic solution behaves in a similar manner. E. W. W.

**The Quantity of Cellulose, Lignin, and Cutin in Pepper and Cocoa.** HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1907, 13, 265—266).—The following percentage amounts of crude fibre, cellulose, lignin, and cutin were found in various samples of pepper and cocoa, the method used for the estimations being that described by König (Abstr., 1906, ii, 905):

	Crude fibre.	Cellulose.	Lignin.	Cutin.
Pepper husks .....	23·54	8·74	12·52	2·28
Black pepper, Tellicherry .....	14·50	4·88	7·83	1·79
White pepper .....	11·59	3·12	6·54	1·66
"    "    coated with chalk .....	5·78	1·11	3·76	0·91
"    "    Singapore .....	5·40	1·16	3·20	1·04
"    "    washed.....	4·97	1·13	2·66	1·00
"    "    Java, washed .....	5·16	0·96	3·21	0·93
Cocoa husks .....	20·21	9·88	9·92	0·41
Cocoa powder .....	9·28	3·57	5·47	0·24

The figures relating to the cocoa husks and cocoa powder are calculated on the dry, fat-, and ash-free substance, and those referring to the peppers on the dry, ash-free substance. W. P. S.

## General and Physical Chemistry.

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**Optical Rotatory Power of Salts in Dilute Solutions.** FREDERICK LAFAYETTE SHINN (*J. Physical Chem.*, 1907, 11, 201—224).—The author has made experiments to ascertain whether the rotatory power of an active salt attains a constant value at high dilution, whether this rotatory power is independent of the inactive component of the salt, and whether any relationship exists between the change in the rotation and the change in the electrical conductivity as the concentration is decreased.

Potassium, sodium, lithium, and ammonium tartrates have the same equivalent rotatory power in 0.05 and 0.025 normal solutions; the rotation caused by butylammonium and barium tartrates is considerably smaller. The rotatory powers of the chlorides, nitrates, and sulphates of strychnine, brucine, cinchonidine, morphine, and quinine have been examined in aqueous solution at much greater dilutions than have been used in previous investigations, the concentration in certain cases falling to 1 gram-equivalent in 1280 litres. The conclusion is drawn that the rotations do not at high dilutions tend to become identical for salts containing the same active base. The curves representing the dependence of the rotatory power on the concentration diverge, some continuing to increase, others attaining a maximum, and then decreasing as the dilution progresses.

The rotation of quinine oleate in chloroform varies with the dilution in much the same way as the rotation of an alkaloid salt in aqueous solution. The results cannot be harmonised with the theory of electrolytic dissociation.

H. M. D.

**Principle of Optical Superposition.** PHILIPPE A. GUYE and MAURICE GAUTIER (*Zeitsch. physikal. Chem.*, 1907, 58, 659—666).—In reply to Rosanoff's recent criticisms (this vol., ii, 207), the authors maintain and further expound the propositions previously advanced by them (*Abstr.*, 1895, ii, 149, 195; see also Guye and Goudet, *Abstr.*, 1896, ii, 134, 458).

J. C. P.

**Latent Fluorescence and Optical Sensitisation.** JOHANNES STARK (*Physikal. Zeitsch.*, 1907, 8, 248—250. Compare this vol., ii, 147).—The fluorescence of molecules in those wave-lengths, for which the absorption in the molecular aggregate is intense, cannot be directly observed in the same manner as the fluorescence for which the absorption in the aggregate is small, the latter in nearly all cases investigated corresponding with wave-lengths near the red end of the absorption spectrum. This fluorescence of the individual molecules which is readily absorbed in the molecular aggregate is called latent fluorescence.

To demonstrate this latent fluorescence, a substance such as silver bromide, with a maximum sensitiveness in the blue and violet, is

covered with a layer of the substance to be tested and the system illuminated by wave-lengths, which are inactive towards the silver bromide, but are strongly absorbed by the substance under examination. By this means latent fluorescence can be detected by the chemical change in the bromide. Erythrosin is found to exhibit weak fluorescence in the blue region with a maximum at  $0.415 \mu$ . Cyanin exhibits strong fluorescence in the blue and violet from  $0.365$  to  $0.490 \mu$  with a maximum at  $0.400 \mu$ .

The author points out that his views determine the conditions which must be satisfied in the employment of optical sensitisers in photographic work.

H. M. D.

### Kauffmann's Fluorescence and Auxochrome Theory.

ARTHUR HANTZSCH (*Ber.*, 1907, 40, 1572—1577).—Polemical. A reply to Kauffmann (this vol., ii, 214, 215).

G. Y.

**Fluorescence of Benzene Derivatives.** JOHANNES STARK and RICHARD MEYER (*Physikal. Zeitsch.*, 1907, 8, 250—255).—The fact that all aromatic compounds investigated exhibit a banded absorption spectrum, and that fluorescence appears to be conditioned by the presence of bands in the absorption spectrum, leads the authors to conclude that the phenomenon of fluorescence must be exhibited by all aromatic compounds. This conclusion has been tested by the examination of the fluorescence spectra of benzene, naphthalene, anthracene, phenanthrene, the three dihydroxybenzenes, benzophenone, xanthone, 3 : 6-dihydroxyxanthone, tetramethyldiaminoxanthone, phthalic acid, phenolphthalein, hydroquinonephthalein, fluoran, and fluorescein in ethyl-alcoholic solution. A parallelism between the absorption spectrum and the fluorescence spectrum is found in all cases. The maximum intensity of the fluorescence spectrum is always displaced relatively to the maximum of the absorption spectrum towards the direction of greater wave-length. The extent of the displacement is considerably influenced by substitution in the benzene nucleus and also by condensation. The presence of the pyrone ring causes a large displacement; whilst in benzophenone the fluorescence spectrum is entirely contained in the ultraviolet, the spectrum of xanthone and its derivatives is in the visible region.

The groups described previously by Meyer as fluorophores are those which cause such displacement as to bring the fluorescent spectrum into the visible region; the actual fluorescent group is, however, the benzene ring itself.

The fluorescence spectra of fluorescein and fluoran have also been examined in sulphuric acid. That of fluorescein is similar to its spectrum in alcohol, but that of fluoran is quite different, and this the authors suppose is due to the formation of an oxonium salt in the acid solution.

H. M. D.

**Phosphorescence of Rare Earths.** JOS. DE KOWALSKI and CHARLES GARNIER (*Compt. rend.*, 1907, 144, 836—839).—Accepting the theory of phosphorescence advanced by Kowalski (*ibid.*, 266) it seemed likely that the various rare earths should behave as

"luminophores" and produce, when mixed in small quantities with "electronogenic" substances, mixtures exhibiting intense and lasting phosphorescence. The mixtures were prepared by dissolving the carefully purified alkaline earth carbonates in nitric acid, adding drop by drop a very dilute solution of the nitrate of the selected rare earth and precipitating the whole with ammonium carbonate. The precipitate was then heated to a red heat with a known quantity of sulphur and either sodium or potassium sulphate and the crucible while still red hot was plunged into melting ice in order to yield a solid supersaturated solution (compare Waentig, *Abstr.*, 1905, ii, 365).

Phosphorescence was excited in the precipitates by ultraviolet rays produced from a mercury lamp in quartz. Under these conditions calcium sulphide in association with potassium sulphate and praseodymium, developed lasting rose-tinted phosphorescence which became red at 200°. With sodium sulphate in place of potassium sulphate, a green phosphorescence was obtained, which on heating became deeper and finally changed to red. The same mixture with neodymium in place of praseodymium gave a green phosphorescence, which on heating became red and at higher temperatures developed a violet tint. Strontium sulphide in presence of sodium sulphate and samarium gave a golden-yellow phosphorescence, which rapidly became less vivid and gave place to a lasting orange-yellow colour. The spectrum in this case showed two lines in the red (the more refrangible had  $\lambda = 604\mu$ ) and one in the green ( $\lambda = 550 - 560\mu$ ). Strontium sulphide in presence of erbium gave a lemon-yellow phosphorescence.

The maximum intensity was found to be produced by one part of samarium in 25,000 of strontium sulphide or in 6000 of calcium sulphide.

All the sulphides examined alone exhibited a feeble green phosphorescence, which is probably due to the presence of traces of copper, and the addition of sodium or potassium sulphate to the mixture intensified both this green phosphorescence and that due to the luminophore added. All the white, fusible salts employed gave similar results, but it was observed that potassium or sodium fluoride had a particularly marked intensifying action on the phosphorescence of strontium sulphide containing samarium.

T. A. H.

**Phosphorescence of Calcium-Manganese Compounds. Determination of the Optimum.** L. BRUNINGHAUS (*Compt. rend.*, 1907, 144, 839—841. Compare Urbain, 1906, ii, 28, 359, and preceding abstract).—The intensity and colour of the phosphorescence induced in mixtures of calcium oxide, sulphate, phosphate, or sulphide (which are called diluents) with varying quantities of manganese compounds (named phosphorogens) by exposure to cathode discharges from a Crookes' tube have been examined and compared with the view of ascertaining the influence of different proportions of the phosphorogen on these properties. The results, which are tabulated in the original, show that the colour is scarcely affected, but the intensity, expressed as 1 for the pure calcium compound, reaches a maximum, expressed as 10, when 0.5% of manganous oxide is present, falls to 2 for a mixture

of equal parts of manganous oxide and calcium oxide, and disappears in the case of pure manganous oxide. The acid radicle present has no influence on the position of the optimum, which appears to depend entirely on the relative number of atoms of manganese and calcium present (1 : 254 in the present instance). Lecoq de Boisbaudran has stated (*Abstr.*, 1887, 3) that calcium sulphide phosphoresces green under the action of cathode rays, but the author finds that the phosphorescence of the sulphide is yellow and that of the phosphate red under these conditions.

T. A. H.

**Triboluminescence of Substances containing Zinc.** ADRIEN KARL (*Compt. rend.*, 1907, 144, 841—843).—When an intimate mixture of manganese nitrate and zinc sulphide is heated to 1200°, a product is formed which exhibits triboluminescence. Substances also exhibiting this property are formed by similarly heating zinc sulphide mixed with silicic, stannic, or titanous acid or with zirconia, praseodymia, or with manganese, silicate, stannate, titanate, or zirconate and other substances. The products formed do not appear to be definite chemical compounds.

T. A. H.

**Photographic Inactivity of Ammonium Amalgam.** G. BABOROVSKÝ and V. VOJTĚCH (*Chem. Zentr.*, 1907, i, 700; from *Physikal. Zeitsch.*, 1906, 7, 846. Compare *Abstr.*, 1906, ii, 725).—The positively charged particles which are emitted by decomposing ammonium amalgam have no photographic activity; the phenomenon is therefore not identical with that of the decomposition of radioactive substances.

E. W. W.

**Absorption of  $\beta$ -Radium Rays by Matter.** JOHN A. McCLELLAND and F. E. HACKETT (*Sci. Trans. Roy. Dubl. Soc.*, 1907, 9, 37—50. Compare *Abstr.*, 1905, ii, 495, 496; 1906, ii, 413).—The variation of the absorption coefficient with the density has been examined further. If  $\lambda$  is the coefficient of absorption of the total radiation,  $\kappa$  the ratio of the energy of the secondary radiation emitted by an elementary layer to the incident energy absorbed by it, and  $\mu$  the true coefficient of absorption, that is, the absorption when secondary radiation effects are eliminated, then  $\lambda = \mu \sqrt{1 - \kappa}$ . By means of this relationship, values of  $\mu$  are calculated from the experimentally determined values of  $\lambda$  and the values of  $\kappa$  recorded in previous papers. The values of  $\lambda$  obtained by two independent methods agree closely, and this, the authors consider, furnishes strong evidence of the general accuracy of the theoretical treatment of secondary radiation in this and previous papers.

It is shown that, whereas the ratio  $\lambda/d$  ( $d$  being the density) varies considerably and irregularly from one metal to another, the ratio  $\mu/d$  increases regularly with the atomic weight. In respect of the values of  $\mu/d$ , the metals examined fall into divisions corresponding with the chemical periods—lead and platinum are in one period, tin, cadmium, and silver in a second, zinc, copper, and nickel in a third, and aluminium in a fourth. The mean values of the ratio for these groups are 23, 18.5, 14, and 8.5 respectively.

H. M. D.

**Effect of High Temperatures on Radium Emanation and its Products.** WALTER MAKOWER and SYDNEY RUSS (*Proc. Roy. Soc.*, 1907, *A*, **79**, 158—166. Compare Makower, *Abstr.*, 1906, *ii*, 259).—The diminution in the activity of radium emanation which has been observed when the emanation is subjected to temperatures between 1000° and 1200° is found to be due to an alteration in the activity of one of the transformation products, radium *B* or *C*, and not to any alteration in the emanation itself, for the rate of decay of the emanation at these high temperatures is found to be the same as at room temperature. The effect of high temperatures on the activity of the deposit obtained on wires immersed in an atmosphere of the emanation has been examined. Two wires were subjected simultaneously to the influence of the emanation, and while one of these, after removal, was maintained at room temperature, the other was heated in an electrical furnace, and the activity of the two wires was compared from time to time by a differential method. Except in one experiment the radiation from the active deposit was found to be less intense in the case of the heated wire. The explanation given is that radium *C* undergoes a sudden change when subjected to a high temperature, the activity being thereby diminished. In an appended note the authors call attention to the discrepancy between their experimental results and those of Bronson, and attribute the difference to the different method of operating.  
H. M. D.

**Anode Rays.** E. GEHRCKE and O. REICHENHEIM (*Chem. Zentr.*, 1907, *i*, 687; from *Ber. deut. physikal. Ges.*, 1906, *4*, 559—566).—When the anode of a gas discharge tube is filled or coated with a sodium salt, intensely yellow torch-like rays of light are emitted, whilst the cathode is enveloped in blue light. The spectrum of the yellow light shows the *D* line, but after a time the light fades. The salts of thallium, lithium, potassium, rubidium, copper, caesium, barium, strontium, and zinc behave in a similar manner, but oxides are inactive. The rays which are named anode rays have been found to be positively charged.  
E. W. W.

**Chemical Action of Cathode Rays.** JOHANN ŠTĚRBA (*Monatsh.*, 1907, *28*, 397—409).—It having been shown by Goldstein (*Abstr.*, 1895, *ii*, 150; 1897, *ii*, 302) that the behaviour of substances when acted on by cathode rays is greatly modified by the presence of small traces of impurities, this work was undertaken with the object of preparing alkali salts as nearly pure as possible and determining their behaviour under the conditions mentioned.

The changes produced in alkali salts by the action of cathode rays has been ascribed to physical changes by Goldstein (*loc. cit.*) and by Abegg (*Ann. Phys. Chem.*, 1898, [iii], **62**, 425), to the formation of alkali subhaloids by Wiedemann and Schmidt (*Ann. Phys. Chem.*, 1895, [iii], **56**, 201), and to that of solid solutions of liberated alkali metal in the excess of salt by Elster and Geitel (*Abstr.*, 1898, *ii*, 201) and by Siedentopf (*Physikal. Zeitsch.*, 1905, **6**, 855). The purification of sodium chloride, nitrate, and sulphate, and potassium chloride and



chlorate, and the results obtained on exposing the purified salts to the action of the cathode rays, are described.

In agreement with the statements of Goldstein and of Wiedemann and Schmidt, it is found that on exposure to the cathode rays, sodium chloride shows a white fluorescence which changes to blue, the salt becoming brown and finally blackish-blue; the salt particles are attracted by the cathode, the cathode light becoming orange and the vacuum diminishing rapidly. The residue is strongly hygroscopic and is found to have an alkaline reaction when tested by Emich's method (Abstr., 1902, ii, 45); both thermo- and lyo-luminescence are observed with the brownish-yellow salt. The formation of free chlorine also is confirmed. The author considers, therefore, that the blackish-blue residue contains metallic sodium. In this connexion it is shown that the gases given off by blue rock-salt from Stassfurt, on solution in water, contain about 3.34% by volume more of hydrogen than the gases obtained from the colourless rock-salt, which points to the presence of about 0.00011% of metallic sodium in the blue salt. Wöhler and Kasarnowski's results obtained with artificially coloured sodium chloride (Abstr., 1906, ii, 22) are confirmed. On exposure to daylight at the ordinary temperature, the salt becomes greenish-blue, violet, and finally a permanent amethyst-violet; this colour change, which is the more rapid the more intense the illumination and the original brownish-yellow colour, takes place below 20°, but not in the dark even when the salt is in contact with uranium oxide or active thorium oxide. At 100° in the dark, the salt becomes rose-coloured, but again brownish-yellow on cooling; on prolonged heating or at high temperatures the colour disappears entirely.

The other salts investigated behave in a similar manner to sodium chloride when exposed to the action of cathode rays; the residue from the nitrate contains nitrite, whilst that from the chlorate contains hypochlorite and chloride in addition to the free alkali metal. It is concluded that the action of the cathode rays leads to decomposition of the alkali salts into their components either directly or by stages.

G. Y.

**The Effect of Cathode Rays on Uranoso-uranic Oxide.** WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Weekblad*, 1907, 4, 242—246. Compare also Hofmann and Strauss, Abstr., 1901, ii, 655; Goldstein, Abstr., 1903, ii, 524).—One hundred mg. of uranoso-uranic oxide were exposed for one hour to cathode rays. On cooling the weight was 71.2 mg. The activity of this preparation in discharging an electroscope was found to be 30% more than that of a similar preparation which had not been exposed to cathode rays.

A. J. W.

**Gaseous Product of Transformation of Polonium.** HEINRICH GREINACHER and M. KERNBAUM (*Physikal. Zeitsch.*, 1907, 8, 339—344).—Two polonium preparations from different sources were enclosed in spectral tubes specially designed to have a minimum capacity, the tubes being examined from time to time for helium or other lines. Two forms of tube were employed each having a capacity of about

2 c.c. Assuming the polonium deposit to weigh 0.001 mg., it was calculated that if helium were formed as one of the disintegration products the quantity produced in 140 days should be equal to 2% of the gaseous contents of the tube, a proportion in which helium should be readily recognised spectroscopically. After eleven months there was no trace of the helium lines even after the tubes had been heated at 150–200° to drive off any helium which might have been occluded by the glass. The hydrogen lines increased in intensity during the period of observation, but the possibility of the presence of traces of water or of hydrogen occluded by the copper plates on which the polonium had been deposited prohibits the conclusion that the polonium is the source of the hydrogen.

H. M. D.

**Radioactivity of Lead. II.** JULIUS ELSTER and HANS GEITEL (*Physikal. Zeitsch.*, 1907, 9, 273–277).—The radioactive precipitate obtained by converting commercial lead oxide into the chloride and saturating the solution with hydrogen sulphide after partial neutralisation has been further examined. A new apparatus is described for the measurement of the range of the  $\alpha$ -particles emitted by feebly radioactive materials. The range of the  $\alpha$ -particles from the active precipitate is found to be about 4 centimetres and the time required for the decay of the activity to half value about 100 days.

These numbers agree approximately with the corresponding constants for radium  $F$ , but the authors consider that the question as to whether radium  $F$  or some other unknown substance (lead  $X$ ) resembling this is the cause of the radioactivity of commercial lead has still to be settled.

H. M. D.

**Total Ionisation of Various Gases by the  $\alpha$ -Rays of Uranium.** T. H. LABY (*Proc. Roy. Soc.*, 1907, A, 79, 206–219).—The total ionisation produced by the  $\alpha$ -rays emitted by uranium oxide,  $U_3O_8$ , in various gases has been examined. The tabulated values of the total ionisation are the same as those found by Bragg for the  $\alpha$ -rays from radium  $C$ . The relative total ionisation is therefore independent of the range and initial velocity of the  $\alpha$ -particles producing it, for the particles from radium  $C$  have probably double the range of those from uranium.

The values obtained by the author for the total ionisation of the various gases do not agree with the numbers calculated from the conductivity and stopping power according to Strutt's formula. On the other hand, the ionisation per c.c. is found to be proportional to the molecular volume of the gas, and the relationship indicated by Bragg is thus confirmed.

H. M. D.

**Ionisation of Various Gases by  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Rays.** R. D. KLEEMAN (*Proc. Roy. Soc.*, 1907, A, 79, 220–233. Compare Abstr., 1906, ii, 720).—Measurements have been made of the ionisation produced by  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays in a large number of different gases. The data indicate that the ionisation is an additive quantity for the three kinds of rays. The atomic ionisation values of hydrogen, carbon, nitrogen, oxygen, sulphur, chlorine, bromine, and iodine for each type

of ray are recorded. The ionisation values of the compound gases calculated from the atomic ionisations agree well with the experimental values except in the case of ammonia and sulphur dioxide. The ionisation in hydrogen is also greater than that calculated from the additive law, and the explanation of this is that more energy is absorbed in the formation of an ion from a hydrogen atom when this is part of a molecule of hydrogen than when it is a component of the molecule of another gas. The ionisation values for the  $\beta$ -rays are almost exactly the same as those for the  $\gamma$ -rays, the only appreciable difference being found in the case of vapours containing iodine. By plotting the atomic ionisations against the atomic weight, curves are obtained which show that the ionisation is a periodic function of the atomic weight. The curves for the three different kinds of rays present the same periodicity. A similar periodic character is presented by the curves, which show the variation of the energy spent in the production of an ion with the atomic weight of the element ionised.

H. M. D.

**Absolute Potential of the Calomel Electrode.** WILHELM PALMAER (*Zeitsch. physikal. Chem.*, 1907, 59, 129—191).—Full details are given of work already reported (Abstr., 1903, ii, 707). Billitzer's work (*Zeitsch. Elektrochem.*, 1902, 8, 638, and succeeding papers) is adversely criticised, and the value assigned by him to the *P.D.* of the *N/10* calomel electrode (namely, +0.1 volt approximately) is shown to be wrong. There is added a full list of papers published since 1875 bearing on electrocapillary phenomena and the determination of absolute potential differences.

J. C. P.

**Changes of Energy Accompanying the Dilution of Zinc and Cadmium Amalgams.** THEODORE W. RICHARDS and GEORGE SHANNON FORBES (*Zeitsch. physikal. Chem.*, 1907, 58, 683—752).—The potentials between amalgams of different concentrations were determined at 23°, and the results are regarded as correct to within 0.00001 volt. In the case of the zinc amalgams, the values found for the potentials are less than those calculated on the basis of the gas laws; in the case of cadmium amalgams, the observed values are greater than the calculated values. In both cases the deviations between observed and calculated values tend to disappear as the amalgams become more dilute. The temperature coefficient of the potential of the cadmium amalgam cells is almost the same as the pressure-temperature coefficient of an ideal gas; that of the zinc amalgam cells is about 3% greater.

The heats of dilution of the amalgams have been determined directly by a trustworthy method, and the results, combined with the temperature coefficient of the *E.M.F.*, have furnished a very accurate confirmation of the Helmholtz formula. Cady's formula (Abstr., 1899, ii, 394) does not account adequately for the deviations from the gas laws.

The densities of the liquid amalgams have been determined accurately, and the magnitude of the contraction occurring on mixture ascertained for each case.

The authors discuss the nature of the zinc and cadmium amalgams from the chemical and the kinetic standpoint. The deviations in the case of the zinc cells are attributed to partial polymerisation; those observed with the cadmium cells are attributed chiefly to abnormal osmotic pressures.

J. C. P.

**Theory of the Tension of Solutions at their Decomposition Values.** UGO GRASSI (*Nuovo Cim.*, 1907, [v], 13, 202—208).—In this mathematical paper, the author shows that by assuming a distribution of electricity in the form of a single layer on the surface of the electrode and in the contiguous region of the solution, conclusions can be drawn regarding the amount of zinc passing into solution which are far more nearly in agreement with the observed facts than those arrived at by Lehfeldt (*Abstr.*, 1900, ii, 62) on the assumption that a double electrical layer exists between the electrode and the solution.

T. H. P.

**Permanent Condition Established Between Polarised Hydrogen Electrodes.** ARNOLD EUCKEN (*Zeitsch. physikal. Chem.*, 1907, 59, 72—117).—The method of investigation adopted was that due to Nernst and Merriam (*Abstr.*, 1905, ii, 674. Compare also Weigert, *Abstr.*, 1906, ii, 417). The theoretical connexion between current and potential in cases where the electrolyte is (1) an acid, (2) an acid + a salt with common ion, is deduced for the conditions of the author's work and is confirmed satisfactorily by his experiments. The limiting current for the case where hydrochloric acid is mixed with a small quantity of potassium chloride can be calculated from the limiting current observed with the acid alone, and from the amount of salt added. Theoretically, the limiting current with acid alone should be twice as great as the limiting current observed in presence of large excess of a salt with common ion, but secondary effects interfered with the experimental confirmation of this conclusion. The supposition that polarisation and resistance approach a constant limiting value as the applied *E.M.F.* increases has been verified in a general qualitative way. With the help of the residual current method, the diffusion coefficients of a number of organic acids (acetic, succinic, tartaric, benzoic, cinnamic, &c.) have been determined.

J. C. P.

**Polarity of Discharge.** D. PACINI (*Nuovo Cim.*, 1907, [v], 13, 182—188).—The author has confirmed the phenomenon observed by Sarasin, Tommasina, and Micheli (*Abstr.*, 1905, ii, 3), but he does not agree with their explanation of the non-superposability of the curves representing the rates of decay of the positive and negative charges of the electroscope.

The author wound the charged wire, after exposure to the air, in the form of a spiral, co-axial with and inside which was placed a cylinder of oxidised brass connected with the knob of the electroscope. When the spiral wire was replaced by a thick paper cylinder which had been moistened with uranium nitrate solution and allowed to dry, it was found that the electroscope lost a positive charge more rapidly than an

equal negative one. The polarity of the discharge is defined by the expression:  $\sigma_p = (t_n - t_p)/t_n$ , where  $t_n$  and  $t_p$  are the respective times required for the leaves of the electroscope to approach by a certain amount when negatively and positively charged. Such polarity is also found to exist when the uranium nitrate is replaced by non-radioactive, crystalline substances. Sodium, magnesium, and ammonium sulphates and potassium dichromate differ from uranium nitrate in exhibiting negative polarity of discharge, that is, with these substances, the negative charge is lost the more rapidly. Quinine hydrogen sulphate first shows positive polarity of discharge, which disappears after a few days; if then left for a day in a moist atmosphere, this substance subsequently exhibits negative polarity. With nickel sulphate, a change from negative to positive polarity occurs if the moist crystals are left in the air for a day. Potassium alum, if deposited from a concentrated solution, exhibits negative polarity, whilst if it is slowly deposited from a weaker solution, its polarity of discharge is positive.

From these results the conclusion is drawn that the condition of the dispersing surface is capable of generating a polarity of discharge sensitive to low potentials (250—1000 volts), the assumption of any emission being unnecessary. Whether the phenomenon depends on chemical actions, or on physical changes occurring in the air, remains to be decided.

T. H. P.

**Electromotive Forces of Concentration Cells.** JOSEPH E. TREVOR (*J. Physical Chem.*, 1907, 11, 283—291).—Helmholtz's differential equation for the *E.M.F.* of a concentration cell is integrated on the assumption that the relation between the vapour pressure and concentration is that required by the theory of dilute solutions, and (1) that Ostwald's dilution law is valid, (2) that the van't Hoff-Rudolphi equation expresses the relationship between the degree of dissociation and the dilution.

H. M. D.

**Thermodynamics of Liquid Cells.** P. HENDERSON (*Zeitsch. physikal. Chem.*, 1907, 59, 118—127).—A formula is deduced which permits the calculation of the contact potentials in liquid cells of higher concentrations than those to which Planck's formula applies. The author's theoretical deductions are tested with satisfactory results by measurements of the contact potentials in such cases as  $\text{H}_2\text{SO}_4/\text{K}_2\text{SO}_4$  and  $\text{HCl}/\text{BaCl}_2$ .

J. C. P.

**Chemistry of the Iron Electrode of the Jungner-Edison Accumulator.** OTTO FAUST (*Zeitsch. Elektrochem.*, 1907, 13, 161—165).—The *E.M.F.* of the combination, 10% zinc amalgam | 20% potassium hydroxide solution | iron electrode, is measured at different stages during the charge and discharge of the electrode. The completely charged electrode gives 0.39 volt. During discharge with a current density of 0.00033 ampere per sq. cm., three periods are observed in which the *E.M.F.* is approximately constant at about 0.47, 0.65, and 1.9 volt respectively. If the electrode is left at rest during the first period the *E.M.F.* returns to 0.39 volt, during the second

period it returns to 0.44 volt, and during the third to about 0.69 volt. The charging curve also exhibits three periods, and the *E.M.F.*'s attained when the electrode is left at rest are the same as those observed during discharge.

The author shows that an electrolytic deposit of spongy iron containing a considerable quantity of occluded hydrogen gives an *E.M.F.* of 0.39 volt; when the occluded hydrogen has escaped (which it does in bubbles), the *E.M.F.* rises to 0.44 volt. These two stages are therefore due to hydrogen and metallic iron respectively. The *E.M.F.* due to ferrous hydroxide was measured (in 20% potassium hydroxide solution) by pasting it on a platinum electrode; it was found to be 0.514 volt. An electrode of ferrous-ferric hydroxide was obtained by electrolysis of a solution of a ferrous salt in ammonia with a platinum anode. This electrode (combined as before with the zinc amalgam electrode) gave an *E.M.F.* of 0.555 volt. The author did not succeed in measuring the potential of ferric hydroxide, but it appears probable that the *E.M.F.* of the third stage in the discharge of the accumulator electrode must be due to this substance.

T. E.

**Constitution of the Atom and Coulomb's Law.** HENRI PELLAT (*Compt. rend.*, 1907, 144, 744—746. Compare this vol., ii, 249).—Discussing the validity of the second hypothesis (the spherical form of the atom) arising out of the electrical theory of the constitution of the atom, the author shows that the flattened form for the latter, suggested previously, would be unstable, in other words, that the atom is spherical. Hence, in order to reconcile theory with experiment, he concludes that Coulomb's law is inapplicable to intra-atomic distances, that is, *the attractive force must increase less rapidly, or the repulsive force more rapidly, than the inverse of the square of the distance.*

In reply to Tommasina's criticism (see following abstract), the author points out that since the existence of neutral monatomic molecules is admitted, it follows that neutral atoms exist, at any rate for some simple substances.

E. H.

**Constitution of the Atom.** THOMAS TOMMASINA (*Compt. rend.*, 1907, 144, 746—747. Compare this vol., ii, 249, and preceding abstract).—The author points out that a fourth condition, the electrical neutrality of the atom considered as a whole, accepted by Pellat as a fact in his consideration of the electrical theory of the constitution of the atom, is really only a hypothesis. Moreover, from this hypothesis it follows that the atoms would possess no chemical affinity and would not unite to form molecules, whereas the converse is the case. Accordingly the atoms can never be electrically neutral.

E. H.

**Direct Determination of the Absolute Value of the Electric Charge on a Univalent Electrolytic Ion. Diameter of an Atom.** HENRI PELLAT (*Compt. rend.*, 1907, 144, 902—904. Compare preceding abstracts).—By means of an equation derived from Stokes's formula for the velocity of a solid sphere moving in a resistant medium and from electrolytic data, the author has obtained values for

the electric charge on a univalent ion agreeing with those obtained indirectly by Townsend and J. J. Thomson from the electric charge on a gaseous ion. From thence the value  $7.8 \times 10^{-9}$  cm. is deduced for the radius of a univalent ion. E. H.

**Multivalent Atoms.** HENRI PELLAT (*Compt. rend.*, 1907, 144, 969—971. Compare this vol., ii, 249, and preceding abstracts).—Multivalent atoms may be regarded as consisting of groups of univalent atoms in juxtaposition, and on this view the constitution assigned by Lorentz and by Larmor to atoms should be regarded as applying to univalent atoms only, and the same is true of the relation  $r = 7.063 \times 10^{11} ne$  deduced previously,  $r$  being the radius of a spherical atom,  $n$  its valency which is now taken as 1 and  $e$  its electric charge. This view of the structure of multivalent atoms affords an explanation of the fact that their mobility is independent of their valency, since their velocity in an electric field is conditioned by the *E.M.F.* and the viscosity, which both vary with the number of atoms in juxtaposition. This consideration enables the difficulty previously referred to (*loc. cit.*) in considering the value of the charge  $e$  on an atom of mercury to be surmounted, and this relation now becomes  $e = 5.425 \times 10^{-40} r^3 / R^3$ , where  $2R$  = the length of the side of a cube containing a single atom of mercury. If  $r$  is taken as equal to  $R$ , the value of  $e$  becomes  $2.3 \times 10^{-20}$ , which is near the value  $2.2 \times 10^{-20}$ , found indirectly by J. J. Thomson. But  $r$  is probably smaller than  $R$ , and using Thomson's most recent value for  $e$ , obtained from observations on gaseous ions,  $R/r$  is 1.65, which indicates that the distance from edge to edge of two neighbouring atoms in liquid mercury is less than the diameter of the atom. T. A. H.

[Electromotive Force of Iron.] E. HEYN (*Zeitsch. physikal. Chem.*, 1907, 58, 760—761).—A criticism of Richards and Behr's recent work (this vol., ii, 222). J. C. P.

**Passive Copper or the Anodic Behaviour of Copper in Solutions of Sodium Hydroxide.** ERICH MÜLLER (*Zeitsch. Elektrochem.*, 1907, 13, 133—145).—The behaviour of a copper anode in a concentrated solution of sodium hydroxide (this vol., ii, 174) is further examined. When a clean copper plate is immersed in a solution of sodium hydroxide (14*N*) which is free from dissolved oxygen, the copper is negative compared with the solution; measured against the *N/10* calomel electrode its potential is  $-0.66$  volt. When a very small current,  $2 \times 10^{-6}$  amp. per sq. cm., is passed, the potential rises at first slowly, then rapidly to about  $-0.54$  volt. If electrolysis is continued with a larger current density, a blue solution of cupric hydroxide is formed, and the potential rises again, at first slowly, then rapidly to  $+0.76$  volt, at which point oxygen is evolved and copper ceases to be dissolved. The first rise is accompanied by the formation of a skin of cuprous oxide, the second by the formation of a skin of cupric oxide. During the last period, a little copper peroxide is always formed. In the earliest period, the change  $\text{Cu} + F \rightleftharpoons \text{Cu}'$  takes place; when the solution is saturated with

cuprous ions, which very soon occurs, a skin of cuprous oxide forms, and the potential rises to the point at which the reaction  $\text{Cu}^+ + F \rightleftharpoons \text{Cu}^{++}$  can occur; this goes on until the solution (in contact with the anode) is saturated with cupric hydroxide; owing to the greater solubility of this substance, this stage lasts longer or requires a larger current; when the skin of solid cupric oxide is formed, the potential again rises until the reaction  $\text{Cu}^{++} + F = \text{Cu}^{+++}$  occurs. The peroxide is, however, unstable, and decomposes spontaneously, giving off oxygen.

T. E.

**Electrical Conductivity of Alloys and the Theory of Electrons.** RUDOLF SCHENCK (*Physikal. Zeitsch.*, 1907, 8, 239—244).—The thermal conductivity ( $k$ ) and the electrical conductivity ( $\sigma$ ) of a metal are both lowered by the addition of small quantities of a second metal with which it forms mixed crystals. The quotient  $k/\sigma$  is greater for the alloy than for the pure metal in all cases which have been examined. From this it follows that the thermal conductivity is lowered to a relatively smaller extent than the electrical conductivity. To explain this the author supposes that the dissolved molecules as well as the electrons take part in the process of heat conduction. The lowering of the thermal conductivity is supposed to be due to a diminution in the mean free path of the electrons and the lowering of the electrical conductivity to an increase in the viscosity.

The relationship between  $k$  and  $\sigma$ , obtained by Drude for pure metals, is applied to alloys, and the concentration of the electrons in the alloys is calculated. From the calculated results the conclusion is drawn that the number of the electrons in a metal is not diminished by the solution of a second metal in the first. Drude's equation connecting thermo-electric forces with the concentration of the electrons in different metals is employed to test this conclusion, and the data indicate approximate equality between the electron concentration in copper on the one hand, and constantan and manganin on the other. The lowering of the electrical conductivity of an alloy when compared with the pure metal is therefore to be attributed to increase in the internal friction.

H. M. D.

**Nature of Metallic and Electrolytic Conduction.** RUDOLF VON HASSLINGER (*Monatsh.*, 1907, 28, 173—207).—The work of previous authors on the metallic and non-metallic states, and on electrolytic and metallic conduction, with special reference to the electrolytic conductivity of elements, is discussed, and, together with the experimental results, described in the present paper, utilised in an attempt to explain metallic conduction by an expansion of the ionic theory.

The resistance of carbon, which at first diminishes as the temperature rises, reaches a minimum and again increases at higher temperatures. Fused sulphur is only a feeble conductor, exhibits polarisation phenomena on passage of an electric current, and serves as an ionising solvent for other substances. Iodine behaves as both a metallic and an electrolytic conductor. Silver sulphide is an electrolytic conductor at the ordinary temperature, but at low temperatures behaves as a



metallic conductor, whilst copper sulphide and ferroso-ferric oxide, which are metallic conductors at the ordinary temperature, are found to conduct electrolytically at high temperatures. G. Y.

**Conductivity of Some Fused Salts and the Method of Determining the Same.** RICHARD LORENZ and H. T. KALMUS (*Zeitsch. physikal. Chem.*, 1907, 59, 17—30).—The conductivities of potassium nitrate, sodium nitrate, potassium dichromate, lead chloride, and bromide in the fused condition have been determined over a considerable range of temperature. The measurements were carried out by Kohlrausch's method, with alternating current and telephone, and the corrections rendered necessary by the special circumstances of temperature, &c., were duly made. For particulars of these as well as for details of the results obtained, the original must be consulted.

J. C. P.

**Ionic Velocities: Magnesium Sulphate and Sulphuric Acid in Dilute Aqueous Solution.** MAURICE HUYBRECHTS (*Ann. Chim. Phys.*, 1907, [viii], 11, 68—101).—The transport numbers in solutions of magnesium sulphate and of sulphuric acid at 18° and 30° were determined by the author in Jahn's laboratory according to the method used by the latter chemist. The sulphuric acid was estimated by its action on the potassium iodide-iodate mixture, the iodine set free being titrated with sodium thiosulphate, and it is considered that for this and other reasons the results are more accurate than those of Tower (*Abstr.*, 1904, ii, 802).

The transport number of the magnesium ion in magnesium sulphate increases rapidly with dilution to a value of 0.386 at 18° in 1/90*N* solution, remaining constant on further dilution; at 30°, exactly the same number is obtained.

For sulphuric acid, two values are obtained at 18°, 0.824 (for the hydrogen ion) from 1/8 to 1/90*N*, and 0.845 for 1/105*N* and beyond. It is suggested that dissociation into three ions is only complete when the latter dilution is reached, but this conclusion is not in accord with the results of freezing-point determinations, which seem to show that dissociation is practically complete in solutions less than 1/10*N*. The values at 30° are slightly lower. The results are in fair agreement with those of Tower.

A bibliography of the subject is appended.

G. S.

**Rate of Migration of Ions in Dilute Solutions.** HANS JAHN (*Zeitsch. physikal. Chem.*, 1907, 58, 641—658).—The transport numbers for hydrochloric and sulphuric acids and a number of salts have been determined, and the variation with concentration and temperature has been studied. The value obtained for the transport number of hydrogen in hydrochloric acid agrees closely with that recorded by Noyes and Sammet (*Abstr.*, 1903, ii, 126). In the case of sulphuric acid the transport number for hydrogen is constant and equal to 0.824 over a considerable range of concentration (from  $V=16$  to  $V=180$ ), but in more dilute solutions distinctly larger values are obtained, a phenomenon that may have something to do with the second stage of

ionisation. The results obtained with various salts are generally in harmony with previous determinations, and indicate that with rise of temperature the value of the transport number approaches 0.5.

Measurements with the transport number were made also with hydrochloric acid, sodium, potassium, and barium chlorides in mixtures of alcohol and water. The transport number of hydrogen in hydrochloric acid increases with the concentration of the alcohol in the mixtures, and the limiting steady value of the transport number is not reached until greater dilutions than when pure water is the solvent. In the case of potassium and sodium chlorides also the presence of alcohol leads to an increased value of the transport number for the cation. In the case of barium chloride, on the other hand, it appears that as the percentage of alcohol in the mixtures increases, the transport number for the anion first increases, then reaches a maximum value, and subsequently decreases.

J. C. P.

**Electro-chemistry of Non-aqueous Solutions.** GIACOMO CARRARA (*Mem. R. Accad. Lincei*, 1906, [v], 6, 268—291).—The author gives a résumé and discussion of the work published, during the past fourteen years, on the electro-chemistry of solutions in solvents other than water.

In dealing with the causes determining electrolytic dissociation, he shows how various hypotheses which have been advanced can be brought into accord. The phenomenon of electrolytic dissociation is due to the chemical action occurring between the solvent and the solute, since the former, by combining with the parts of the molecule which become ions, causes a predisposition to ion-formation and also furnishes the energy necessary for the dissociation; the dielectric constant then allows the ions, when they are once formed, to exist together in the solvent without recombining.

The electro-chemical laws of non-aqueous solutions and the chemical behaviour of solutes in different solvents are next examined. It is here shown that no essential differences exist between aqueous solutions and those in other solvents and that, when all the factors bearing on the phenomenon are considered, the theory of dissociation is capable of explaining all apparently contradictory exceptions.

T. H. P.

**Solubility of Electrolytes.** JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1907, 59, 212—217. Compare this vol., ii, 328).—By way of extension of the earlier paper (*loc. cit.*), the author deduces a general expression for the solubility of any electrolyte in any solvent. He finds  $c = C\lambda(1 + \lambda)$ , where  $c$  is the concentration of the electrolyte in its saturated solution,  $C$  is its dissociation constant, and  $\lambda$  is a constant almost independent of the solvent. The quantities  $c$  and  $C$  have been determined by Walden for tetraethylammonium iodide in a number of organic solvents, and the author shows that in this case  $\lambda$ , the specific salt constant, is nearly independent of the solvent. It may be found also by the formula  $\lambda = (1 - a)/a$ .

J. C. P.

**Thermomagnetic Analysis of Meteoric and Artificial Nickel-Iron Alloys.** S. W. J. SMITH (*Proc. Roy. Soc.*, 1907, A, 79, 132—133).—The author has studied in detail the changes in permeability which

accompany changes of temperature between  $0^{\circ}$  and  $850^{\circ}$  (1) for a typical specimen of "octahedral" meteoric iron, (2) for a sample of nickel steel containing about the same percentage of iron as the meteorite, (3) for a sample of nearly pure iron. Evidence has been obtained of the connexion between permeability and change in the state of crystallisation, and an attempt is made to interpret the permeability-temperature curves in terms of the theory of solid solutions. The analogy between the behaviour of supersaturated solutions and of nickel-iron alloys, especially with reference to the relation of the "metastable" and "labile" states, is discussed.

The thermomagnetic data show that meteoric iron is composed mainly of a nickel-iron alloy containing 6—7% of nickel, and that it contains, in addition, a small quantity of a complex alloy which, whilst its total percentage of nickel is from 25—30, has a nickel-rich constituent with about 40% of nickel. These conclusions are in harmony with the chemical data.

J. C. P.

#### Electric Furnace Reactions under High Gaseous Pressures.

ROBERT S. HUTTON and J. E. PETAVEL (*Proc. Roy. Soc.*, 1907, *A*, 79, 155—157).—The principal processes studied were the formation of calcium carbide, carborundum, and nitric acid, the direct reduction of alumina by carbon, and the fusion of quartz. In the experiments on calcium carbide, it was found that a high pressure of carbon monoxide during the reaction does not appreciably diminish the yield. If the carbide is cooled in an atmosphere of carbon monoxide, a back reaction occurs at about the freezing point of the substance, but the effect is limited to the surface of the ingot and is therefore of slight importance when work is carried out on a large scale. Experiments on the fusion of quartz in atmospheres of air and hydrogen at pressures up to 2500 lb. per square inch indicated a marked decrease in the volatilisation of the fused product, but no appreciable increase in its fluidity and transparency. The diminished vaporisation of silica just referred to probably explains the very limited formation of carborundum which occurs under pressure, since it is generally supposed that this product results from the interaction of silica vapour and carbon. In a study of the direct reduction of alumina by carbon it has been shown (1) that metallic aluminium can be produced by a purely thermal reaction; (2) that the lowest temperature at which this reaction can take place coincides with the melting point of alumina; (3) that the metal is first produced in the form of vapour. In ordinary circumstances, however, the metal vapour immediately interacts with the carbon monoxide, and to collect the pure metal it is therefore necessary (1) to dilute and remove the carbon monoxide, (2) to limit the vaporisation of the metal by working under high gaseous pressures. In this way it has been possible to prepare and collect 40—50 grams of aluminium.

In each of two series of experiments made on the formation of oxides of nitrogen, it is shown that there is an increase of efficiency attributable to pressure.

J. C. P.

**Specific Heat of Some Elements, Alloys, and Compounds between  $-185^{\circ}$  and  $+20^{\circ}$ .** PAUL NORDMEYER and AUGUST L. BERNOULLI (*Ber. deut. physikal. Ges.*, 1907, *5*, 175—183).—The method

employed in determining the specific heat was that already described by Forch and Nordmeyer (Abstr., 1906, ii, 521). The following are the values of the specific heat obtained for the chief substances investigated: sodium, 0.234; magnesium, 0.223; silicon, 0.123; calcium, 0.157; titanium, 0.082; chromium, 0.086; iron, 0.095; nickel, 0.092; molybdenum, 0.063; barium, 0.068; tantalum, 0.033; tungsten, 0.036; gold, 0.035; mercury, 0.032; thallium, 0.038; ice, ( $-185-0^{\circ}$ ), 0.345; benzene, 0.176.

J. C. P.

**Latent Heat of Fusion of Ice.** LEO F. GUTTMANN (*J. Physical Chem.*, 1907, 11, 279—282).—A consideration of the possible sources of error in Bunsen's and Regnault's determination of the latent heat of fusion of ice leads the author to the conclusion that Regnault's figure is nearer the true value. Various observers have found a difference between the density of old and new ice, and this gives rise to considerable uncertainty in Bunsen's value. Recalculating this, by using the more recently determined values of the specific heat of ice and water, 79.59 is obtained. A. W. Smith's electrical measurements (*Physical Review*, 1903, 17, 193), when recalculated, give 79.67, and this the author considers to be the most accurate value yet obtained.

H. M. D.

**Depression of the Freezing Point in Dilute Solutions of Highly Dissociated Electrolytes. II.** HANS JAHN (*Zeitsch. physikal. Chem.*, 1907, 59, 31—40. Compare Abstr., 1905, ii, 145).—The investigation has been extended on the lines already described (*loc. cit.*) to solutions of potassium iodate, bromate and chlorate, sodium iodate, bromate and chlorate, as well as to solutions of sodium, potassium and lithium chlorides, more dilute than those examined previously. The results are expressible by empirical formulæ similar to those recorded in the earlier paper. It is noteworthy that in the most dilute solutions examined the mass action law appears to be valid.

J. C. P.

**Form of the Freezing Point Curves in Binary Systems.** RUDOLF RUER (*Zeitsch. physikal. Chem.*, 1907, 59, 1—16).—A theoretical paper. It is shown that in a binary system, forming a liquid and a solid phase, the two phases have the same composition at all concentrations (and only at those concentrations) at which the tangent to the freezing point curve is parallel to the concentration axis. Roozeboom has pointed out (Abstr., 1900, ii, 132) that where the two components form an uninterrupted series of mixed crystals the freezing point curve may belong to one of three types. The author suggests the possible existence of a fourth type in which the freezing point curve has a point of inflexion, and thinks that the freezing point curves for the systems Br + I (Meerum Terwogt, Abstr., 1906, ii, 15) and Mg + Cd (Grube, *ibid.*, ii, 355) furnish experimental support for his view.

J. C. P.

**Supercooled Liquids.** STEWART W. YOUNG and W. E. BURKE (*J. Amer. Chem. Soc.*, 1907, 29, 329—339. Compare Abstr., 1906, ii, 281).—With the object of confirming the results hitherto published,

which were based on observations on the various hydrates of sodium thiosulphate, the behaviour of fused *p*-nitrotoluene on cooling has been thoroughly investigated. The method employed was to heat in a thermostat a large number of small sealed tubes, 6 mm. internal diameter, containing the *p*-nitrotoluene, for definite periods of time to temperatures respectively  $10^{\circ}$  and  $30^{\circ}$  above the m. p. of *p*-nitrotoluene ( $51.2^{\circ}$ ); the temperature of the bath was then lowered to, and maintained for ten minutes at, temperatures respectively  $5^{\circ}$ ,  $10^{\circ}$ ,  $15^{\circ}$ , &c., below the m. p., and the number of tubes which had solidified at each temperature noted. The following are the most important influences which determine the degree of supercooling to which a fused substance may be subjected. The longer the time of heating and the higher the temperature to which the tube is heated, the greater the difficulty of bringing about solidification; the tube undergoes a sort of sterilisation. To a certain extent, the effect produced by heating is permanent; thus tubes which have been heated for a long time at rather high temperatures do not return to their original condition, for when subjected subsequently to the same treatment the fused substance remains liquid much longer in such tubes than in those which have not been so treated; to a great extent, however, this property is nullified by a subsequent solidification. The reaction which produces this sterilisation is not reversible in the liquid state, since the maintaining of the substance in the liquid state at temperatures just above the m. p. after previous treatment at higher temperatures results only in increased sterilisation. The effect of allowing the substance to remain a long time in the solid state is to produce a greater sterilisation on subsequent heating than would occur if the time in the solid state had been short. It is possible by means of the nuclear hypothesis to explain the influence of the time and temperature of heating, but not the influence of the time in the solid state.

W. H. G.

**Curved Capillary Layer and the Theory of Boiling.** GERRIT BAKKER (*Zeitsch. physikal. Chem.*, 1907, 59, 218—243).—The author applies his theories (Abstr., 1905, ii, 304; 1906, ii, 655) to the surface layer of the bubbles which form in a boiling liquid. The boiling of a liquid depends on differences of temperature at various points in the heated liquid. If it were possible to heat a liquid so that at any given moment the temperature were the same at all points, the liquid would never boil. It would ultimately reach a certain temperature at which the whole of the liquid would be vaporised with explosive violence.

J. C. P.

**Vaporisation.** RUD. TANDLER (*Zeitsch. physikal. Chem.*, 1907, 58, 753—759).—From the Clapeyron-Clausius equation the author deduces the relationship  $\log_e p/p_0 = C \log_e T/T_0$ , where  $C = \lambda_0/RT_0$  (Trouton's rule); in these formulæ,  $p$  is the vapour pressure of a liquid at the temperature  $T$ ,  $p_0$  and  $\lambda_0$  are the vapour pressure and latent heat of vaporisation at some standard temperature  $T_0$ . If the boiling temperature under 760 mm. mercury pressure is taken as the standard temperature  $T_0$ , and if  $p/p_0 = \pi$ , and  $T/T_0 = \tau$ , then the foregoing formula

may be written  $\pi = \tau^c$ , and it is found with the help of data already available that for a great many substances  $C = 10.6$ . The constancy of the values obtained for  $C = (\log_e p - \log_e p_0) / (\log_e T - \log_e T_0)$  is held to characterise vaporisation as a colligative process. The cases where  $C$  exhibits deviations from 10.6 are those where association and dissociation phenomena are involved, and an attempt is made to indicate in a general theoretical manner the influence of these factors.

Using the relationship  $\lambda_0 / RT_0 = C = 10.6$ , the author shows that the boiling point elevation constant ( $E$ ) may be expressed as follows:  $E = T_0 M / 100C$ , or  $E = T_0 M / 1060$ , where  $T_0$  is the boiling point of the solvent and  $M$  its molecular weight.

J. C. P.

**Determination of the Partial Vapour Pressures of Binary Mixtures from Measurements of the Total Pressures and of One Partial Pressure from Measurements of the Other.** EMIL BOSE (*Physikal. Zeitsch.*, 1907, 8, 353—358).—A graphical method of obtaining the partial pressures from the total vapour pressure of a binary liquid mixture is described. The method consists in the primary assumption of partial pressure curves expressing the variation of the pressure with the composition of the liquid; these are then compared with the requirements of the Duhem-Margules equation connecting the partial pressures of the mixture with its composition, and the assumed curves are corrected so as to make the new curves agree more closely with the equation. This correction and approximation process is carried out a second, and, if necessary, a third time. The partial pressure values obtained in this way agree much more closely with the experimental data obtained by Zawidzki (compare Abstr., 1901, ii, 6) than do the values calculated by Zawidzki's formula. Tabulated numbers for carbon disulphide—acetone and acetic acid—pyridine mixtures show this clearly.

By a slight modification of the above graphical method, the partial pressure of one component may be deduced when that of the other is known. The partial pressure of water for twenty ammonia—water mixtures at  $0^\circ$  has been ascertained, and the values are tabulated.

H. M. D.

**Vapour Pressure of Aqueous Nitrate Solutions.** AZABIAH T. LINCOLN and DAVID KLEIN (*J. Physical Chem.*, 1907, 11, 318—348).—The vapour pressure of water and of concentrated aqueous solutions of lithium, sodium and potassium nitrates has been measured at  $25^\circ$  by the air-bubbling method. The air was passed through water at a temperature higher than  $25^\circ$ , then through a lead coil 5 feet long, a Woulff bottle containing the solution under examination, and finally through the saturator consisting of a horizontal tube 20.5 inches long and 1.5 inches in diameter, with two arms, 5.5 inches long, at right angles to the length of the tube. The saturator was shaken laterally at the rate of 200 strokes per minute. The coil, Woulff bottle, and saturator were all immersed in a thermostat maintained constant to within  $0.02^\circ$ .

Preliminary experiments with water showed that the apparatus yielded consistent results, the measured vapour pressure being inde-

pendent of the rate of passage of the air, and the same value was obtained whether the air was previously supersaturated with water vapour or not.

From the vapour pressures of the nitrate solutions the molecular weight of the dissolved electrolyte is calculated by means of the van't Hoff-Raoult formula. The calculated molecular weight of potassium nitrate increases with the concentration; that of sodium nitrate is practically constant, whilst that of lithium nitrate decreases. The observed behaviour of sodium nitrate, and more especially lithium nitrate, is said to be at variance with the theory of electrolytic dissociation; in fact, the calculated molecular weight of lithium nitrate in the strongest solution (57 grams of salt per 100 grams of water) is only one-fourth of that corresponding with the formula. H. M. D.

**Compressibility and Vapour Tension of Mixtures of Methyl Ether and Sulphur Dioxide: Formation of a Compound of these Two Substances.** E. BRINER and E. CARDOSO (*Compt. rend.*, 1907, 144, 911—913. Compare Abstr., 1906, ii, 424, 529, 657; this vol., ii, 11).—The authors have obtained the following values for the vapour tension of liquefied methyl ether and sulphur dioxide, both separate and when mixed:

*Vapour Tension in Atmospheres.*

Temperature.	Pure gases.		Mixtures.		
	$\text{OMe}_2$ .	$\text{SO}_2$ .	$\frac{1}{2}\text{OMe}_2 \frac{1}{2}\text{SO}_2$ .	$\frac{2}{3}\text{OMe}_2 \frac{1}{3}\text{SO}_2$ .	$\frac{3}{4}\text{OMe}_2 \frac{1}{4}\text{SO}_2$ .
56.1°	12.5	9.5	6.7—7.7	7.65—9.7	6.6—6.8
77.1	20.3	16.1	12.8	14.0—16.9	12.1—12.5
108.7	36.8	32.3	27.4—28.4	32.6—35.1	26.7—27

The figures for the mixtures refer to the beginning and end of liquefaction. The low pressure, and small variation of pressure observed for the mixture of equal parts of methyl ether and sulphur dioxide, indicate the formation of a compound,  $\text{OMe}_2\text{SO}_2$ , analogous to Friedel's  $\text{OMe}_2\text{HCl}$ . When the temperature is raised, the phenomena characteristic of the critical point are observed at 153°. The critical constants of the compound  $\text{OMe}_2\text{SO}_2$  are  $t_c = 152.5^\circ$ ,  $p_c = 62$  atmospheres, thus lying between the constants of methyl ether and those of sulphur dioxide. Comparison of the curves  $pv = f(p)$  for the constituent gases and their mixtures shows that at 56° and 77° the values of  $pv$  for mixtures are less than those for the gases singly, and that the lowest relative value of  $pv$  corresponds with the mixture of equal volumes of the gases, thus indicating that the compound is already formed in the gaseous phase.

At the end of the experiments it was found that the tube used for containing the mixtures had become slightly tarnished, probably owing to a secondary reaction analogous to that observed with the compound  $\text{OMe}_2\text{HCl}$ . E. H.

**Fenchone as an Ebullioscopic Solvent.** ENRICO RIMINI and F. OLIVARI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 665—670).—Measurements with anthracene, carbazole, anthraquinone, and benzil

give the mean value, 59.4, for the molecular rise in boiling point of fenchone, a number which is near those for menthone (62.5) and camphor (58.5). The Trouton-Schiff formula gives the value 67.9.

The following are the molecular formulæ of various inorganic compounds dissolved in fenchone:  $S_8$ ;  $As_4O_6$ ;  $AsI_3$ ;  $SbI_3$ ;  $BiI_3$ ;  $HgCl_2$ ;  $HgBr_2$ , and  $HgI_2$ .

Fenchone is especially suitable as a solvent in accurate ebullioscopic measurements, owing to its stability and to its high constant.

T. H. P.

**Thermal Changes in the Dissolution of Unsaturated Substances and their Bromine Additive Compounds in Carbon Tetrachloride.** WLADIMIR LUGININ and IWAN A. KABLUKOFF (*J. Chim. Phys.*, 1907, 5, 186—202. Compare this vol., ii, 72).—The measured heats of solution of various unsaturated compounds and the corresponding bromine additive compounds in carbon tetrachloride have been used to calculate the thermal equivalent of the reaction between free bromine and the undissolved unsaturated compound. The following numbers corresponding with the addition of one molecule of bromine are recorded:  $\beta$ -methyl- $\Delta^2$ -butylene, 27226; allyl alcohol, 28456; allyl acetate, 27598; allyl bromide, 27296; allyl chloride, 27264; *l*-pinene, 35779 (?); *d*-pinene, 35759 (?); carvene, 27812 (?); limonene, 28751 (?); cinnamyl alcohol, 24040; oleic acid, 28719; elaidic acid, 21968; erucic acid, 39577 calories.

H. M. D.

**Organic Solvent and Ionising Media. VII. Heats of Solution and Dissociation.** PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1907, 59, 192—211. Compare this vol., ii, 231).—Solubility and conductivity determinations for potassium iodide have been carried out at 0° and 25° in ethyl alcohol, acetonitrile, and acetone as solvents. The heat of solution in each case has been calculated by van't Hoff's or van Laar's equation (see *loc. cit.*), and there is good agreement, both in sign and magnitude, between the calculated value and the value determined experimentally.

The heat of dissociation of potassium iodide and of tetraethylammonium iodide in a number of organic solvents has been calculated by Arrhenius' equation. For each electrolyte, values of the heat of dissociation are found which vary only very slightly with the nature of the solvent. The conclusion is drawn that the heat of dissociation of a given binary electrolyte is independent of the nature of the solvent, provided the electrolyte exists in each solvent in the same molecular condition and dissociates into the same ions. The dissociation of a gram-molecule of potassium iodide into its ions is accompanied by the liberation of about 1000 cal. The dissociation of tetraethylammonium iodide into its ions is accompanied by the absorption of about 60 cal.

J. C. P.

**Application of the Method of Limiting Densities to Permanent Gases. Constant of Perfect Gases.** PHILIPPE A. GUYE (*Compt. rend.*, 1907, 144, 976—978. Compare D. Berthelot, this vol., ii, 154, 155).—The molecular weight of a



permanent gas is given by the relation  $M = RL/n$ , where  $L$  is the weight of a litre of a gas (at  $0^\circ$ , under 1 atmosphere pressure and where  $\text{lat.} = 45^\circ$  and  $h = 0$ ) and  $n$  is the number of gram-molecules of a perfect gas contained in  $R$  litres. The constant  $R$  is the volume of a gram-molecule of a perfect gas at  $0^\circ$  and under 1 atmosphere pressure, and is generally taken as 22.412 litres. The author gives a résumé of our present knowledge regarding the factors  $L$  and  $n$  in this relation. The following are adopted as the best values of  $L$  available :

O <sub>2</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	CO.	NO.	CO <sub>2</sub> .	N <sub>2</sub> O.	HCl.
1.4290	0.08987	1.2507	1.2504	1.3402	1.9768	1.9777	1.6398
			NH <sub>3</sub> .	SO <sub>2</sub> .			
			0.7708	2.9266			

According to the principle of limiting densities,  $n$  should be given by the relation  $n = 1/(1 - A_0^1)$ , where  $A_0^1$  represents the variation of the gas from Boyle's law between 0 and 1 atmosphere, and if this principle is accurate, the value for  $R$  given by the relation  $R = M/L(1 - A_0^1)$  ought to be constant. Instead, its value increases with the critical temperature of the gas, and varies  $1/2800$  between the gases hydrogen and nitric oxide. The variation is regular, and has the value  $+1/22,400$  (approx.) for the relation  $R^1 = 22,410(1 + 10^{-8}T_c^2)$ . The conclusion is drawn that the corrected value of  $A_0^1$  should be  $(A_0^1 - 10^{-8}T_c^2)$ , and the value 22,410 previously suggested by Guye and Friderich should be accepted for  $R$ .  
T. A. H.

**Determination of the Viscosity of some Fused Salts.** RICHARD LORENZ and H. T. KALMUS (*Zeitsch. physikal. Chem.*, 1907, 59, 244—251).—The viscosities of sodium and potassium nitrates, potassium dichromate, lead chloride and bromide have been determined at various temperatures from their melting points upwards. The product of viscosity and conductivity (see this vol., ii, 430) generally diminishes as the temperature rises, a result analogous to what has been observed with aqueous solutions. This decrease per  $100^\circ$  rise in temperature amounts to about 4.5% for potassium and sodium nitrates, 24% for lead chloride, and 22% for lead bromide.  
J. C. P.

**Possible Explanation of the Increase in Viscosity which Results when the Alcohols are Mixed with Water, and of the Negative Viscosity Coefficient of Certain Salts when Dissolved in Water.** HARRY C. JONES and W. R. VEAZEY (*Amer. Chem. J.*, 1907, 37, 405—410).—The fact that the viscosity of mixtures of water and methyl or ethyl alcohol is greater than that of either of the pure liquids is regarded as due to a diminution in the degree of association of each solvent (compare Jones and Murray, *Abstr.*, 1903, ii, 637), resulting in an increase in the number of the molecules, a diminution of their size, and a consequent increase in the total frictional surfaces which come into contact with one another. This comparatively small association of the molecules of the mixed solvents explains the fact which has been repeatedly observed (Jones

and McMaster, Abstr., 1906, ii, 737; see also Abstr., 1903, ii, 55; 1905, ii, 73; 1906, ii, 66) that in mixtures in which the viscosity is a maximum the conductivity of many dissolved electrolytes shows a minimum value.

It has been found that solutions of potassium thiocyanate in water are less viscous than pure water. Wagner (Abstr., 1890, 441) has shown that potassium chloride and nitrate, rubidium chloride, and caesium chloride also show the same phenomenon. This negative viscosity coefficient is explained as being due to the fact that potassium, rubidium, and caesium have much larger atomic volumes than any other elements. The ions of the salt thus being very large as compared with the molecules of the solvent cause a diminution in the amount of the frictional surfaces, and, consequently, a decrease of friction. In support of this, it is shown from Wagner's work (*loc. cit.*) that the viscosity coefficient is less for rubidium chloride than for potassium chloride, and less for caesium chloride than for rubidium chloride. It is pointed out that the negative viscosity coefficient is not shown by all potassium salts for the following reason. The influence of a salt on the viscosity of a solvent does not depend on the cation only, but on the algebraic sum of the effects of both ions, which may be either positive or negative. Examples are given to illustrate this fact. E. G.

**Osmotic Pressure and Depression of the Freezing Points of Solutions of Dextrose.** II. HARMON N. MORSE, JOSEPH C. W. FRAZER, and B. F. LOVELACE (*Amer. Chem. J.*, 1907, 37, 324—360).—An account has been given previously (Abstr., 1901, ii, 543; 1902, ii, 553; 1903, ii, 272; 1904, ii, 651; 1905, ii, 575; 1906, ii, 600) of the construction of an osmotic cell and the various precautions required in its use.

It has been found that during the course of an experiment the solution in the cell becomes slightly diluted owing to various causes (see next abstract).

A series of determinations have been made of the osmotic pressure of dextrose at concentrations from  $N/10$  to  $N$ , and at temperatures between  $18^{\circ}$  and  $26^{\circ}$ . The various measurements are tabulated and summarised and the results are compared with those obtained previously with sucrose (Abstr., 1906, ii, 601). It is found, as in the case of sucrose, that dextrose in aqueous solutions at temperatures in the neighbourhood of  $20^{\circ}$  exerts an osmotic pressure equal to that which a molecular-equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to that of the solvent in the pure state. At temperatures near  $0^{\circ}$ , however, both sucrose and dextrose exert pressures somewhat in excess of the calculated gas pressure. From the results, it must be concluded that between  $18^{\circ}$  and  $26^{\circ}$  both sucrose and dextrose exist in solution in the anhydrous condition unless it is assumed that the absolute amount of water abstracted from the solution is the same for all solutions, that is, wholly independent of the concentration.

Determinations of the depression of the freezing points of dextrose

solutions have shown that the depression is proportional to the weight of dextrose dissolved in the fixed quantity of water, this relation again indicating that dextrose does not, even at the freezing point of the solution, combine with any of the solvent. E. G.

**Osmotic Pressure of Cane Sugar Solutions in the Vicinity of the Freezing Point of Water.** HARMON N. MORSE, JOSEPH C. W. FRAZER, and W. W. HOLLAND (*Amer. Chem. J.*, 1907, 37, 425—467. Compare preceding abstract).—The authors describe a large number of experiments on the osmotic pressure of aqueous solutions of sucrose at temperatures near 0°. Every solution underwent some loss of rotation whilst in the cell, and this is ascribed to inversion of the sucrose; it is pointed out, however, that not all the diminution in optical activity is due to this cause, a portion of the loss being due to a dilution of the solution in the cell, which occurs when the cell is being closed at the beginning and opened at the end of an experiment. The dilution which occurred in the cells was not due to leakage of the solutions through the membranes; it is mainly due (1) to the slipping of the manometer in the stopper or the crowding upwards of both manometer and stopper when the former could not slip in the latter, and (2) to the sucking in of water from the wall while the cell was being closed for a measurement and again while it was being taken apart after an experiment. The first of these difficulties has been overcome by improvements in method and manipulation, but now the dilution due to the second cause is probably a little greater than formerly.

The various experimental errors involved in the measurements in question are discussed in detail in a manner unsuitable for abstraction.

The authors submit the important fact that the osmotic pressure of sucrose solutions in the vicinity of the freezing point of water considerably exceeds the calculated gas pressures for the same temperatures. The fact of an excess of osmotic over gas pressure at low temperatures appears, they consider, to be established, whatever may be the view accepted as to the proper method of correcting the observed pressure for loss in rotation. A. McK.

**Application of van der Waals' Equation to Solutions.** EARL OF BERKELEY (*Proc. Roy. Soc.*, 1907, A, 79, 125—131).—In an inquiry how far the results of the direct measurements of osmotic pressure recently made by the author and Hartley (this vol., ii, 234) can be represented by an equation on van der Waals' lines, the following formulæ are found to fit the experimental data fairly well: (1)  $(A/v - p + a/v^2)(v - b) = RT$ ; (2)  $(A/v + p - a/v^2)(v - b) = RT$ . In (1)  $v$  is the volume of solvent which contains 1 gram-molecular weight of solute, in equation (2)  $v$  is the volume of solution which contains the gram-molecular weight. Pending further experimental work, these equations must be regarded as holding good over a limited range. On theoretical grounds equation (2) is to be preferred for moderate concentrations. J. C. P.

**Molecular Condition of Salts Dissolved in a Fused Salt.** HARRY W. FOOTE and L. H. LEVY (*Amer. Chem. J.*, 1907, 37, 494—506).—The heat of fusion of sodium chlorate has been determined, and the

constant for sodium chlorate calculated in the molecular weight formula,  $M = ks/\Delta L$ , by means of the van't Hoff formula  $k = 2T^2/\lambda$ , in which  $T$  = the absolute melting point and  $\lambda$  the heat of fusion in calories of 1 gram of sodium chlorate. The heat of fusion was calculated from determinations of the amount of heat evolved by sodium chlorate in a water calorimeter when the salt had been heated at two temperatures above the melting point and at two temperatures below, the formula used being  $\lambda = Q - c_1(t_a - t_s) - c_2(t_s - t_b) - H$ , where  $\lambda$  = heat of fusion of 1 gram of sodium chlorate,  $t_a$  and  $t_b$  = respectively temperatures slightly above and below the melting points of sodium chlorate,  $t_s$  = melting point of sodium chlorate,  $255^\circ$ ,  $c_1$ ,  $c_2$  = respectively the specific heats of liquid and solid sodium chlorate near the melting point,  $Q$  = heat evolved by 1 gram of sodium chlorate cooled from temperature  $t_a$  to  $22^\circ$ , and  $H$  = heat evolved by 1 gram of sodium chlorate cooled from temperature  $t_b$  to  $22^\circ$ .

The lowering in the freezing point of sodium chlorate produced by small amounts of other salts has been determined with considerable accuracy.

The molecular weights of a number of chlorates and sodium salts have been calculated from the data obtained and found to be nearly normal.

The results indicate that there is little or no polymerisation, but they do not prove that dissociation is absent, as nearly normal molecular weights would be obtained if the solute were very largely dissociated and the solvent somewhat less so. A. McK.

**The Anisotropic Liquid Phases of Dihydrocholesteryl Butyrate and the Question as to the Necessary Presence of an Ethylene Double Linking for the Occurrence of these Phenomena.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 701—704).—Dihydrocholesteryl *n*-butyrate, which consists of thin colourless and transparent laminæ, is converted at  $82.1^\circ$  into a doubly refracting liquid, which at  $86.4^\circ$  passes into an isotropic liquid, these transition phenomena being unaccompanied by any colour changes. On cooling the isotropic liquid, it reverts to the anisotropic condition at  $86.4^\circ$  and then at  $84^\circ$  passes into a much more strongly doubly refracting liquid form, which on continued cooling crystallises at about  $80^\circ$  in flat needles with the production of vivid interference colours, commencing with a brilliant violet, which gradually changes into blue, and finally into a radiating green. The solid phase appears to be dimorphous and monotropic, for the needle aggregates rapidly assume a spherulite structure, and the flat needles are not re-obtained on warming.

Since the dihydrocholesteryl ester contains no double linking, the colour changes which accompany the melting of the cholesteryl esters cannot be attributed to the presence of such a double linking, nor can the existence of three liquid phases be explained by stereo-isomerism.

H. M. D.

**Formation of Crystalline Liquids by Mixing Substances.** DANIEL VORLÄNDER and A. GAHREN (*Ber.*, 1907, 40, 1966—1969).—Neither anisic acid (m. p.  $184^\circ$ ) nor  $\alpha$ -anisylidenepropionic acid (m. p.

154°) forms liquid crystals when melted alone, but when mixed and then melted, liquid crystals are obtained. The following crystalline liquid mixtures were also studied: anisic acid with  $\alpha$ -anisylidenebutyric acid, *p*-acetoxybenzoic acid, *p*-benzoyloxybenzoic acid, *p*-carbethoxybenzoic acid, piperonylacrylic acid, *p*-methoxyphenylpropionic acid, piperic acid, and sorbic acid respectively, and  $\alpha$ -anisylidenepropionic acid with *p*-ethoxybenzoic acid, 6-methoxy-*m*-toluic acid, ethyl hydrogen terephthalate, cinnamic acid,  $\alpha$ - $\beta$ -hydropiperic acid, piperonylacrylic acid, *p*-methoxyphenylpropionic acid, and piperic acid respectively. A. McK.

**Influence of Molecular Structure in Conditioning the Formation of Liquid Crystals.** DANIEL VORLÄNDER (*Ber.*, 1907, 40, 1970—1972).—An attempt is made to show a relationship between the structure of the molecule and the formation of liquid crystals. To quote one example, liquid crystals are not formed from meta and ortho benzenoid derivatives, but only from para ones. If a third substituent is introduced into the molecule of a para-substituted benzenoid compound, the tendency of the resulting compound to form liquid crystals is diminished. A. McK.

**Physical Properties of Emulsions and their Relationship with Crystalline Liquids.** EMIL BOSE (*Physikal. Zeitsch.*, 1907, 8, 347—353).—The abrupt change in the viscosity which has been found to occur at the temperature of transformation of anisotropic liquids into the isotropic forms has been cited as an important argument against the emulsion theory of crystalline liquids. The author shows that such abrupt changes may also be expected at the critical solution temperature of a pair of liquids which have widely different viscosity values and for which the limiting solubility curves are widely separated at temperatures immediately below the critical solution temperature. The sudden alteration in the viscosity on transition from the anisotropic crystalline liquid condition to the isotropic form is probably due to the same causes, and the observed volume and thermal changes which accompany such transformations can also be explained quite readily in terms of the emulsion theory. H. M. D

**Settling of Clay Emulsions.** HUGO HERMANN (*Zeitsch. anorg. Chem.*, 1907, 53, 413—418).—When clay is shaken up with a strong solution of an electrolyte and the mixture is then kept, the clay separates first at the surface from the water, giving rise to a plane surface of separation which slowly descends. This separation into layers is only complete with 5—8% of clay and does not take place if the electrolyte concentration is too small.

Measurement of the rate at which the separating surface descends shows that there is an initial retardation after which the movement is regular; the rate is somewhat diminished by increase of temperature. There is some evidence to show that there is considerable pressure in the interior of the settling emulsion. No satisfactory explanation of the phenomenon has been found. G. S.

**Suspensions in Dilute Alkaline Solutions.** WILLIS R. WHITNEY and ALONZO STRAW (*J. Amer. Chem. Soc.*, 1907, **29**, 325—329).—The object of this investigation was to study the effect of alkali on the stability of suspensions of various kinds, as it is known that the presence of a trace of alkali increases the stability of colloids.

Equal volumes of an emulsion of turpentine and water, for example, were placed in test tubes of equal size and varying quantities of sodium hydroxide added to all except one. The tubes were then corked and violently shaken at the same time; after remaining until the emulsion had partially clarified, the tubes were photographed and the quantity of alkali in each then determined volumetrically. It is found that up to a certain point an increase in the quantity of alkali is accompanied by an increase in the stability of the emulsion, but above this point the stability decreases. For example, an emulsion of turpentine and water is most stable when the concentration of the alkali in the water is about 0.008*N* sodium hydroxide; the point of maximum stability of a carvene-water emulsion corresponds with about 0.0002*N* sodium hydroxide. Other emulsions, also suspensions of China clay and lamp-black in water, are similarly affected by alkali.

In all probability, the effect produced by the alkali is due to an increase in the surface-tension of the solution.

The paper is illustrated by photographs of the tubes. W. H. G.

**Relation Between the Coefficients of Affinity and the Hydrolysis of the Salts of *iso*Nitroso-ketones.** HARALD LUNDÉN (*J. Chim. Phys.*, 1907, **5**, 145—185. Compare Abstr., 1906, ii, 265 and 828).—The affinity coefficients of aniline, ammonia, acetic acid, and *isonitrosomethylpyrazolone* have been measured between 15° and 40°, and that of *isonitrosoacetone* at 25°.

On account of the small conductivity of the free acid and the small degree of hydrolysis of the alkali salts, the affinity coefficient of an acid for which the value lies between  $10^{-7}$  and  $10^{-10}$ , cannot be determined accurately from such measurements. The measurement of the hydrolysis of the ammonium or aniline salt is found, however, to be quite satisfactory. In the case of a base, the affinity coefficient of which is of this order of magnitude, the measurement of the hydrolysis of the acetate gives satisfactory results.

A knowledge of the degree of electrolytic dissociation of salts containing a weak acid and a weak base is required in the application of this method, and the author has determined and tabulated the conductivities and degrees of dissociation of ammonium acetate and benzoate. At the same concentration, the dissociation of these is smaller than that of potassium chloride and acetate.

*iso*Nitrosomethylpyrazolone is an amphoteric electrolyte; its acid affinity coefficient as measured by its conductivity and the hydrolysis of the aniline salt is 0.90, 1.18, and  $1.70 \times 10^{-6}$  at 15°, 25°, and 40° respectively. The basic coefficient is less than  $10^{-14}$ .

The acid affinity coefficient of *isonitrosoacetone* is  $3 \times 10^9$  at 25°, the basic coefficient less than  $10^{-14}$ .

From the degree of hydrolysis of the salts and the affinity coefficients at different temperatures, the heats of neutralisation of aniline,

ammonia, and acetic acid are calculated and found to be in agreement with thermochemical measurements. The calculated heat of neutralisation of isonitrosomethylpyrazolone is +8900 cals., the heat of dissociation -4600 cals. (28°).

Phthalimide has no measurable basic properties; its acid affinity coefficient is 2.6 and  $4.2 \times 10^{-8}$  at 15° and 40° respectively. The conductivity of its aqueous solutions changes with time.

Generalising from the results, the author draws the conclusion that Hantzsch's criteria for the distinction between normal and pseudo-acids are untenable, and that the only safe indication of such change in an acid when it enters into combination with a base is to be found in the slow rate of neutralisation of the acid.

H. M. D.

**The System—Lime, Nitric Acid, and Water.** FRANK K. CAMERON and W. O. ROBINSON (*J. Physical Chem.*, 1907, 11, 273—278).—The authors have determined the composition of the solutions obtained by agitating a series of calcium nitrate solutions with excess of calcium hydroxide at 25° until equilibrium was reached. About six weeks was necessary for this in some cases. When the concentration of the calcium hydroxide is plotted as a function of the calcium nitrate concentration, a system of four curves with three inversion temperatures is obtained. By means of the method of triangular representation and the determination of the composition of the filtered solid residues, the nature of the solid phase corresponding with each curve is deduced. The solid phases and the composition of the solution expressed in grams per 100 grams of water is given by the following summary:

Solid phases in contact with solution.	CaO(as Ca(OH) <sub>2</sub> ).	Ca(NO <sub>3</sub> ) <sub>2</sub> .
Ca(OH) <sub>2</sub> .....	0.118	0.0
Ca(OH) <sub>2</sub> and solid solution } CaO, $x$ N <sub>2</sub> O <sub>5</sub> , $y$ H <sub>2</sub> O..... }	0.170	20.73
Solid solution CaO, $x$ N <sub>2</sub> O <sub>5</sub> , $y$ H <sub>2</sub> O } and CaO, N <sub>2</sub> O <sub>5</sub> , $3\frac{1}{2}$ H <sub>2</sub> O..... }	0.440	83.03
CaO, N <sub>2</sub> O <sub>5</sub> , $3\frac{1}{2}$ H <sub>2</sub> O and } Ca(NO <sub>3</sub> ) <sub>2</sub> , 4H <sub>2</sub> O }	0.203	135.3
Ca(NO <sub>3</sub> ) <sub>2</sub> , 4H <sub>2</sub> O .....	0.0	139.3

H. M. D.

**Velocity of Reaction in Electrolytic Gas** ALLAN WINTER ROWE (*Zeitsch. physikal. Chem.*, 1907, 59, 41—71).—The velocity of combination of hydrogen and oxygen has been studied by passing a mixture of the gases in equivalent proportions through a porcelain tube heated to various high temperatures. Comparison of the issuing gas with that passed into the tube showed how far combination had taken place. It appears from consideration of Bodenstein's (Abstr., 1899, ii, 733; 1904, ii, 245) and the author's experiments, that in addition to the direct combination of the gases there is a catalytic action at the surface of the porcelain. This catalytic action depends probably on a diffusion process and corresponds with a chemical reaction of the first order. The influence of the catalytic factor is much augmented by packing the tube with porcelain, by accelerating

the passage of the gases, and by keeping the temperature down. The temperature coefficient of the velocity for a chemical reaction is much greater than that for a purely physical process like diffusion; hence it comes that at high temperatures the influence of the purely chemical interaction between hydrogen and oxygen predominates. The author shows that at high temperatures the course of the reaction nearly coincides with that of a termolecular change. Altogether, the results obtained are to be regarded as supporting Nernst's theory of reaction velocity in heterogeneous systems, and as indicating that the purely chemical reaction between hydrogen and oxygen takes place according to the equation  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ .

[There is no reference to Bone and Wheeler's work on the same subject (Abstr., 1906, ii, 434).]  
J. C. P.

**Chemical Kinetics of the Decomposition of Oxalic Acid in Concentrated Sulphuric Acid.** DAVID M. LICHTY (*J. Physical Chem.*, 1907, 11, 225—272).—A detailed account of work already published (compare Bredig and Lichty, Abstr., 1906, ii, 602). It may be further noticed that the alkali sulphates also retard the reaction, the influence exerted by these being about one-tenth of that exerted by an equal weight of water. The electrical conductivity and the rate of decomposition of oxalic acid are recommended as very delicate methods of measurement of the amount of water in very concentrated sulphuric acid solutions.  
H. M. D.

**Supposed Change in Weight in Certain Chemical Reactions.** II. ANTONINO LO SURDO (*Nuovo Cim.*, 1906, [v], 12, 299—306. Compare Abstr., 1904, ii, 720).—Landolt (*Zeitsch. physikal. Chem.*, 1906, 55, 589—621; Abstr., 1906, ii, 528) has stated that the author's results (*loc. cit.*) agree with those of Heydweiller (*Ann. Physik.*, 1901, [iv], 5, 394), whereas they are really more in accord with those of Landolt (*loc. cit.*) himself.

In a further study of the reaction between silver nitrate and ferrous sulphate, the observed changes in weight lie within the limits of experimental error.  
T. H. P.

**Grouping of the Chemical Elements.** C. E. STROMEYER (*Mem. Manchester Phil. Soc.*, 1907, 51, [vi], 1—15).—An unsuccessful attempt to find a formula which would express the atomic weights in terms of the positions in Mendeléeff's groups.  
H. M. D.

**Isomorphism of the Elements.** GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, 53, 446—456).—The isomorphism of the elements is deduced from the miscibility in the crystalline condition, or, in other words, from their capacity to form mixed crystals in binary systems, and the question is investigated as to how far elements of analogous properties, or elements belonging to a natural group, are isomorphous. As an approximate arrangement of the elements according to their chemical analogy, the system of Staigmüller (Abstr., 1902, ii, 129) is chosen. The data as to the formation of mixed crystals are taken chiefly from the papers of the author and his co-workers.



In general, elements belonging to the same natural group form mixed crystals, but no compounds, whereas those belonging to widely different groups enter into chemical combination, but do not form mixed crystals. However, elements belonging to closely related groups also form complete series of mixed crystals in certain cases, and isomorphism does not altogether exclude the power of entering into chemical combination. It is suggested, in analogy with Mitscherlich's rule as to compounds, that elements which form mixed crystals are similarly constituted, and this is borne out by a comparison of their spectra. When elements are only partially miscible, it is shown that, with very few exceptions, the element with the higher melting point dissolves more of the element with lower melting point than vice versa, from which it follows that the temperature of crystallisation is of even more importance than the chemical analogy as regards the capacity of the elements to form mixed crystals. G. S.

**Calculation of Physico-Chemical Constants.** H. STANLEY REDGROVE (*Chem. News*, 1907, 95, 193).—In the study of certain physical properties it is frequently found that the ethylene linking exerts a certain specific influence; it is now suggested as very probable that the single carbon linking also exerts such an influence (compare Thomsen, *Abstr.*, 1905, ii, 436), and that atomic constants for hydrogen in  $H_2$  are different from those for hydrogen in hydrocarbons. If this is so, then the generally accepted values for atomic constants are incorrect, and the true values are unobtainable.

J. C. P.

**Lecture Apparatus [Combustion, &c.].** NICOLAE TECLU (*J. pr. Chem.*, 1907, [ii], 75, 224—234).—The author describes and figures apparatus for lecture experiments showing (a) the flames of coal gas in air and of air in coal gas, (b) the combustion of hydrogen in oxygen and of oxygen in hydrogen, (c) the explosion of mixtures of coal gas and air, oxygen, or oxygen and carbon dioxide, and (d) the preparation of hydrogen by the action of sodium on water. G. Y.

**Convenient Air-Bath and Hot Plate.** EDWARD DEMILLE CAMPBELL (*J. Amer. Chem. Soc.*, 1907, 29, 283—286).—A small combined air-bath and hot plate is described, which is recommended for heating solutions when a temperature higher than that of the water-bath is required and when it is necessary to avoid local over-heating. For details of the apparatus, the description and diagram in the original must be consulted. It has been found useful in the course of some work on the oxalates of thorium, cerium, lanthanum, neodymium, and praseodymium. When these salts are heated at 305—335°, they are completely converted into soluble basic and normal carbonates.

E. G.

**Gas Generator.** A. KLEINE (*Zeitsch. angew. Chem.*, 1907, 20, 655—656).—This piece of apparatus is so designed that practically all the acid is exhausted before it becomes necessary to recharge with fresh acid. It consists of a four-necked Woulff's bottle *D*, above which are

arranged three pipette-shaped reservoirs. The tube of the reservoir *A*, which contains the marble, zinc, or ferrous sulphide, just passes into *D*; the upper end of *A* is fitted with a glass tap. The tube of another reservoir *C* passes to the bottom of *D*, whereas that of the third, *B*, extends only half-way into *D*. The upper ends of *B* and *C* are fitted with pieces of rubber tubing and pinch-cocks. The fourth neck of *D* is fitted with a stopper through which passes a glass syphon, also closed by means of a pinch-cock. The reservoir *C* is closed, *D* is completely filled with dilute acid, and *B* half-filled with acid; on opening the glass tap, acid rises in *A* and gas is evolved. When the tap is closed, acid flows back into *D*; the saturated portion settles to the bottom of *D*, and the unsaturated rises into *B*. When the acid in *D* is used up, air is blown into *B* and the saturated acid driven into *C*; the unsaturated acid from *B* enters *D*. The acid in *C* is now used to drive the acid into *A*, *B* of course being closed by means of a pinch-cock. When all the acid has become neutralised, air is blown through *A*, and acid driven into *B* and *C*. The glass tap is then closed, the pinch-cock closing the syphon opened, and the acid empties itself from the apparatus.

W. H. G.

**Easily Constructed Arrangement for Filtering Alkaline Solutions.** R. RINNE (*Chem. Zeit.*, 1907, 31, 411—412).—An arrangement for filtering solutions out of contact with carbon dioxide. Inverted over the funnel fitted to the pump-flask and connected to it by means of a wide rubber band is a funnel of equal diameter, but having a short, wide stem; this stem is fitted with a doubly-bored stopper, through one hole of which passes the end of a calcium chloride tube packed with soda-lime. A glass tube bent at right angles passes through the other hole, and is connected by means of rubber tubing to a glass tube bent at an acute angle, which passes to the bottom of a flask, containing the solution to be filtered, through one hole of a double-bored stopper with which the flask is fitted. Through the other hole of this stopper passes the end of a calcium chloride tube packed with soda-lime.

The air in the apparatus is first displaced by air free from carbon dioxide, by connecting the pump-flask to a pump and drawing air through the soda-lime tube fitted to the inverted funnel. The solution is then transferred to the funnel fitted with a filter, by blowing air into the flask containing the solution through the soda-lime tube fitted to this flask.

W. H. G.

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### Inorganic Chemistry.

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Behaviour of the Halogens to One Another, Especially the Systems Chlorine-Bromine and Chlorine-Iodine. BARTA J. KARSTEN (*Zeitsch. anorg. Chem.*, 1907, 53, 365—392. Compare Meerum Terwogt, Abstr., 1906, ii, 15; Lebeau, Abstr., 1906, ii, 843).—It

is shown in agreement with Lebeau (*loc. cit.*) that chlorine and bromine do not enter into chemical combination either in the vapour or liquid phase. Iodine monochloride, which, according to Stortenbeker (Abstr., 1889, 102), is not appreciably dissociated in the liquid phase, is now shown to be stable in the form of vapour.

The curves representing the commencement and end of solidification respectively in the system chlorine-bromine fall regularly from the melting point of bromine,  $-7.3^{\circ}$ , to that of chlorine,  $-102^{\circ}$ . From 20—90% of chlorine the curves are from  $10$ — $14^{\circ}$  apart. It follows that the two elements form a continuous series of mixed crystals, and that there is no indication of chemical combination, which would be shown by an approximation of the two curves at one or more intermediate points.

The boiling point curve of the system has also been fully investigated. The composition of the vapour and that of the liquid with which it is in equilibrium at the boiling points of mixtures of the components in varying proportions are plotted against the corresponding boiling points. In this case also the curves do not approximate at intermediate points, so that no chemical combination takes place.

The boiling point curve of the system chlorine-iodine has also been determined. In this case the curves representing the composition of liquid and vapour respectively incline towards each other, and almost touch at a point at which the components are present in atomic proportions, so that the compound  $\text{ICl}$  exists in the vapour phase, and is only slightly dissociated at  $100^{\circ}$ , the boiling point of the mixture in question.

In conclusion, the mutual combining capacity of the halogens is discussed. The further apart the halogens are in the periodic table the greater is the mutual affinity, and, further, chlorine and bromine are nearer to one another, in other words, have less mutual affinity than bromine and iodine.

G. S.

**Hypohalogenous Acids and Hypohalogenites. I. Kinetics of the Hypoiodites and Hypobromites in Strongly Alkaline Solution.** ANTON SKRABAL (*Monatsh.*, 1907, 28, 319—382. Compare Abstr., 1905, ii, 449; Graebe, Abstr., 1902, ii, 556; Kretzschmar, Abstr., 1904, ii, 814; Bray, Abstr., 1906, ii, 221).—It is shown that in the formation of iodates from hypoiodites in alkaline solution, iodine is formed as the intermediate product. The iodine combines with the excess of hypoiodite forming the *hypotri-iodite*,  $\text{M'I}_3\text{O}$ , which, as an unstable compound of iodine with the hypoiodite, reacts as free iodine. The velocity of the iodate formation is determined by the rate of the reaction of the hypotri-iodite with the alkali, by which the iodide and iodate are formed. The kinetic equation,  $-dc/dt = K([\text{HIO}]^2[\text{I}']/[\text{OH}'])$ , derived from this view of the reaction is experimentally confirmed, and is in agreement with Forster's measurements (Abstr., 1904, ii, 163).

The formation of iodates from hypoiodites when the concentration of the iodine ions is small, and of bromates from hypobromites, are found also to be reactions of the second order, but the relation of the velocities of the reactions to the ionic concentrations is less regular.

The velocities of the formation of halogenates from hypohalogenites increase in the order: chlorine, bromine, iodine, and are shown to be in the proportion,  $1 : 3 \times 10^4 : 3 \times 10^6$ .

The action of halogens on hypohalogenites is considered to take place chiefly according to the scheme: (1)  $\text{HXO} \rightarrow \text{X}' + \text{OH}'$ ; (2)  $\text{X}' + \text{X}' \rightarrow \text{X}_2$ , (I)  $\text{HXO} \rightleftharpoons \text{X}_2 + \text{OH}'$ ; (3)  $\text{X}_2 \rightarrow \text{X}' + \text{X}'$ ; (4)  $\text{X}' \rightarrow \text{X}' + \text{XO}_3'$ , (II)  $\text{X}_2 \rightarrow \text{X}' + \text{XO}_3'$ . If in consequence of the conditions the equilibrium (I) is not established with sufficient rapidity, the reaction takes place to a proportionate extent according to the scheme: (1)  $\text{HXO} \rightarrow \text{X}' + \text{OH}'$ ; (2)  $\text{X}' \rightarrow \text{X}' + \text{XO}_3'$ , (I)  $\text{HXO} \rightarrow \text{X}' + \text{XO}_3'$ . But if the velocity of (1) is extremely small, the reaction proceeds directly to the formation of the stable end products: (1)  $\text{HXO} + \text{H}' \rightarrow \text{X}'$ ; (2)  $\text{X}' \rightarrow \text{X}' + \text{O}_2$ , (I)  $\text{HXO} \rightarrow \text{X}' + \text{O}_2$ . These schemes are in agreement with the observed facts: (1) the reaction is sometimes of the first, but at other times of the second, order; (2) the nature of the products is dependent on the velocity of the reaction; (3) the formation of the halogenate is accelerated by addition of the halogenide; (4) the velocity of the reaction, especially in the case of the hypobromites, is greatly increased by high concentrations of the hydroxyl ions, and (5) the initial acceleration in freshly prepared halogen solutions is observed also when the concentration of the halogenide is constant during the reaction.

The velocity of the reaction of halogens with hypohalogenites and the stability of the reaction products are shown to be causally related to the electro-affinities of the halogens. Gay-Lussac's law of the progression of chemical reactions in stages is discussed and defined.

G. Y.

**Manufacture of Chlorates and Hypochlorites with a View to High Current Efficiency.** ANSON G. BETTS and R. H. SHERRY (*J. Amer. Chem. Soc.*, 1907, 29, 340—345).—Although the current efficiency in the preparation of chlorate and hypochlorite is greatly increased by the addition of an alkali chromate, it cannot be employed in the manufacture of hypochlorite for bleaching purposes owing to the strong colour. The effect of adding other substances was therefore investigated, and, although in several cases the efficiency is increased to a considerable extent, none work so well as sodium chromate. Cathodes of iron, magnesium, aluminium, and nickel were also tried in the preparation of chlorate, with the result that a magnesium cathode was found to give an efficiency nearly equal to that produced by the addition of alkali chromate to the solution; however, one part of magnesium is lost for 50 parts of chlorate made. A high efficiency is also obtained in the manufacture of hypochlorite by using a magnesium cathode. The percentage loss of magnesium is reduced considerably by employing a large number of cells and using carbon electrodes in the first and magnesium electrodes in the other cells, a certain proportion of the solution being transferred periodically from the first cell to the second, and so on. By employing three cells, it was possible to convert from 35—50% of the salt with an efficiency of 60%, the power required for 100 lbs. of chlorine being

450 H.P. hours, and the loss of magnesium, 0.2 lbs. per 100 lbs. of chlorine.  
W. H. G.

**Absolute Atomic Weight of Bromine.** GUSTAV D. HINRICHS (*Compt. rend.*, 1907, 144, 973—975).—Using the data afforded by Baxter's recent determination of the atomic weight of bromine (*Abstr.*, 1906, ii, 740) and applying the method of calculation suggested previously (*Abstr.*, 1893, ii, 317), the author concludes that the value 80 should be accepted for the atomic weight of bromine in place of 79.952 adopted by Baxter, who used the values 107.93 for silver and 35.473 for chlorine in place of the numbers 108 and 35.5, which the author has previously shown to be the correct values for these elements (*Abstr.*, 1894, ii, 276).  
T. A. H.

**Preparation of Anhydrous Hydrogen Fluoride.** GUIDO GOLDSCHMIEDT (*Monatsh.*, 1907, 28, 297—298).—A copper retort may be used in place of the platinum usually employed in the preparation of anhydrous hydrogen fluoride by distillation of potassium hydrogen fluoride (compare Moissan, *Abstr.*, 1886, 849, 976; 1899, ii, 593).  
G. Y.

**Decomposition of Water Vapour in Contact with Hot Platinum Wire.** ALFRED HOLT, jun. (*Phil. Mag.*, 1907, [vi], 13, 630—635).—The author has estimated the dissociation of water vapour at high temperatures by heating a platinum wire in contact with it at low pressures and collecting the electrolytic gas produced. The values obtained for the amount of dissociation are slightly higher than those obtained by Nernst and Wartenberg (*Abstr.*, 1906, ii, 729) and by Langmuir (*ibid.*, ii, 848) at the lower temperatures. With rising temperature, the author's values become relatively smaller, until at 2000° abs. they are only about one-seventh of the quantities obtained by the other workers. The cause of this discrepancy is being investigated.  
J. C. P.

**Explosion of Pure Electrolytic Gas.** HAROLD B. DIXON and LAWRENCE BRADSHAW (*Proc. Roy. Soc.*, 1907, A, 79, 234—235).—With the object of finding whether the interaction of hydrogen and oxygen depends on the presence of water molecules formed previously, the authors have made a photographic analysis of the explosion flame in the dried and undried gases. The photographs were taken on a film moving vertically downwards with great rapidity, while the flame, started by a spark, travelled horizontally. The hydrogen and oxygen were made by electrolysis of very pure barium hydroxide, and to ensure the removal of water the mixed gases were placed in contact with phosphoric oxide in the dark for about two months before being exploded. As far as can be judged from the photographs, the absence of water vapour does not influence the explosion when once the flame has been started by a spark.  
H. M. D.

**The Firing of Gaseous Mixtures by Compression.** LAWRENCE BRADSHAW (*Proc. Roy. Soc.*, 1907, A, 79, 236—241).—Photographs of

the explosion flame, obtained by firing electrolytic gas by means of a spark in a glass tube, one end of which is drawn out to a capillary, indicate the advance of a second luminous wave from the capillary end of the tube. Experiments with different forms of tubes indicate that two of the conditions essential to the setting up of the wave are that end of the tube must be funnel-shaped and rigid. The distance from the firing wires to the end of the tube must be less than that required for the development of the detonation-wave in the gaseous mixture. The facts indicate that the second luminous wave is due the ignition of the explosive mixture by a wave of compression which is propagated with a velocity approximately equal to that of a sound-wave.

The phenomenon is more evident when a mixture of carbon disulphide and oxygen in the proportion  $2\text{CS}_2 : 3\text{O}_2$  is fired.

H. M. D.

#### Determination of the Limiting Explosive Mixtures of Gases.

NICOLAE TECLU (*J. pr. Chem.*, 1907, [ii], 75, 212—223).—An apparatus for making and exploding mixtures of gases of known composition is described and figured. The results of a series of experiments with mixtures of air with hydrogen, coal gas, methane, and acetylene are tabulated. The mixtures capable of being exploded by means of an electric spark are found to lie between the following limits in composition: 9.73—9.96 to 62.75—63.58% of hydrogen, 4.36—4.82 to 23.35—23.63% of coal gas, 3.20—3.67 to 7.46—7.88% of methane, and 1.53—1.77 to 57.95—58.65% of acetylene. Whilst the sensitiveness of these four gases to explosion with air diminishes in the order: acetylene, methane, coal gas, hydrogen; the range of explosiveness of the mixtures with air increases in the order: methane, coal gas, hydrogen, acetylene, and in the proportions: 1:4.21:12.7:13.5. Contraction takes place on explosion of mixtures containing less than 7.03%, or more than 49.79%, but expansion on explosion of mixtures containing 7.03—41.92%, whilst neither expansion nor contraction is observed with mixtures containing 41.92—49.79% of acetylene.

G. Y.

**Amorphous Sulphur: Study of the Two Forms of Liquid Sulphur as Dynamic Isomerides.** CHARLES M. CARSON (*J. Amer. Chem. Soc.*, 1907, 29, 499—517).—The experiments are described which lead to the conclusions previously recorded (Smith and Carson, this vol., i, 20).

E. G.

#### Blue Colour of Sulphur and of Certain of its Compounds.

EMANUALE PATERNÒ and ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 465—476. Compare Knapp, Abstr., 1888, 1163; Milbauer, Abstr., 1905, i, 121; 1906, i, 405; Giles, Abstr., 1901, i, 262).—The authors discuss the blue colour (1) of ultramarine; (2) of the blue modification of sulphur; (3) obtained by adding an alkali polysulphide to boiling alcohol or acetone, and describe their own investigations bearing on these points.

Knapp (*loc. cit.*) regards the blue colour of ultramarine as due to the presence of sulphur in a special state of aggregation, but the authors

are in agreement with Hofmann's view (Ultramarin, Braunschweig, 1902) that ultramarin cannot contain free sulphur, as they find that this substance retains its blue colour after being heated to bright redness for some time.

The blue (or green) variety of sulphur obtained by Orloff (Abstr., 1901, ii, 499; 1902, ii, 315) seems to be formed also by prolonged boiling of sulphur bromide with cadmium sulphide in presence of toluene; with sulphur iodide no reaction occurs. The properties of blue sulphur and ozone do not allow of an analogy being drawn between these two substances (compare Orloff, *loc. cit.*).

With 95% alcohol, traces of a polysulphide give a blue, and larger quantities a green, coloration, but only when the alcohol is heated; in the cold, the liquid assumes a yellow colour. The reaction is sharper with potassium or sodium polysulphide than with the ammonium compound, but, in any case, the coloration is only transitory. With acetone the colorations are more intense and more persistent, the best results being obtained by adding an alcoholic solution of potassium polysulphide to boiling acetone; even in the cold these solutions give a blue coloration, but this changes to green and ultimately to yellow with less quantities of the polysulphide than when boiling acetone is employed. The view that these colorations are due to a limited decomposition of the polysulphide is supported by the observations that intense and moderately persistent colorations are obtained with basic solvents such as pyridine, ethylamine, and allylamine, which are able to form saline compounds with persulphidic acid, whilst with water, the most highly dissociating solvent, no coloration is formed.

When sulphur is vaporised in a transparent, quartz vessel, it is seen that it has at first a deep, reddish-yellow colour, which, at higher temperatures, becomes very faint, and is ultimately replaced by a characteristic, pale-blue colour, this disappearing when the vapour cools. The same blue colour is observed when sulphur is volatilised in an atmosphere of carbon dioxide, but not when an atmosphere of sulphur dioxide is employed.

When potassium thiocyanate is heated, it melts at  $172.3^{\circ}$  to a colourless liquid, which begins to turn blue at  $430^{\circ}$ , the colour gradually deepening to an intense indigo if this temperature is maintained. When the salt is cooled, the colour begins to fade at about  $300^{\circ}$ , but only disappears completely in the neighbourhood of the melting point. If the blue liquid is maintained at above  $500^{\circ}$ , it changes to an opaque, incandescent, red liquid, but again becomes blue immediately on cooling; even at this temperature there is no appreciable separation of free sulphur, although the thiocyanate retains a yellow colour after cooling. When heated in a current of oxygen at above  $400^{\circ}$ , potassium thiocyanate loses in weight rapidly, sulphate and polysulphide being formed.

Observations were also made on the influence on the blue colour of mixing various salts with the thiocyanate.

Curves are given representing the absorption spectra (1) of a polysulphide in boiling acetone, pyridine, ethyl or propyl alcohol, or allylamine; in ethylamine at  $0^{\circ}$  or glycerol at  $160-180^{\circ}$ ; (2) of



fused potassium thiocyanate at different temperatures, and (3) of increasing thicknesses of a solution in sulphur in fuming sulphuric acid.

T. H. P.

**Liquid Hydrogen Sulphide as a Solvent.** GIUSEPPE MAGRI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 518—525. Compare this vol., ii, 237).—The author describes the method of employing the apparatus, previously described (*loc. cit.*), for measurements at low temperatures on inorganic solvents and on solutions in these solvents. The following are the results obtained up to the present.

The values obtained by Walden and Centnerszwer (*Abstr.*, 1902, ii, 245) for the physical constants of sulphur dioxide near its boiling point and of solutions of potassium iodide and ammonium thiocyanate in this solvent are, in general, confirmed.

Hydrogen sulphide, whether prepared from ferrous sulphide or synthesised from sulphur and hydrogen, boils under ordinary pressure at  $-62^{\circ}$ , a thermometer in the boiling liquid indicating  $-60^{\circ}$ ; its freezing point is  $-83^{\circ}$ . The following physical constants were determined at  $-60^{\circ}$ : D 0.95 (water=1); internal friction, 0.00417 dyne per sq. cm.; dielectric constant, 10.2 (air=1); surface tension, 25.434 dynes per cm.; conductivity, much below  $4 \cdot 10^{-7}$ .

The salts of energetic bases do not dissolve in liquid hydrogen sulphide, but compounds of the non-metals among themselves are soluble in it and determine a certain conductivity. Hydrogen sulphide also dissolves iodine, a 1.1% solution having a conductivity of  $1.34 \cdot 10^{-5}$  at  $-60^{\circ}$ . If this conductivity is due to dissociation of the hydrogen sulphide into hydrogen and sulphur ions, the solution should contain sulphur iodide dissociated into its ions. Such chemical interchange between the hydrogen sulphide and iodine is, however, apparently contradicted by the observation that a 1.2% solution of sulphur iodide in hydrogen sulphide has a conductivity  $5.81 \cdot 10^{-6}$ , which is much less than that of the iodine solution. Most probably the conducting power is to be ascribed to the iodine molecule itself, which may be regarded as formed from ions, thus:  $I_2 = I' + I'$  or  $2I_2 = 3I' + I'''$ .

T. H. P.

**Purification and Testing of Selenium.** RICHARD THRELFALL (*Proc. Roy. Soc.* 1907, A, 79, 167—174).—The author has examined the methods for the purification of selenium and the detection in it of small quantities of tellurium. The method described by Ekman and Petterson is recommended for the purification and Oppenheim's method for the detection of tellurium, the limit of this test being somewhere between 0.1% and 0.025% of tellurium. Traces of tellurium cannot be detected spectroscopically. The separation is best effected by repeated sublimation of the mixed oxides in a current of dust-free, dry air at  $360^{\circ}$ . Selenium purified by the above method is found to contain a trace of arsenic.

H. M. D.

**Behaviour of Selenium towards Light and Temperature.** IV. and V. ROBERT MARC (*Zeitsch. anorg. Chem.*, 1907, 53, 298—318).—In former papers (*Abstr.*, 1904, ii, 105; 1906, ii, 226, 280, 742) it has been shown by two independent methods that crystalline selenium exists in

two forms, *A* and *B*, the former being a non-conductor and the latter a good conductor of electricity. In the dark, the equilibrium mixture consists almost exclusively of *A*, and the equilibrium is displaced in the direction of *B* by raising the temperature. The transition has now been observed microscopically, the round granular crystals of *A* first formed at 140° changing to the longer crystals of *B* when heated for some time at 200°. Further, *B* appears to be rather less soluble in carbon disulphide than the other modification.

The action of light on selenium has also been studied. The equilibrium mixture at the ordinary temperature is sensitive to light, but when heated at 200° for some time (so that practically only *B* is present) and then rapidly cooled, this is no longer the case; however, when kept at the ordinary temperature, it becomes more and more sensitive as the equilibrium becomes displaced in the direction of *A*. It is therefore considered that light displaces the equilibrium from *A* to *B*, as does rise of temperature. It is shown that the effect in question is really photochemical and not due to simultaneous heating, and, further, that the sensitiveness is the same in dry air, in carbon dioxide, and in a vacuum.

Owing to the very slight transparency of selenium, only an extremely thin layer is affected by light, but there is some evidence that the particles thus affected diffuse slowly towards the interior, a fresh layer being thus exposed.

In the light of the above observations, the conditions to be observed in constructing sensitive selenium cells are discussed. G. S.

**Equilibrium of Ammonia.** FRITZ HABER and ROBERT LE ROSSIGNOL (*Ber.*, 1907, 40, 2144—2154).—The authors have determined the state of equilibrium of ammonia at high temperatures. Haber and van Oordt (*Abstr.*, 1905, ii, 159, 384, 814) have obtained an approximate value in the neighbourhood of 1000°; they find that in 10,000 mols. of ammonia, only 1.5—2.5 remain undecomposed. In the present experiments, the authors use an improved form of Haber and van Oordt's apparatus; iron, manganese, nickel, or chromium being employed as catalyst. The value *k*, obtained from  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ , at atmospheric pressure is  $1.48 \times 10^{-4}$  at 1000°, and  $4.68 \times 10^{-4}$  at 750°. The agreement is very good between the experimental values of *k* and those calculated from van't Hoff's thermochemical equation, on the assumption that the heat of formation of ammonia at constant pressure is independent of the temperature. C. S.

**Electrolytic Reduction of Hydroxylamine and of Nitrous Acid.** OTTO FLASCHNER (*Monatsh.*, 1907, 28, 209—246).—Haber's method of reduction with a limited potential (*Abstr.*, 1900, i, 281) cannot be applied to all cases, but only if the decrease in the amount of oxygen contained in the substance reduced is accompanied by a fall in the oxidation potential. As this cannot be foreseen, the effect of lowering the cathode potential can be known only experimentally. Moreover, the velocity of the reduction is affected by the metal employed as the electrode in such a manner that the effect caused by a difference in potential may be disguised. It is not certain that in

every case the substance reduced passes through the intermediate stages; the formation of the intermediate products can be assumed only with probability from kinetic considerations. It is found that in the electrolytic reduction of hydroxylamine and nitrous acid, the results obtained are in agreement with the curves representing the *E.M.F.* required for decomposition. Since nitrous acid is completely reduced with even extremely low cathode potentials, intermediate products cannot be obtained by the method of limited potentials. Whilst the reduction of hydroxylamine, or of nitrous acid, is affected only slightly by variations in temperature, the rate of reduction varies with the metal used as the cathode, the greatest velocity being found with a cathode of platinised platinum; this effect is ascribed to the catalytic action of the platinum black. With a copper cathode, nitrous and nitric acids are reduced only to ammonia. When reduction takes place without evolution of gas, a considerable part of the current employed in each case remains unaccounted for. G. Y.

**The Lead Chamber Process and the Oxides of Nitrogen.** FRITZ RASCHIG (*Zeitsch. angew. Chem.*, 1907, 20, 694—722. Compare Abstr., 1905, ii, 23 and 700).—Polemical. A reply to Lunge and Berl (compare Abstr., 1906, ii, 438). The chief point at issue is the following. The present author distinguishes between the so-called "first product" resulting after a quarter of a second's contact between one volume of nitric oxide and three volumes of oxygen and the "after product" which is formed after twenty-five seconds. The "first product" is supposed to consist of a mixture of nitrogen trioxide with oxygen, which in the course of twenty-five seconds is converted into a mixture of nitrogen peroxide and oxygen. Lunge and Berl, on the other hand, do not accept the formation of the trioxide, but consider it probable that at first only half of the nitric oxide is oxidised by the oxygen, the rest of the nitric oxide remaining as such in contact with the excess of oxygen. By mixing nitric oxide with air or varying proportions of pure oxygen, and analysing the mixtures both by absorption with concentrated sulphuric acid and with *N*/10 sodium hydroxide as well as by passing the gas through stannous chloride and titrating back the amount of unoxidised chloride by means of *N*/10 iodine solution, the author has found that it is possible to get various higher stages of oxidation of nitrogen according to the proportions in which the original gases were mixed. Thus, from the analysis of a mixture of nitric oxide with an excess of air, he concludes that in the "first product" the "apparent stage of oxidation" may be represented by the symbols  $N_2O_3 + O$  and not  $N_2O_3 + O_2$ . Although the system  $N_2O_3 + O$  has the same composition as  $N_2O_4$ , he does not regard it as identical with nitrogen peroxide, but prefers to call it *isonitrogen peroxide* or *oxy-nitrogen trioxide*,  $ON_2O_3$ . The "after product," on the other hand, is not  $N_2O_4 + O_2$ , but  $N_2O_5$ , which is isomeric with the ordinary oxide of that formula, and is therefore named *isonitrogen pentoxide*. If, however, nitric oxide is mixed with a large excess of pure oxygen, the first and after products are in a still higher state of oxidation, represented by the formulæ  $N_2O_6$  and  $N_2O_7$  for nitrogen hex- and hept-oxide respectively. The two gases behave towards most

reagents like nitrogen trioxide and peroxide respectively, and can only be recognised by their behaviour towards such a powerful reducing agent as stannous chloride; all attempts to isolate them have hitherto failed, and they appear only to be stable in the presence of a large excess of oxygen. Inasmuch as the *isohex-* and *hept-*oxides are only formed in presence of an excess of pure oxygen, these two gases are never formed in ordinary practice, and only the *isoper-* and *penta-*oxides are ever realised in the lead chamber process. A study of the solubilities of these two oxides in sodium hydroxide has led to the conclusion that in order to obtain a large yield of nitrite from the gases produced by the action of the electric discharge on air, the gases should be absorbed by very strong sodium hydroxide as soon as possible after their formation, when they will consist for the most part of *iso-*nitrogen peroxide. The solution should be allowed to become hot during the process, as this can but increase the yield of nitrite. Finally, the author considers that Lunge and Berl's experiments can be interpreted as a complete confirmation of his view that nitrous acid and not nitrosulphonic acid is the active catalytic agent in the chamber process; he also agrees with Littmann's view that the formation of nitrosulphonic acid is positively detrimental to the process, and that manufacturers should therefore try to prevent its formation. P. H.

**Reaction between Bromic, Hydriodic, and Arsenious Acids, and the "Induction" by Hydrogen Bromide of the Reaction between Bromic and Arsenious Acids.** FRED C. BOWMAN (*J. Physical Chem.*, 1907, 11, 292—305).—The oxidation of arsenious acid in solutions containing bromic and hydriodic acids has been examined with the object of ascertaining whether the oxidation is effected by the hypobromous and bromous acids which have been supposed to be formed in the reduction of bromic acid by hydriodic acid or by the iodine which is the end-product of the oxidation of the hydriodic acid.

It is shown that the rate of reduction of bromic acid by hydriodic acid is not affected by the presence of arsenious acid except in so far as the oxidation of the latter affects the concentration of acid and iodide in the solution.

The arsenious acid oxidised corresponds with the iodine liberation during the reaction and is very much smaller than the amount which would be oxidised if the oxidation were affected by hypobromous and bromous acids formed as intermediate products. The reduction of bromic acid by hydriodic acid does not therefore "induce" the oxidation of arsenious acid. H. M. D.

**Solidification Pressure in Moissan's Preparation of Diamonds.** CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1907, 4, 211—214. Compare Moissan, *Abstr.*, 1893, ii, 275, 320; 1894, ii, 189; 1896, ii, 644; 1905, ii, 160).—A theoretical paper, in which the views expressed by Moissan are criticised. A. J. W.

**Presence of Europium in Stars.** JOSEPH LUNT (*Proc. Roy. Soc.*, 1907, A, 79, 118—125).—In measurements of the radial velocity of

$\alpha$ -Boëtis and  $\beta$ -Geminorum, the results for the calcium line at  $\lambda$  4435·851 (Rowland) are discordant, and consideration of the available evidence indicates europium as the disturbing element. Recent investigation by other workers has indicated the presence of europium also in the chromosphere. J. C. P.

**Some Properties of the Alkali Protoxides.** ETIENNE RENGADÉ (*Compt. rend.*, 1907, 144, 753—756).—The alkali protoxides have been prepared according to the method described previously (Abstr., 1906, ii, 850, and this vol., ii, 83), but without using the silver boat. Sodium oxide ( $D_0$  2·25) is slightly yellow when hot; potassium oxide ( $D_0$  2·32) is white at the ordinary temperature, clear yellow at  $200^\circ$ ; rubidium oxide ( $D_0$  3·72) is pale yellow when cold, golden-yellowish when hot; caesium oxide ( $D_0$  4·78) has a fine red colour when cold. The oxides are similar in properties to that of caesium. They decompose above  $400^\circ$  into dioxide and metal; form an equimolecular mixture of hydroxide and amide when treated with liquid ammonia; are reduced by hydrogen at  $180$ — $200^\circ$  to a mixture of hydroxide and hydride which, when heated to  $300^\circ$  in a vacuum, dissociates with sublimation of the metal; are not attacked by cold fluorine or chlorine, but react violently (with incandescence) when heated with these gases; become incandescent but do not evolve gas when slightly heated with iodine in a vacuum, the residue giving a colourless solution in water from which iodine is precipitated by dilute acids; form poly-sulphide and sulphate when gently heated with sulphur; do not react with boron or sugar carbon below  $400^\circ$  (above which the oxides decompose); react violently with water, are dissolved by alcohol, and do not combine when cold with carbon dioxide, but do so at  $300^\circ$  forming carbonate.

Caesium oxide, when cold, does not absorb oxygen, but at  $150^\circ$  the peroxide,  $Cs_2O_4$ , is formed; it inflames when heated slightly in sulphur dioxide forming a mixture of sulphide and sulphate; in hydrogen sulphide ignition occurs at the ordinary temperature. When kept in the evacuated tubes in which they were prepared, caesium oxide gradually changes from red to black, and rubidium oxide acquires a coppery colour with a metallic reflex. These changes only occur when the tube contains the alkali metal, and on heating the resulting products at  $60$ — $80^\circ$  in a vacuum they regain their original colours, whilst a sublimate of the alkali metal is formed. Caesium and rubidium therefore have an appreciable vapour tension at the ordinary temperature, and their vapours are easily absorbed by the corresponding oxides, forming very easily dissociated substances. Similar phenomena are less clearly observed with potassium, but not with sodium. The vapours of the alkali metals seem to diffuse very slowly, as their absorption by the oxide occurs more rapidly on the side nearer the alkali metal and is almost entirely stopped by a constriction in the tube between the metal and oxide (compare Wood, *Phil. Mag.*, 1904, [vi], 8, 296). E. H.

**Scheele's Sodium Hydroxide Process.** ERNST BERL and G. AUSTERWEIL (*Zeitsch. Elektrochem.*, 1907, 13, 165—172).—The process

in question is based on the reaction  $2\text{NaCl} + 4\text{PbO} + \text{H}_2\text{O} = 2\text{NaOH} + 3\text{PbO}, \text{PbCl}_2$ . Lead oxide, prepared by heating white lead at  $400^\circ$ , had the solubility  $1.02 \times 10^{-3}$  gram-mol. per litre, whilst the solubility of a purchased sample was  $2.64 \times 10^{-4}$  gram-mol. per litre.

When lead oxide is shaken with  $N/2$  sodium chloride solution a white oxychloride,  $4\text{PbO}, \text{PbCl}_2, 2\text{H}_2\text{O}$ , is formed. The solubility of this substance in water is, at  $18^\circ$ ,  $5.15 \times 10^{-5}$ , at  $48^\circ$ ,  $6.6 \times 10^{-5}$ , and at  $74^\circ$ ,  $7.9 \times 10^{-5}$  gram-mol. per litre. Lead oxide and  $N$ -sodium chloride solutions yield the yellow oxychloride,  $3\text{PbO}, \text{PbCl}_2$ , the solubility of which in water at  $18^\circ$  is  $5.9 \times 10^{-5}$ , at  $48^\circ$ ,  $1.4 \times 10^{-4}$ , and at  $74^\circ$ ,  $7.4 \times 10^{-4}$  gram-mol. per litre.

The solubility of lead oxide in solutions of sodium hydroxide of various strengths at  $18^\circ$  and  $74^\circ$  is determined, and the conclusion is drawn that in solutions containing less than one molecule of sodium hydroxide per litre the lead oxide dissolves as  $\text{NaHPbO}_2$ , whilst in stronger solutions the salt,  $\text{Na}_2\text{PbO}_2$ , is formed to some extent. The dissociation constant of the monobasic acid,  $\text{H}_2\text{PbO}_2$ , at  $18^\circ$  is  $1.1 \times 10^{-12}$ . The equilibrium attained when sodium chloride solutions act on lead oxide at  $18^\circ$ ,  $48^\circ$ , and  $74^\circ$  is then studied. It is found that the ratio of the concentrations of the hydroxyl and chlorine ions in the solution is constant. The values of the ratio  $[\text{OH}]/[\text{Cl}]$  are at  $18^\circ$ , 1.0, at  $48^\circ$ , 0.75, and at  $74^\circ$ , 0.58. These values hold for solutions containing less than one molecule of sodium chloride per litre; with stronger solutions the lead oxide becomes coated with oxychloride, so that equilibrium cannot be attained.

The regeneration of lead oxide from the oxychloride by means of the reaction  $4\text{PbO}, \text{PbCl}_2 + \text{Ca}(\text{OH})_2 = 5\text{PbO} + \text{CaCl}_2 + \text{H}_2\text{O}$  is also studied. The ratio of the concentrations of hydroxyl and chlorine ions in the solution is again found to be constant; at  $18^\circ$  it is 1.05, and at  $74^\circ$ , 0.55.

T. E.

**Higher Oxides of Rubidium.** ÉTIENNE RENGADÉ (*Compt. rend.*, 1907, 144, 920—922. Compare Erdmann and Köthner, *Abstr.*, 1897, ii, 96).—In the apparatus previously described (*Abstr.*, 1906, ii, 444), known weights of rubidium are treated gradually with measured volumes of pure oxygen. After absorption of the gas, the product is heated rapidly to fusion and then immediately allowed to cool. By using a volume of oxygen corresponding with the formation of the dioxide,  $\text{Rb}_2\text{O}_2$ , a yellowish-white substance, fusing at  $600^\circ$  to a brown liquid and solidifying to a mass of felted needles, is obtained. By slightly increasing the quantity of oxygen, the colour of the solidified mass changes to deep brown and black, the latter being the colour of all the further products until sufficient oxygen is used to form the peroxide,  $\text{Rb}_2\text{O}_4$ , which is yellow. The peroxide is only yellow, however, if kept fused for some time and then cooled in oxygen at atmospheric pressure. It dissociates when heated in a vacuum, and at  $600^\circ$  the dissociation pressure of oxygen is about 3 cm. If the oxygen produced is removed by a mercury pump, after some hours the evolution of gas ceases. The black residue dissolves rapidly in water with evolution of oxygen and formation of hydrogen peroxide, whilst the proportion of rubidium corresponds with the formula  $\text{Rb}_2\text{O}_3$ . This

trioxide is more readily obtained by treating rubidium with the theoretical volume of oxygen and fusing the product. It forms a black mass, m.p. below  $500^{\circ}$ ,  $D_0^{\circ}$  3.53 (for the peroxide and dioxide,  $D_0^{\circ}$  is respectively 3.05 and 3.65). The author concludes that a black oxide intermediate between the peroxide and dioxide is formed by the direct oxidation of rubidium. E. H.

**Ammonium.** HENRI MOISSAN (*Compt. rend.*, 1907, 144, 790—791).—Ammonium amalgam can be obtained (1) by the action of sodium amalgam on an ammonium salt, (2) by electrolysis of a moist ammonium salt with a mercury cathode. The first reaction is only possible in the presence of an excess of sodium, even at  $-40^{\circ}$  when the sodium is removed, by repeated washing with a solution of an ammonium salt in liquid ammonia, or otherwise, the so-called ammonium amalgam ceases to exist. Accordingly the equation  $\text{NaHg} + \text{NH}_4\text{Cl} = \text{NaCl} + \text{NH}_4\text{Hg}$  is incorrect. When a solution of the double iodide of ammonium and mercury in liquid ammonia, or, better, a solution of 3 grams of ammonium iodide and 0.5 gram of mercuric iodide in 20 c.c. of water, is electrolysed at  $-40^{\circ}$  between platinum electrodes carrying a current of 2.5 amperes at 110 volts, there is formed at the cathode a mass of blue filaments which rapidly become entangled. This substance is only stable during the passage of the current, and on stopping the latter it immediately decomposes with evolution of hydrogen and formation of a grey cloud of mercury. It is soluble in mercury and the solution has all the properties of ammonium amalgam. E. H.

**Existence of Potassammonium and Sodammonium.** ALEX-ANDRE JOANNIS (*Ann. Chim. Phys.*, 1907, [viii], 101—110).—Polemical against Ruff and Geisel (*Abstr.*, 1906, ii, 228), who consider that the potassammonium and sodammonium described by the author do not exist. The arguments and more particularly the experimental results adduced by these observers in support of their view are severely criticised. G. S.

**Bleaching Powder.** HUGO DITZ (*Zeitsch. angew. Chem.*, 1907, 20, 754—757. Compare *Abstr.*, 1906, ii, 26).—Polemical against Schwarz (this vol., ii, 167). The author maintains that bleaching powder does not contain free calcium hydroxide, but is a mixture of the compound  $\text{CaO}, \text{CaOCl}_2, \text{H}_2\text{O}$  and the compound  $\text{CaOCl}_2, \text{H}_2\text{O}$ ; the latter substance in the anhydrous form  $\text{CaOCl}_2$  is not present in bleaching powder. W. H. G.

**Acid Sulphates. II. Acid Calcium-Sodium Sulphate.** JOH. D'ANS (*Zeitsch. anorg. Chem.*, 1907, 53, 419—422. Compare *Abstr.*, 1906, ii, 351).—To a saturated solution of calcium sulphate in sulphuric acid at the room temperature, glauberite (sodium sulphate) was added and the solution then diluted with 10% sulphuric acid. After some days, an acid calcium-sodium sulphate separated in tufts of small, doubly-refracting needles; the compound is immediately decomposed by water.

The limits of concentration within which the compound exists at 25° were determined, and it was then found that when specimens were prepared from solutions corresponding with different parts of the field the composition was not constant; the higher the proportion of sulphuric acid, the smaller is the proportion of calcium sulphate. It is considered that an isomorphous mixture, represented by the empirical formula  $x\text{Ca}_3\text{Na}_6(\text{SO}_4)_8 \cdot 5\text{H}_2\text{O} + \text{Na}_3\text{H}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  ( $x$  varying from 3 to 1.6), separates from solution. G. S.

**Temperature of Formation of Strontium and Barium Carbides.** MOREL KAHN (*Compt. rend.*, 1907, 144, 913—915. Compare this vol., ii, 166).—Mixtures of strontium or barium oxide (1 mol.) with sugar charcoal (3 atoms), when heated for twenty to twenty-five minutes at the temperature of melting platinum (1775°) in the furnace described by Moissan (*Abstr.*, 1902, ii, 122), give products which have not been fused, but contain strontium and barium carbides respectively. Moissan has shown that calcium carbide is not formed without fusion of the calcium oxide employed. E. H.

**Reduction of Magnesia by Charcoal.** PAUL LEBEAU (*Compt. rend.*, 1907, 144, 799—801).—On heating magnesia mixed with sugar charcoal in a carbon crucible in the electric furnace, the loss of magnesia by volatilisation in a given time is three to four times as great as when magnesia alone is heated similarly, thus indicating that reduction takes place. When 50 grams of a mixture of magnesia and charcoal, contained in a carbon tube in which was also placed a copper tube cooled by a current of water, are heated for eight minutes by a current of 700—800 amperes at 110 volts, 10 grams of an almost black, compact product are obtained on the copper tube. It is shown to consist of magnesium, magnesium carbide, and carbon. This product evolves gas slowly on treatment with water, rapidly with hydrochloric acid, the gas consisting of about 20% of acetylene and 80% of hydrogen. It follows that in the electric furnace magnesia is reduced by charcoal to a mixture of magnesium and magnesium carbide, which is largely destroyed by the furnace gases. The reduction takes place at a temperature possibly slightly above the boiling point of magnesia. In the fused magnesia, fragments of carbon are found which have preserved their irregular shape, but have been completely transformed into graphite. E. H.

**Chemistry of Thallium. I.** L. F. HAWLEY (*J. Amer. Chem. Soc.*, 1907, 29, 300—304).—The following modification of Willm's method is recommended for the estimation of thallium. The potassium permanganate solution is standardised by means of a pure thalious salt dissolved in a definite quantity of water and in presence of a definite amount of hydrochloric acid. The titrations must always be made under precisely the same conditions. It has been observed that the thallium factor, the weight of thallium oxidised by 1 c.c. of a permanganate solution, varies with the quantity of thallium present in the solution. This variation is shown by means of a curve in which the



thallium factors are plotted as ordinates and the volumes of permanganate solution as abscissæ. From this curve the factor to be employed in an estimation can be read directly from the amount of permanganate used. In carrying out the experiments required for the construction of the curve, fused thalious sulphate was used for standardising, all titrations were made in hot solutions, the volume of liquid titrated was always 60 c.c., and the hydrochloric acid present was equivalent to 4 c.c. of the concentrated acid of D 1.2. Under these conditions the thallium factor remains nearly constant, about 35 c.c. of permanganate solution corresponding with about 0.10 gram of thallium, but below that amount it decreases rapidly. A study is being made of the causes of this variation.

*Thallium fulminate*,  $\text{Tl}_2\text{C}_2\text{O}_2\text{N}_2$ , obtained by treating mercury fulminate suspended in water with thallium, is slightly yellow when dry, but becomes brown on exposure to the air. *Thallium aluminate*,  $\text{Tl}_4\text{Al}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ , prepared by the action of aluminium on thalious hydroxide, forms a white powder and is slowly hydrolysed by water. *Potassium thallic chromate*,  $\text{KTI}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ , obtained by adding potassium hydroxide to a solution of thallic hydroxide in chromic acid, is a yellow, crystalline salt which is rapidly hydrolysed by water unless a large excess of the chromic ion is present. E. G.

**Constitution of Copper Alloys.** LÉON GUILLET (*Compt. rend.*, 1907, 144, 845—848. Compare Abstr., 1906, ii, 357, and Shepherd, Abstr., 1904, ii, 662).—A series of buttons was prepared by superposing copper and the metals zinc, tin, antimony, cadmium, aluminium, manganese, magnesium, and nickel, the latter being taken one at a time so as to form binary alloys. It was observed in polishing these buttons for microscopic examination that in each case a fragile layer was reached, presenting a similar structure and developing a white colour when treated with ferric chloride dissolved in hydrochloric acid. Further, the succession of constituents passed through before reaching this fragile layer appeared to be the same except in the cases of the copper-cadmium and copper-manganese buttons. In the former case the compound  $\text{Cu}_2\text{Cd}$  separates, even when small quantities of cadmium are present, and so long as the alloy is relatively rich in copper no solid solution appears to be formed (compare Sahmen, Abstr., 1906, ii, 543). Of the alloys examined, the  $\alpha$ -constituents can be rolled or hammered in the cold and those composed of two solid solutions of which one is an  $\alpha$ -solution can be rolled when warmed. T. A. H.

**Limit of Silicuration of Copper.** ÉMILE VIGOUROUX (*Compt. rend.*, 1907, 144, 917—920. Compare Lebeau, Abstr., 1906, ii, 29, 168).—Mixtures of 81.74 grams of pure copper, 28.26 grams of pure crystallised silicon, and 200 grams of pure lead, bismuth, or antimony, contained in a porcelain boat, are heated at  $1200^\circ$  in a stream of hydrogen for about three hours. In the experiment with lead the product consists of (1) lead containing small quantities of copper and silicon, (2) a silicide containing 83.4—84.0% of copper, 9.53—9.35% of combined silicon, and 6.4% of free silicon. With bismuth, the product is composed of (1) bismuth containing small quantities of copper

and silicon, (2) crystallised silicon, and (3) a silicide containing 83·8—84·2% of copper, 10·84—10·78% of combined silicon, and 5·3% of free silicon. Antimony does not give a mechanically separable mixture, but a product containing 35·8—36·0% of copper, 3·60—4·10% of combined silicon, 4·20% of free silicon, and 56·5—56·17% of antimony. In each case the proportion of copper to combined silicon agrees within the limits of experimental error with the formula  $\text{Cu}_4\text{Si}$ . The author draws the conclusion that the maximum amount of silicon absorbed by copper to form a silicide is not affected by the presence of lead bismuth or antimony, that this maximum amount of silicon in copper silicide is about 10%, and that whilst the silicide rises to the surface of the lead and bismuth, it remains disseminated throughout the antimony.

E. H.

**Cuprous Iodide.** GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 528—531).—When cuprous iodide is heated with cupric chloride (or bromide), it loses all its iodine and is converted into cuprous chloride (or bromide):  $2\text{CuI} + 2\text{CuCl}_2 = 4\text{CuCl} + \text{I}_2$ . On the other hand, when cuprous chloride (or bromide) is dissolved in a concentrated alkali chloride solution, through which a current of carbon dioxide is kept passing, and the liquid subsequently shaken vigorously with a solution of iodine in xylene, the latter loses all its iodine, which is transformed into cuprous iodide according to the equation:  $4\text{CuCl} + \text{I}_2 = 2\text{CuCl}_2 + 2\text{CuI}$ . The action of iodine on cuprous salts is hence perfectly comparable with that which it exerts, in small degree, on ferrous or stannous salts. The concentration of the salts and the temperature determine the predominance of one or the other of the inverse reactions represented by the two equations given above. These reactions form a particular case of a more general equilibrium expressed by the ionic equation:  $\text{Cu}^{++} + \text{I}' \rightleftharpoons \text{Cu}' + \text{I}$ .

T. H. P.

**Electrolytic Preparation of Amalgams.** GEORGE MCP. SMITH and JAMES R. WITHEROW (*J. Amer. Chem. Soc.*, 1907, 29, 321—324).—The method proposed by Shepherd (*Abstr.*, 1903, ii, 210) as a lecture experiment for the electrolytic preparation of sodium amalgam has been employed in the preparation of potassium, barium, strontium, calcium, and lithium amalgams. A thick, pasty potassium amalgam is obtained from a potassium sulphate electrolyte with current of 3—4 amperes and 18—22 volts, the temperature being 70—90°. A solid amalgam containing 1·5% of potassium is obtained as a matt of brilliant needles from potassium hydroxide at a temperature of 60—70°, and with a current of 3—4 amperes and 9—12 volts. A harder amalgam, containing 1·66% of potassium, is obtained by using a potassium nitrate electrolyte at 60° and with a current of 3—5 amperes and 5·5—8·8 volts. A 1·43% barium amalgam is obtained as a thick mass of needle-like crystals from barium nitrate, with a current of 3—5 amperes and 11—13 volts at a temperature of 90°. Although the potassium and sodium amalgams are readily obtained by this method, the other amalgams are obtained only with great difficulty, owing to the decomposability of the amalgams and clogging of

the porous cell. The strongest strontium amalgam, containing 0.7% of the metal, is obtained from strontium nitrate; both lithium acetate and calcium acetate give only weak amalgams. With the exception of the potassium amalgam, none of these amalgams are pure, being contaminated with more or less potassium, derived probably from the porous cup.

W. H. G.

**Reversible Metallic Displacements in Aqueous Solutions.** GEORGE MCP. SMITH (*Amer. Chem. J.*, 1907, 37, 506—542. Compare Abstr., 1905, ii, 450).—Whilst the solid crystalline amalgams of the alkali and alkaline earth metals are regarded as definite chemical compounds, the corresponding liquid amalgams, on the other hand, have generally been regarded as mercurial solutions of these metals in the monatomic condition. The author does not agree with the latter view, and submits evidence to show that the liquid amalgams of the metals of the alkalis and alkaline earths, with the possible exception of magnesium, are solutions in mercury of compounds of the general formula  $MHg_m$ , containing only 1 atom of the amalgamated metal in the molecule. The solid amalgams are regarded as analogous to hydrated salts.

The preparation of potassium, sodium, lithium, barium, strontium, and calcium amalgams, and the action of various salt solutions on these amalgams is described. It is experimentally shown that the following sixteen pairs of metals are reversibly displaceable in aqueous solutions, K-Na, K-Li, K-Ba, K-Sr, K-Ca, K-Mg; Na-Li, Na-Ba, Na-Sr, Na-Ca, Na-Mg; Li-Sr, Li-Ca; Ba-Mg; Sr-Ca, Sr-Mg. In the presence of mercury, lithium can be displaced from a mixed solution of its chloride and hydroxide by magnesium with the formation of lithium amalgam. In like manner, barium can be displaced from its chloride solution by the amalgams of the more electronegative metals, strontium and calcium.

The stability of the compounds of the type  $MHg_m$ , increases in the following order:  $LiHg_m$ ,  $KHg_m$ ,  $NaHg_m$  for the alkali compounds, and  $CaHg_m$ ,  $SrHg_m$ , and  $BaHg_m$  for those of the alkaline earths.

The same equilibrium is obtained by the action of an equimolecular solution of sodium and potassium chlorides on either potassium, sodium, or lithium amalgam.

A. McK.

**Solubility of Mercuric Chloride in Mixed Solvents.** M. DUKELSKI (*Zeitsch. anorg. Chem.*, 1907, 53, 327—337. Compare Herz and Anders, this vol., ii, 159; Timoféeff, Abstr., 1891, 1313).—In 1898 the author determined the solubility of mercuric chloride in the following binary organic solvents through a wide range of temperature (usually 0—50°), the components being taken in equivalent, and in some cases also in other proportions: methyl alcohol with chloroform, with carbon tetrachloride, and with ethylene chloride; ethyl alcohol with benzene and with chloroform; and ethyl acetate with benzene, with carbon tetrachloride, and with chloroform. The results are now published in accessible form. The solubility of mercuric chloride in the simple solvents is taken from the previous observations of Timoféeff (*loc. cit.*) and others, and in some cases has been specially determined.

The observed values are compared with those calculated on the assumption that each of the components of the solvent exerts its effect independently, but, owing to the complicated nature of the phenomena, it has not been found possible to draw any general conclusions.

G. S.

**Formation of Hydrosols and Organosols of Metallic Sulphides.** ALFRED LOTTERMOSER (*J. pr. Chem.*, 1907, [ii], 75, 293—306. Compare this vol., ii, 78).—The methods which have been employed by various authors in the preparation of hydrosols of metallic sulphides are discussed. Many of these hydrosols appear to be capable of existence only in presence of an excess of hydrogen sulphide; on the other hand, a stable hydrosol, as in the case of the formation of the hydrosol of arsenious sulphide in presence of a large excess of hydrogen sulphide, may be prepared by the action of a limited amount of hydrogen sulphide if the concentration of the ions present in the original solution and formed by the reaction is less than that necessary for the precipitation of the hydrogel. The hydrosol of arsenious sulphide is gradually hydrolysed, forming arsenious acid and evolving hydrogen sulphide, no precipitation of the hydrogel taking place. It is considered probable that when a hydrosol exists in presence of an unremovable excess of hydrogen sulphide, this must be ascribed to adsorption of the gas.

When mercuric sulphide is treated with hydrogen sulphide and water (Winssinger, *Abstr.*, 1888, 911; Linder and Picton, *Trans.*, 1892, 61, 114; Picton, *ibid.*, 137), the hydrosol is not formed until the solution has been saturated with hydrogen sulphide. The above considerations have led the author to prepare the hydrosol of mercuric sulphide by the action of hydrogen sulphide on mercuric cyanide, since this in aqueous solution has only an extremely small ionic concentration which is hardly increased by the action. The hydrosol formed by passing hydrogen sulphide into a cold saturated solution, containing 12 grams of mercuric cyanide per 100 c.c., is deep brown and can be freed from hydrogen cyanide by dialysis, the formation of the hydrogel being prevented by a slow current of hydrogen sulphide, the greater part of which is expelled finally by a current of carbon dioxide. The resulting hydrosol is unstable, but if the hydrogen cyanide is removed by distillation under reduced pressure in an atmosphere of hydrogen sulphide, there is obtained a stable hydrosol which is oily and opaque,  $D_{17}^{20}$  1.0638, or after some days, 1.0370. The mercuric sulphide in the hydrosol is calculated to have  $D$  8.148, which approximates to the sp. gr. of red, crystalline, sublimed mercuric sulphide,  $D_{4}^{15.8}$  8.1587. If, however, the mercuric sulphide in the hydrosol contains absorbed water (van Bemmelen, *Abstr.*, 1897, ii, 137; 1899, ii, 12, 84), its sp. gr. is probably lower than that here calculated. When examined ultramicroscopically by the arc light, the hydrosol gives a bluish-white diffraction disc, whilst with concentrated solutions of the hydrosol, large, bright points of light are observed; the hydrosol obtained from dilute solutions of the cyanide show a less bright disc, which on further dilution of the solution breaks up into numerous points of feeble illumination. The pure hydrosol is stable when boiled, but the hydrogel

is precipitated if the impure hydrosol is boiled under atmospheric pressure, or by the action of electrolytes.

A deep brown hydrosol of copper sulphide is obtained in the same manner by the action of hydrogen sulphide on cold cuproglycine solutions, whilst an olive-green hydrosol is formed from the hot dilute solution, or if the brown hydrosol is boiled.

The relation of the colour of hydrosols to the size of their particles is discussed and illustrated by reference to the hydrosols of silver, tellurium, and gold.

Organosols have been prepared by the action of hydrogen sulphide on mercuric cyanide and cuproglycine in alcoholic solution, and on ethyl cuproacetoacetate in indifferent solvents such as ether and benzene.

G. Y.

**Catalytic Properties of the Rare Earth Elements. I.** GIUSEPPE A. BARBIERI and A. VOLTINO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 399—403).—Meyer and Marckwald (Abstr., 1901, ii, 21) have shown that the velocities with which the oxalates of the rare earth metals are decomposed by nitric acid vary with the electro-chemical characters of the elements, the most stable oxalate being that of the most positive metal.

Quantitative experiments made by the authors show that the oxidation of oxalic acid by nitric acid is greatly accelerated by cerous sulphate, whilst the corresponding salts of lanthanum, praseodymium, neodymium, and yttrium exert no appreciable influence on the velocity of the reaction. The positive catalytic action of the cerous salt finds a ready explanation in the oxidisability of cerous to ceric salts by nitric acid (this vol., ii, 466, 467), and consists evidently in a transference of oxygen from the nitric acid to the oxalic acid by way of the ceric salt. In the intensity of its catalytic effect on this reaction, cerium stands between manganese and iron, whilst cobalt is intermediate between iron and nickel. In the estimation of the unoxidised oxalic acid by titration with permanganate solution, it is found that the reduction of the latter is very rapid even at the ordinary temperature when cerium salts are present; manganous salts exert a similar influence. Quantitative investigation of the influence of various sulphates on the reaction between oxalic acid and permanganate shows that the catalytic action of cerous sulphate approximates to that of manganous sulphate, whilst those of praseodymium, neodymium, and lanthanum sulphates are much less and stand nearer, in this respect, to cobalt and nickel sulphates.

T. H. P.

**New Tanning Materials: Mineral Tanning Agents.** FELICE GARELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 532—538).—The author's investigations deal with the use of salts of the rare earth metals as tanning materials. Hide powder rapidly decomposes or hydrolyses lanthanum, didymium, and cerous salts, fixing the hydrated oxides. The behaviour of these salts is hence similar to that of chromium and aluminium salts. Similar results were obtained with ceric ammonium nitrate and with zirconium and thorium nitrates. Ceric ammonium nitrate and also ceric sulphate give leather which has a pale yellow colour and is resistant to the action of water; the leather

obtained with thorium or zirconium nitrate is very soft and flexible, and is white. With ceric salts, partial reduction is produced by the hide, the oxygen thus absorbed by the latter favouring the formation of a leather possessing stability and good quality.

It is suggested that the large quantities of crude cerium salts separated from monazite sand during the preparation of thorium for incandescent mantles might be utilised in the tanning industry.

T. H. P.

**Cerium Sesquioxide.** ALFRED BURGER (*Ber.*, 1907, 40, 1652—1655).—When cerium dioxide is reduced by calcium, and the calcium oxide and excess of calcium removed by a solution of ammonium chloride at  $-10^{\circ}$  or by a solution of sugar at  $0^{\circ}$ , a yellowish-green powder remains which has approximately the composition of the sesquioxide; it burns at  $200^{\circ}$  forming cerium dioxide, and combines with oxygen at the ordinary temperature. C. S.

**Oxidation of Cerous to Ceric Compounds.** GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 395—399).—Objection has been raised, mainly on account of the instability of the salts  $CeX_4$ , to the position assigned by Mendeléeff to cerium in the first part of the fourth group of the periodic system, the elements on either side of it, zirconium and thorium, being only quadrivalent (compare Biltz, *Abstr.*, 1902, ii, 201).

The author points out that it is not absolutely accurate to state that ceric compounds are unstable, whilst cerous compounds are stable. What is really unstable is the ceric ion  $Ce^{++++}$ , which is readily transformed into the cerous ion  $Ce^{+++}$ . The author's experiments indicate that, in an alkaline medium, in which ceric ions cannot exist, ceric compounds are stable, whilst cerous compounds act as reducing agents. Further, in an acid medium, when the conditions are such as to diminish the concentration of the ceric ions, the oxidation of cerous salts can be effected by nitric acid alone.

When sodium hydroxide solution is added to a solution containing cerous chloride and cupric (or mercuric) chloride, cuprous (or mercurous) oxide is precipitated. This reducing action of cerous salts distinguishes the latter from the salts of all the other rare earths and indicates that they are more nearly allied to manganous salts.

When cerous nitrate is boiled with nitric acid (D 1.4), about 6—8% undergoes oxidation to the ceric salt; in presence of alkali nitrate, the proportion oxidised may reach 33%. This oxidation appears contradictory to the great instability and intense oxidising power of the ceric ion, but in solutions rendered strongly acid with nitric acid and containing alkali nitrate, the ceric ion probably forms a moderately stable, complex anion,  $Ce(NO_3)_6^{--}$ , with the  $NO_3^{-}$  anion. It has, indeed, been shown by Meyer and Jacoby (*Abstr.*, 1901, ii, 510) that, during the electrolysis of double nitrates of quadrivalent cerium, coloured ceric ions migrate towards the anode. Since also cerous nitrate tends to form double salts with alkali nitrates, it may be assumed that highly nitrated solutions of cerous nitrate contain complex cerous-nitric anions, which are probably oxidised to ceric-nitric complexes by hot

concentrated nitric acid; the latter may also transform non-dissociated cerous nitrate into non-dissociated ceric nitrate. T. H. P.

**Ceric Hydroxide.** GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 525—528).—According to Brauner (Abstr., 1904, ii, 485), the ceric hydroxide obtained by decomposing hydrated cerium peroxide at 100°, when treated in a platinum capsule with dilute sulphuric acid, dissolves with vigorous evolution of ozonised oxygen and yields cerous sulphate; in a porcelain dish, however, neither reduction nor evolution of gas occurs, the ceric hydroxide being transformed into ceric sulphate. On the other hand, ceric hydroxide prepared by oxidation of cerous hydroxide by means of chlorine yields only ceric sulphate when treated with dilute sulphuric acid in presence of platinum.

On repeating these experiments, the author finds that the ceric hydroxide obtained by either of the above methods gives, with dilute sulphuric acid, a solution in which about 93—95% of the cerium exists in the quadrivalent form. T. H. P.

**New Method of Preparing Ceric Salts: Ceric Iodate.** GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 644—647).—Cerous salts may be converted into the corresponding ceric salts by heating with concentrated nitric acid, provided that: (1) the cerous salt is soluble in nitric acid; (2) the acid of the cerous salt is non-volatile and does not react with nitric acid, and (3) the ceric salt formed is either insoluble or only slightly soluble in nitric acid.

*Ceric iodate*,  $\text{Ce}(\text{IO}_3)_4$ , prepared by heating together either cerous iodate and nitric acid (D 1·4), or cerous nitrate (1 mol.), iodic acid, (4 mols.) and nitric acid (D 1·4), is obtained as an anhydrous, yellow, crystalline powder, and undergoes slight hydrolysis when treated with water. One hundred c.c. of boiling concentrated nitric acid dissolve 0·34 gram of the salt, which separates unchanged when the acid is evaporated. When ceric iodate is treated with hydrogen peroxide solution acidified with sulphuric acid, iodine is evolved. As iodic acid and the iodates decompose hydrogen peroxide without undergoing change (compare Tanatar, Abstr., 1899, ii, 414), the liberation of iodine from ceric iodate, and hence the reduction of the iodic acid must be ascribed to the presence of cerium, which need not be in the quadrivalent condition. This decomposition of iodic acid is effected by manganese salts, but not by salts of lanthanum, neodymium, praseodymium, yttrium, samarium, or erbium. T. H. P.

**New Method for the Separation of the Yttrium Earths.** CHARLES JAMES (*Chem. News*, 1907, 95, 181—182. Compare Bettendorff, this vol., ii, 172).—The oxalates of the rare earths obtained from gadolinite, freed from those earths giving insoluble double sodium sulphates, are treated with a solution of ammonium carbonate made by saturating dilute (1—5) ammonium hydroxide with the solid salt. On warming, the oxalates dissolve completely, and from the solution a precipitate is soon obtained on boiling. This is filtered off and the

filtrate re-treated in the same manner, and some five fractions thus obtained of approximately equal size. Fraction I is a crystalline powder with a faint pink tinge; it consists principally of yttrium carbonate together with small quantities of the carbonates of didymium, holmium, dysprosium, and erbium. Fraction II is similar in appearance to Fraction I; its solution gave no didymium absorption bands, whilst those of holmium, dysprosium, and erbium were stronger. Fraction III takes longer to form, is rose-coloured, and consists of a mixture of carbonates and oxalates. The absorption bands of the solution were similar to the original material. Fraction IV is deposited very slowly and is salmon-coloured. Its solution in nitric acid gave an intense erbium spectrum; that of holmium and dysprosium had become weak. Fraction V, obtained by evaporating to dryness and calcining, is a dense, pink oxide. Its solution in nitric acid gives an intense erbium spectrum, holmium and dysprosium being very weak. This last fraction is converted into oxalate and separated by the above method into four fractions. The fourth fraction thus obtained yields a white oxide practically free from holmium and dysprosium. It gave erbium bands and also a thulium band in the red, and contained a fair amount of ytterbium and some thorium. By this method it is thus possible to separate quickly erbium from holmium, dysprosium, and terbium.

The first fractions when treated by Muthmann and Rolig's method (Abstr., 1898, ii, 518) yield a yttrium oxide containing traces of terbium; the latter is removed by employing the chromate method of Muthmann and Böhm (Abstr., 1900, ii, 209). W. H. G.

**Preparation of Aluminium Bromide.** GABRIEL GUSTAVSON (*J. pr. Chem.*, 1907, [ii], 75, 328. Compare Abstr., 1901, ii, 316).—Contrary to Lassar-Cohn's statement (*Arbeitsmethoden*, 1907, 354) the action of bromine on aluminium must be carried out in a tube, a retort being used only as receiver. The method as described by Lassar-Cohn is dangerous. G. Y.

**Aluminium Sulphide and its Compounds with Manganese and Iron Sulphides.** MARCEL HOUDARD (*Compt. rend.*, 1907, 144, 801—804. Compare this vol., ii, 92).—A mixture of aluminium turnings and manganese sulphide contained in a carbon boat placed in a porcelain tube is heated to dull redness for an hour in a current of hydrogen sulphide, and then the temperature is raised to a white heat for half an hour. The product is attacked by cold water with evolution of hydrogen sulphide and deposition of aluminium hydroxide, but the greater part, composed of brownish-yellow crystals, is insoluble. The latter after being powdered and treated with acetic acid to remove aluminium sulphide gives analytical results agreeing with the formula  $\text{Al}_2\text{S}_4\text{Mn}$ . If the original mixture contains excess of manganese sulphide, the product consists of a pale golden-yellow mass throughout which green crystals of manganese sulphide are disseminated.

A similar experiment with a mixture of aluminium turnings and ferrous sulphide gives a product containing deep, brownish-red crystals and others of a greenish, almost black colour. Both substances when



powered and treated with acetic acid give analytical results approximating to the formula  $\text{Al}_2\text{S}_4\text{Fe}$ , but the agreement is not so close as with the manganese compound. The first contains an excess of iron and a deficit of aluminium from the theoretical, whilst the proportions are reversed in the second substance. E. H.

**Melting Points of some Cryolite-Alumina Mixtures.** FRANCIS R. PYNE (*Trans. Amer. Electrochem. Soc.*, 1906, 10, 63—65).—The weighed mixtures were fused in a crucible of graphitised carbon, and the temperatures of solidification measured by a thermo-couple. The results are :

% $\text{Al}_2\text{O}_3$ .	Melting Point.	% $\text{Al}_2\text{O}_3$ .	Melting Point.
0	1000°	7	982
3	974	8	992
4	960	10	980
5	915	15	994
6	960	20	1015

The curve plotted from these figures has two minima, one at 5%, the other at about 9%  $\text{Al}_2\text{O}_3$ . T. E.

**Action of Finely-divided Iron on Water.** S. BIRNIE (*Chem. Weekblad*, 1907, 4, 291—296).—The author finds that at temperatures between 0° and 100° finely-divided iron reacts with water, evolving hydrogen, and that the presence of oxide of iron considerably accelerates the velocity of reaction. A. J. W.

**Alloys of Iron with Tin and Gold.** EDUARD ISAAC and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, 53, 281—297).—No well-defined compound has been obtained from the alloys in question, but iron and tin seem to form at least one compound as a result of secondary changes after partial solidification has taken place.

Tin and iron are only partially miscible in the fused state ; at 1140°, from 50—89% of tin, two layers are present. The latter metal is soluble to the extent of about 19% in crystallised  $\gamma$ -iron. At 1140° the layer rich in iron decomposes into mixed crystals and a fused mass, and at 893° the mixed crystals react with the fused mass to form a compound the formula of which could not be determined definitely ; it may be  $\text{Fe}_3\text{Sn}$ . These changes are indicated by breaks in the cooling curve ; at 780° there is a third break, probably indicating a polymorphous transition of the compound, and there is a fourth break at 496°. From 89—100% of tin, the freezing point curve falls very rapidly.

Alloys containing as little as 2.5% of iron affect the magnetic needle. The temperature at which iron loses its magnetic character is practically unaffected by the presence of tin.

Iron and gold are miscible in all proportions in the fused state, and form an interrupted series of mixed crystals on solidification, the break extending from 28—63% of gold ; at lower temperatures, owing partly to the change of iron into another form, the break extends from 18—85% of gold. At 1168° the saturated mixed crystals with 28% of gold react with the fused mass to form a second series of mixed crystals. At

95% of gold the freezing point curve shows a minimum about  $24^{\circ}$  below the melting point of the pure metal.

The transition temperature of iron is not affected by the presence of gold.

The alloy containing 10% of gold is rather harder than iron; beyond this point, the hardness slowly diminishes, and those containing more than 70% of gold are considerably softer than iron. G. S.

**Experimental Studies on the Reduction and Formation of Carbide by Iron.** RUDOLF SCHENK, H. SEMILLER, and V. FALKE (*Ber.*, 1907, 40, 1704—1725).—The authors have reinvestigated the equilibrium pressure obtained in the system Fe, FeO, C, CO, and  $\text{CO}_2$  at varying temperatures with the idea of reconciling the results obtained previously (Abstr., 1905, ii, 519, 526; 1906, ii, 363) with those obtained by Baur and Glässner (Abstr., 1903, ii, 423). It is now shown that, although the curves for carbon monoxide-charcoal and for graphite are very nearly coincident, they have absolutely nothing to do with one another, and that for the complete determination the proportion of the two oxides in the gas phase must be known. A further complication introduced is the formation of iron carbide (cementite,  $\text{Fe}_3\text{C}$ ) by the action of carbon monoxide on iron. The experiments were carried out below  $700^{\circ}$ , as above this temperature mixed crystals of iron and cementite make their appearance.

From the results obtained from the systems (I) Fe, FeO, C (amorphous), CO, and  $\text{CO}_2$ ; (II) Fe, FeO, C (graphite), CO, and  $\text{CO}_2$ ; (III)  $\text{Fe}_3\text{C}$ , FeO, C (amorphous), CO, and  $\text{CO}_2$ ; (IV)  $\text{Fe}_3\text{O}_4$ , FeO, C (amorphous), CO, and  $\text{CO}_2$  a graphic representation in space with the co-ordinates, temperature, pressure, and composition of the gas phase can be constructed and the conditions for the formation of iron carbide calculated. The conclusion arrived at is that the cementation of iron is only possible when the gas contains 96—99% of carbon monoxide; this conclusion was experimentally verified by heating reduced white pig-iron and carbon monoxide, when slightly lower values were obtained.

The heat of formation of iron carbide calculated from these observations with the aid of van't Hoff's equation is 8940 cal., cementite being an exothermic compound (compare Benedicks, *Metallurgie*, 1906, 3, Nos. 12—14; Campbell, *J. Iron and Steel Inst.*, 1901, 59, 217).

W. R.

**2:1-Ferroso-ferric Oxide.** OTTO HAUSER (*Ber.*, 1907, 40, 1958—1960).—When ferroso-ferric ammonium carbonate (Abstr., 1905, ii, 715) is added to a hot concentrated aqueous solution of potassium hydroxide and a current of coal gas passed through the mixture, a dark coloured *ferroso-ferric oxide* separates, which, when dried at  $100^{\circ}$ , has the formula  $\text{Fe}_6\text{O}_7 \cdot 5\text{H}_2\text{O}$  or  $\text{Fe}_2\text{O}_3 \cdot 4\text{FeO} \cdot 5\text{H}_2\text{O}$ . It is very readily acted on by oxygen to form the hydrated sesquioxide,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , which differs from the ordinary sesquioxide in being much darker, very strongly magnetic, and convertible at about  $300^{\circ}$  into the anhydrous oxide, which is also magnetic. A. McK.

**Transitions of Ferrous Sulphide.** FRIEDRICH RINNE and H. E. BOEKE (*Zeitsch. anorg. Chem.*, 1907, 53, 338—343).—It is known that commercial ferrous sulphide has a transition point about  $130^{\circ}$  (compare Treitschke and Tammann, *Abstr.*, 1906, ii, 547). The authors have now observed that whereas two specimens of the sulphide (troilite and another) occurring in meteoric iron show the same transition, no break in the cooling curve occurs with a third natural specimen or with a sulphide prepared by heating the elements together without access of air.

When the sulphide last mentioned had been fused previously with excess of iron, however, it showed the transition point. When 7% of iron or more was present, the change took place sharply at  $137^{\circ}$ , but with less iron it was not so sharp and occurred at lower temperatures; with less than 4% the break in the cooling curve could no longer be detected. It is therefore considered that iron and the sulphide form mixed crystals at  $138^{\circ}$  which are saturated at 7% of iron and are readily transformed into another modification. The way in which iron facilitates the transformation has not been elucidated satisfactorily.

The fact that the transformation takes place so sharply in troilite, which does not contain excess of iron, is accounted for by the catalytic action of a small proportion of carbon it contains. G. S.

**Ferrous and Ferric Sulphides.** HENRY N. STOKES (*J. Amer. Chem. Soc.*, 1907, 29, 304—307).—Experiments are described which show that the precipitate obtained on adding alkali sulphides to solutions of ferric salts is not a mixture of ferrous sulphide and sulphur as is commonly stated, but consists of ferric sulphide. When the precipitate is treated with an alkaline solution of zinc hydroxide, ferric hydroxide and zinc sulphide are produced. Ferric sulphide is also formed on the addition of alkali polysulphides to solutions of ferrous salts. When ferric sulphide is boiled with water, it is converted into ferric hydroxide and hydrogen sulphide. If ferrous sulphide is treated with ammoniacal zinc chloride, no reaction takes place at the ordinary temperature, but at  $160$ — $170^{\circ}$  in a sealed tube a mixture of ferrous hydroxide and zinc sulphide is produced.

E. G.

**Action of Various Solutions on Pyrites and Marcasite.** HENRY N. STOKES. (*J. Amer. Chem. Soc.*, 1907, 29, 307—314).—When either pyrites or marcasite is heated in a sealed tube, the air having been displaced by carbon dioxide, with either lead or zinc carbonate and a solution of potassium hydrogen carbonate, a residue is obtained which contains ferric oxide and either lead or zinc sulphide, whilst thiosulphate is found in solution. When cupric or silver carbonate is employed, sulphate is found in solution and no other sulphur acid; in this case it is probable that thiosulphate is first formed, but is decomposed by the copper or silver salt. Treatment in a sealed tube with a solution of sodium carbonate in the absence of air produces only a partial conversion of the pyrites or marcasite into ferric oxide,

whilst in solution are found sodium sulphide, sodium thiosulphate, and a polysulphide of sodium. When, however, pyrites or marcasite is heated with a solution of an alkali carbonate in a platinum crucible placed in a platinum digester, the air of which has been displaced by carbon dioxide, and containing on the bottom a layer of either lead carbonate or cuprous oxide, the conversion into hematite is complete. The whole of the sulphur in pyrites is oxidised to sulphuric acid when heated with neutral copper chloride solution at  $200^{\circ}$  in the absence of air. The reaction between pyrites and marcasite and either cupric sulphate or lead chloride also results in the formation of sulphuric acid, but the sulphur is not completely oxidised, a portion remaining in the form of either a copper sulphide or galena. These results show that pyrites and marcasite are decomposed by circulating alkaline waters which carry away the sulphur in the form of alkali sulphide and thiosulphate and leave hematite or hydrated ferric oxide, but since this change occurs in the absence of free oxygen, the occurrence of ferric oxides as transformation products of pyrites is not in itself proof of the action of aerated water or other oxidising agents.

*Identification of Chalcocite.*—A fragment of chalcocite boiled for a moment with 10% ferric chloride solution, acidified with hydrochloric acid, becomes blue, whilst enargite remains unaltered in appearance by this treatment.

W. H. G.

**Roussin's Salts.** ITALO BELLUCCI and F. CARNEVALI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 654—662. Compare this vol., ii, 29).—The authors have prepared a number of ferronitrosulphides of the type  $\text{Fe}_4(\text{NO})_7\text{S}_3\text{R}'$ , some of which are described in the present paper. The tetramethylammonium and tetraethylammonium compounds differ from all the others which have been examined in being insoluble in ether and in possessing extraordinary stability, since they are not decomposed by boiling with 50% potassium hydroxide solution.

*Pyridine ferronitrosulphide*,  $\text{Fe}_4(\text{NO})_7\text{S}_3\text{H}, \text{C}_5\text{NH}_5$ , forms a black, shining, crystalline precipitate, soluble in alcohol, ether, or acetone and sparingly so in water.

*Aniline ferronitrosulphide*,  $\text{Fe}_4(\text{NO})_7\text{S}_3\text{H}, \text{NH}_2\text{Ph}$ , dissolves in nitrobenzene or aniline, to a moderate extent in water, alcohol, ether, or acetone, and sparingly in chloroform or benzene.

*Tetramethylammonium ferronitrosulphide*,  $[\text{Fe}_4(\text{NO})_7\text{S}_3]\text{NMe}_4$ , separates from acetone in black, triclinic crystals [F. ZAMBONINI.  $a : b : c = 0.8648 : 1 : 1.3125$ ;  $\alpha = 87^{\circ}29'34''$ ;  $\beta = 106^{\circ}7'10''$  and  $\gamma = 93^{\circ}44'10''$ ;  $D^{19} 2.056$ ], soluble in alcohol and slightly so in water.

*Tetraethylammonium ferronitrosulphide*,  $[\text{Fe}_4(\text{NO})_7\text{S}_3]\text{NEt}_4$ , is deposited from acetone in triclinic crystals [F. ZAMBONINI.  $a : b : c = 1.0221 : 1 : 1.0247$ ;  $\alpha = 85^{\circ}8'19''$ ,  $\beta = 97^{\circ}8'2''$  and  $\gamma = 99^{\circ}17'41''$ ;  $D^{18} 1.883$ ], slightly soluble in water, alcohol, or benzene.

*o-Phenylenediamine ferronitrosulphide*,  $[\text{Fe}_4(\text{NO})_7\text{S}_3\text{H}]_2, \text{C}_6\text{H}_4(\text{NH}_2)_2$ , is soluble in water, alcohol, acetone, or ether.

*Luteocobaltic ferronitrosulphide*,  $[\text{Fe}_4(\text{NO})_7\text{S}_3]_3\text{Co}(\text{NH}_3)_6$ , dissolves in alcohol, water, ether, or acetone.

T. H. P.

**Electrolytic Deposition of Nickel-Zinc Alloys.** EUGENE P. SCHOCH and ALCAN HIRSCH (*J. Amer. Chem. Soc.*, 1907, 29, 314—321).—Although zinc has a greater electrolytic solution tension than nickel, yet a bath which contains much more nickel than zinc yields an alloy containing far more zinc than nickel. The object of this investigation was to discover the cause of this phenomenon.

Four series of nickel-zinc alloys were made, the alloys being deposited on a lead cathode. For the four series the ratios of nickel to zinc in the electrolyte were radically different, but during each series the ratio was kept practically constant by running nickel and zinc anodes the necessary ampere hours. In general, it is found that the ratio of zinc to nickel (by equivalents) in the alloy is from 4.5 to 14 times their ratio in the electrolyte, according to the concentrations of the latter. When the solutions are fairly dilute and do not differ extensively in the relative concentrations of the nickel and the zinc salts, the cause produces a constant factor. For example, two solutions of about equal concentration were prepared; the ratio of nickel to zinc (by equivalents) in (a) was 0.29 : 1; in (b) 0.74 : 1. With current densities above 2 amperes the alloys obtained were practically of constant composition. The alloy obtained from (a) with C.D. = 3 amperes contained 4.6% of nickel; hence the ratio of zinc to nickel (by equivalents) in the alloy equals 5.4 times their ratio in the electrolyte. The alloy obtained from (b) with the same current density contained 11.2% of nickel; hence the ratio of zinc to nickel (by equivalents) in the alloy equals 5.3 times their ratio in the electrolyte. The authors are unable at present to say anything as to the nature of the cause itself.

W. H. G.

**Nickel-Tin Alloys.** LÉON GUILLET (*Compt. rend.*, 1907, 144, 752—753. Compare Vigouroux, this vol., ii, 354).—Nickel and tin are capable of forming four solid solutions and one compound. (1) A magnetic solution  $\alpha$  containing 0—5% of tin; (2) a non-magnetic solution  $\alpha$  containing 0—5% of tin; (3) a solution  $\beta$  containing 38—41% of tin; (4) a solution  $\gamma$  containing 55—60% of tin; (5) the compound NiSn which forms crystals visible to the naked eye. Other alloys slowly cooled are constituted as follows. Those containing 5—38% of tin are formed of the solution  $\alpha$ , or of the solution  $\beta$  containing the eutectic  $\alpha$ — $\beta$ ; those containing 41—55% of tin, of the solutions  $\beta$  and  $\gamma$ ; those containing 60—67% of tin, of the solution  $\gamma$  and the compound NiSn, and finally those containing 65—100% of tin, of the compound NiSn, or of tin containing the eutectic  $\gamma$ —Sn. The alloys containing less than 38% of tin are only magnetic at the ordinary temperature, possess transformation points corresponding with their passage into the non-magnetic state, and all contain the solution  $\alpha$  (either in a free or eutectic state), which is the sole magnetic constituent of the nickel-tin alloys. The alloys formed of the solution  $\alpha$  and those formed of tin and the eutectic Sn— $\gamma$  are ductile and possess the mechanical properties of nickel or tin; all the others, except those containing more than 90% of tin, are extremely hard or fragile, the solution  $\alpha$  being the most fragile.

E. H.

**Higher Oxide of Nickel.** ITALO BELLUCCI and E. CLAVARI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 647—654. Compare Abstr., 1905, ii, 823).—Fresh evidence is adduced in support of the non-existence of an oxide of nickel having the formula  $\text{Ni}_2\text{O}_3$ . The work of Zedner (Abstr., 1906, ii, 65, 595) and that of Riesenfeld (Abstr., 1906, ii, 723) are criticised.

T. H. P.

**Preparation and Properties of a New Variety of Chromium.** ARMAND BINET DU JASSONNEIX (*Compt. rend.*, 1907, 144, 915—917).

—Chromium boride (this vol., ii, 30, 95), together with a large excess of copper, is heated at the boiling point of the latter metal for three to four minutes in a magnesia crucible in an electric furnace. Through the copper ingot obtained, a brilliant, white metal is disseminated in the form of thin filaments or snow-like crystals. From this ingot, nitric acid dissolves the copper and a small quantity of chromium, but no boron, and leaves a spongy, black mud, which, when washed with water, suddenly acquires a brilliant, metallic appearance, whilst the wash-waters become deep brown. The spongy, metallic residue is composed of very fine felted filaments, and crystals grouped in star- or fern-like forms. It contains 1—2% of boron, which is removed by a second fusion with copper. The chromium so prepared has the appearance described above and  $D^{17} 7.1$ . It shows the chemical properties of pure fused chromium (Moissan, Abstr., 1894, ii, 452), but is more reactive. It is not oxidised by the air at the ordinary temperature, but in contact with a flame it ignites and burns like tinder. When heated to whiteness in nitrogen, it gives a friable, bronze-coloured mass containing 80—90% chromium, and dissolving in hot hydrochloric acid with evolution of hydrogen and nitrogen and formation of a small quantity of ammonium chloride. It is attacked by cold concentrated hydrochloric acid, violently by concentrated sulphuric acid, but not by nitric acid. When dissolved in hydrochloric acid, it leaves a slight residue of fused chromium oxide, very dense, and of a deep green colour. The brown wash-waters (above), after filtration, retain their opacity for several months, but when treated with acid or ammonium chloride they rapidly give an amorphous, black precipitate. When evaporated to dryness they give a brownish-black, mirror-like deposit. Both precipitate and deposit behave like Férée's protoxide (Abstr., 1901, ii, 513). Probably both this and the green oxide are formed by the oxidation of chromium by the gases dissolved in copper at high temperatures.

E. H.

**Isomerism of Chromium Sulphates and the "Masked State."** ALBERT COLSON (*Bull. Soc. chim.*, 1907, [iv], 1, 438—446. Compare Abstr., 1905, ii, 94, 255, 460, 592; 1906, ii, 74, 233; this vol., ii, 177, 267, 356).—The normal green chromium sulphates are divided into three classes, according as three (trebly masked sulphates), two (doubly masked sulphates), or one (singly masked sulphates) of their acid radicles are not precipitated by solution of barium chloride in the cold. The trebly masked sulphates have the formula  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ , and are further characterised by a heat of formation,

in solution, of 33,000 cals. The doubly masked sulphates have the formula  $\text{Cr}_2(\text{SO}_4)_3 \cdot 7.5 \text{H}_2\text{O}$  or  $\text{Cr}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ , and have the heat of formation in solution 36,000 cals. The singly masked sulphates are not obtainable pure, but have the heat of formation 43,500 cals. in the dissolved state.

The author accepts the facts stated by Wyruboff (Abstr., 1902, ii, 565) as to the masked state of the acid radicles in these and other chromium salts, but rejects his explanation of this phenomenon, which presupposes a difference in constitution between esters and salts which does not exist. It is suggested that the masking of each acid radicle is due to the admission into the molecule of 1 mol. of water and the formation of such a grouping as  $(\text{OH}) \cdot \text{Cr} \cdot (\text{HSO}_4)$ , and this view is in harmony with the physical constants for solutions of these salts already recorded (*loc. cit.*).  
T. A. H.

**Chromium Trioxide.** MAURICE R. READ (*Chem. News*, 1907, 95, 169).—When gently heated in a current of hydrogen or coal-gas, chromium trioxide is converted into a semi-fused powder, grey in the central portions, purple at the ends, and beneath these a layer of green chromic oxide. Similarly, when heated in a stream of carbon dioxide, the trioxide yields a small quantity of a brownish-purple substance resembling that mentioned above, but there is no combustion in the tube as when hydrogen or coal-gas are employed. When heated in nitrogen, the trioxide is converted into a dull blue substance, dark green beneath. The purple, brownish-purple, and blue residues above mentioned, as well as chromium trioxide, when introduced into a Bunsen flame emit a brilliant, white light. A similar livid whiteness is obtained by passing the vapour of chromyl chloride into a non-luminous flame.  
W. H. G.

**A New Tungsten Silicide,  $\text{WSi}_2$ .** ED. DEFACQZ (*Compt. rend.*, 1907, 144, 848—851).—This silicide was prepared by heating copper silicide with amorphous tungsten in an electric furnace, using a current of 800—900 amperes at 50 volts (compare Lebeau, Abstr., 1899, ii, 427) and washing the resulting product successively with nitric acid, sodium hydroxide solution, warm hydrofluoric acid, and water. The crystals having a lower specific gravity than 3.4 (principally carbon silicide) were eliminated by washing with methylene iodide. The same product may also be obtained by reducing a mixture of silica and tungstic anhydride with sulphur and aluminium (compare Hollemann, Abstr., 1904, ii, 813), the crystals being isolated from the button produced by the method already described, nitric acid being replaced by hydrochloric acid.

The silicide,  $\text{D}^0 9.4$ , is dimorphous, and when prepared by the second method occurs in brilliant, bright, grey, prismatic needles, but when obtained from copper silicide forms masses of brilliant, grey crystals. It is not magnetic, and remains unaltered at  $900^\circ$  in air, is decomposed by copper at  $1200^\circ$ , forming copper silicide and tungsten, and is not affected by sulphuric acid or *aqua regia*, but is attacked by a mixture of hydrofluoric and nitric acids, yielding tungstic anhydride as a residue. Fused alkali hydroxides or carbonates convert it into the alkali sili-

cate and tungstate, but melted potassium hydrogen sulphate is without action. Dry chlorine attacks the silicide easily at about  $450^{\circ}$ , yielding a mixture of silicon tetrachloride and tungsten hexachloride, and this reaction is utilised for the analysis of the compound, the mixed chlorides being condensed, decomposed by water, and from the residue, dried at  $125-130^{\circ}$ , the silica and tungstic anhydride may be separated by Marignac's process (fusion with potassium hydrogen sulphate), or by the method described by Friedheim, Henderson, and Pinegal (Abstr., 1905, ii, 614).

The author points out that it is necessary, in preparing the silicide, to follow his directions implicitly, as under different conditions other crystalline silicides are formed, which are still under investigation. Crystalline silicides of molybdenum have also been obtained by these methods.

T. A. H.

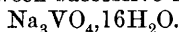
**Composition and Some Properties of the Normal Uranyl Chromate.** N. A. ORLOFF (*Chem. Zeit.*, 1907, 31, 375).—A saturated solution of uranium trioxide in chromic acid yields, on evaporation, yellow needles of the *normal uranyl chromate*,  $\text{UO}_2\text{CrO}_4 \cdot 3\text{H}_2\text{O}$ . At  $15^{\circ}$ , 1 part of this salt dissolves completely in 13.3 parts of water, forming a pure yellow solution, which on evaporation at  $100^{\circ}$  gives an amorphous, brown mass, soluble in water to a brown solution. Uranyl chromate dissolves slowly in alcohol at the ordinary temperature; this solution decomposes on boiling, also when exposed to the action of sunlight, with the separation of a brown precipitate. The filtrate from this precipitate when evaporated to dryness yields an amorphous, brown mass, partially soluble in water; it probably consists of a mixture of uranyl chromate and chromous uranate. Potassium chromate added to an aqueous solution of uranyl chromate precipitates the *basic salt*,  $\text{UO}_3 \cdot 2\text{UO}_2\text{CrO}_4 \cdot 8\text{H}_2\text{O}$ ; when uranyl acetate is employed, the *basic salt*,  $\text{UO}_3 \cdot \text{UO}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$ , is obtained. The formation of the basic salt points to the conclusion that in solution, uranyl chromate behaves as a mixture of uranic and chromic acids.

W. H. G.

**Complex Compounds of Quinquevalent Vanadium and Quadrivalent Elements. II. Compounds of Sodium Stannate with Sodium Orthovanadate, Sodium Orthophosphate, and Sodium Orthoarsenate.** WILHELM PRANDTL and OSKAR ROSENTHAL (*Ber.*, 1907, 40, 2125—2133. Compare Abstr., 1905, ii, 395).—An amorphous, yellow *substance*,  $3\text{SnO}_2 \cdot \text{V}_2\text{O}_5 \cdot \text{Na}_2\text{O} \cdot x\text{H}_2\text{O}$  or  $4\text{SnO}_2 \cdot \text{V}_2\text{O}_5 \cdot \text{Na}_2\text{O} \cdot x\text{H}_2\text{O}$ , is obtained when a solution of sodium orthovanadate and stannic chloride or sodium stannate is carefully neutralised. By cooling or diluting a solution of stannic vanadate in hot concentrated sodium hydroxide, *substances* crystallising in white, glistening needles are obtained; the same compounds are formed when a solution containing sodium stannate and sodium orthovanadate is crystallised, or by fusing tin dioxide, vanadium pentoxide, and sodium hydroxide, and crystallising the fused mass. These substances are *sodium stannovanadates*, members of a series the compositions of which

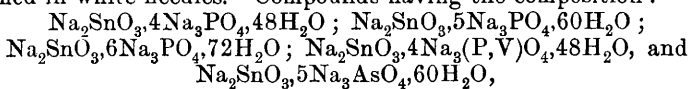


lie between  $\text{Na}_2\text{SnO}_3, 3\text{Na}_3\text{VO}_4, 32\text{H}_2\text{O}$  and  $\text{Na}_2\text{SnO}_3, 6\text{Na}_3\text{VO}_4, 80\text{H}_2\text{O}$ , the constant difference between successive members being



These substances all form double-refracting, transparent, rhombic crystals of arragonite habit; the particular member obtained in the preceding preparations depends on the concentration of the constituents and on the temperature.

Analogous potassium or ammonium salts have not been obtained, but by mixing sodium stannate and sodium phosphate or arsenate in alkaline solution, or by dissolving stannic phosphate or arsenate in sodium hydroxide, *substances* similar to the stannovanadates are formed in white needles. Compounds having the composition:

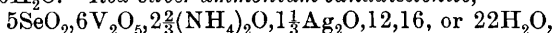


have been thus prepared.

C. S.

**Vanadium Selenium Compounds.** WILHELM PRANDTL and FRITZ LUSTIG (*Zeitsch. anorg. Chem.*, 1907, 53, 393—412).—The paper contains an account of *vanadiselenious acid*,  $3\text{V}_2\text{O}_5, 4\text{SeO}_2, 4\text{H}_2\text{O}$ , and of certain well-defined red and yellow alkali salts of this acid which have been already described (*Abstr.*, 1905, ii, 395). Some other red and a few orange-coloured salts have also been prepared.

*Red lithium vanadiselenite*,  $5\text{SeO}_2, 6\text{V}_2\text{O}_5, 4\text{Li}_2\text{O}, 30\text{H}_2\text{O}$ , is very soluble in water; in a vacuum over sulphuric acid it loses  $22\text{H}_2\text{O}$  and at  $100^\circ$ ,  $26\text{H}_2\text{O}$ . *Red silver-ammonium vanadiselenite*,



obtained by interaction of silver nitrate and excess of red ammonium vanadiselenite, forms long, flat, rectangular, glistening, black crystals. *Red sodium vanadiselenite*,  $5\text{SeO}_2, 6\text{V}_2\text{O}_5, 4\text{Na}_2\text{O}, 20\text{H}_2\text{O}$ , is very soluble in water, and decomposes partially after a time with formation of sodium trivanadate,  $\text{Na}_2\text{O}, 3\text{V}_2\text{O}_5, 5\text{H}_2\text{O}$ .

Orange-coloured salts of vanadiselenious acid were obtained by the action of excess of selenious acid on the alkali vanadates at a high temperature, and subsequent evaporation. The formulæ of these salts are complicated, and vary somewhat with the proportions in which the components are used. Two sodium salts had the respective formulæ  $12\text{SeO}_2, 7\text{V}_2\text{O}_5, 2\text{Na}_2\text{O}, x\text{H}_2\text{O}$  and  $10\text{SeO}_2, 7\text{V}_2\text{O}_5, 2\text{Na}_2\text{O}, 13\text{H}_2\text{O}$ , whilst the potassium salts obtained from four solutions of the components in varying proportions had a different formula in each case.

All the vanadiselenites lose selenious acid on boiling with water, and they are therefore to be regarded as loose compounds of alkali vanadates with selenious acid in varying proportions.

G. S.

**A New Chloride of Tantalum.** CAMILLE CHABRIÉ (*Compt. rend.*, 1907, 144, 804—806).—By the reduction of tantalum pentachloride with sodium amalgam, the author has obtained a *tantalum dichloride*,  $\text{TaCl}_5, 2\text{H}_2\text{O}$ , in the form of an emerald-green, microcrystalline powder. The substance has a spectrum identical with that of tantalic anhydride, it is soluble in water when freshly prepared, but

on keeping in the air it is transformed into a brown substance without losing its crystalline form. When heated to redness on platinum foil, it decomposes with incandescence, leaving a residue of tantalum pentoxide. On treatment with nitric acid (at  $100^{\circ}$ ), not tantalic acid, but a reddish-brown powder is formed. The latter appears to be an intermediate oxidation product between tantalum pentoxide and dioxide, since it is reduced by stannous chloride and hydrochloric acid to the original green substance, and is oxidised on heating to the pentoxide. Nitric acid or bromine water turns the green solution of the chloride yellow, and the colour is restored by stannous chloride. Prolonged action of bromine water gives tantalum pentoxide. E. H.

**Columbium, its Preparation and Properties.** WERNER VON BOLTON (*Zeitsch. Elektrochem.*, 1907, 13, 145—149).—Pure columbium pentoxide was moulded into filaments (by mixing it with a little paraffin) and these were heated to whiteness for four or five hours in carbon powder. The filaments of tetroxide obtained in this way conduct electricity. When such a filament is heated to whiteness in a vacuum by a direct current it is but little changed, a small portion at the positive end only being reduced to metal. By using an alternating current, however, the filament is converted into the metal in a quarter of an hour. This method yields very small quantities of the metal. Larger quantities were prepared as follows: columbium pentoxide and powdered aluminium react together when the mixture is heated at one point, yielding a hard, metallic regulus of sp. gr. 7.5, and containing 2.8% to 3.2% of aluminium as well as some unchanged oxide. By heating this material in a vacuum (a current of 185 amperes at 40 volts for fifteen hours is required for 20 grams of metal) the whole of the impurities are vaporised, leaving perfectly pure columbium.

The pure metal has the following properties. The specific heat between  $21^{\circ}$  and  $100^{\circ}$  is 0.071, which gives 6.67 for the atomic heat. The specific gravity is 12.7 or 12.75 after rolling into thin foil. The electrical resistance of a wire 1 metre long and 1 sq. mm. cross section is 0.187 ohm; this was found to increase with the temperature. The hardness of the metal is about the same as that of wrought iron. It can be hammered out into foil 0.05 mm. thick, and it is possible, although rather difficult, to draw it into wire; it can be welded at a red heat.

In 10% sulphuric acid a columbium anode does not allow current to pass even at a pressure of 120 volts. This behaviour is being utilised in the construction of an electrolytic transformer. The pure metal has a coarsely crystalline structure. It volatilises to a considerable extent when heated in a vacuum; during the purification process about a quarter of it vaporises along with the impurities. Its melting point is  $1950^{\circ}$ . When heated in an atmosphere of hydrogen, the metal is converted into a dark grey powder containing 1.12% of hydrogen, corresponding with the compound  $\text{CbH}$ . The metal is oxidised very slowly by oxygen, owing to the formation of a skin of oxide. It decomposes ammonia yielding a nitride. The carbide, with 3% carbon, is very hard and brittle. The metal is insoluble in nitric, hydrochloric, and sulphuric acids, or in *aqua regia*; it dissolves slowly

in hydrofluoric acid, rapidly in contact with platinum. Aqueous solutions of the alkalis have no action, but fused alkalis or potassium nitrate dissolve it, forming columbates. Sulphur and selenium react violently when heated with columbium. Columbium does not dissolve in mercury, but it alloys with iron in all proportions. Chlorine, at a red heat, yields the pentachloride. T. E.

**Observations on a Property of Moissan's Platinum Amalgam.** PAUL LEBEAU (*Compt. rend.*, 1907, 144, 843—845).—The author confirms Moissan's observation (*ibid.*, 593) that platinum amalgam when shaken with various liquids has the property of forming semi-solid, buttery masses of much greater volume than that of the original amalgam. Similar masses are formed by calcium or lithium amalgams when shaken with benzene or carbon tetrachloride. The product formed by the action of lithium amalgam on carbon tetrachloride decomposes in a few minutes, producing lithium chloride and carbonaceous matter. The amalgams of the other metals of the platinum group do not exhibit this phenomenon. The property is shown by platinum amalgam containing as little as 0.038% of platinum when shaken with water, and is destroyed by mixing it with amalgam of zinc, calcium, lead, or tin. The volume of the mass formed is dependent not only on the nature of the liquid, but also on the state of the platinum from which the amalgam was made, being much greater when the latter is finely divided, although even in this case the effect is diminished if the metal be strongly heated before the amalgam is made. Microscopic examination of sections cut from the mass, obtained by shaking platinum amalgam with a solution of gelatin and then cooling to the freezing point of mercury, show that it has a structure similar to that of soap lather, so that it is probably due entirely to surface tension. T. A. H.

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## Mineralogical Chemistry.

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**Artificial Coloration of Minerals.** PAUL GAUBERT (*Compt. rend.*, 1907, 144, 761—763).—Minerals of the serpentine group, especially chrysotile and pilolite, absorb not only basic colouring matters, but also the acid colours, picric and picramic acids, and potassium and ammonium picrates. When, however, the minerals have been previously heated to redness, methylene-blue is absorbed, but not picric or picramic acid or fluorescein. Different coefficients of absorption of light are observed in different faces of artificially coloured crystals of phthalic acid and chrysolite, according to their various indices, thus showing that the colour is not due to a chemical combination. Absorption of methylene-blue by chrysolite proceeds best in the transverse section of the fibre; fibres of this mineral 3 cm. long by 0.5 cm. diameter require at least three days for the complete penetration of the dye, and the quantity of dye absorbed amounts to

1/180 of the weight of the crystal. The amount of colour absorbed and rate of absorption vary with the dye, and the mineral is coloured less rapidly after heating to redness for some seconds. The author concludes that the artificial coloration of chrysotile and other crystalline minerals is a purely physical phenomenon (compare Suida, *Abstr.*, 1905, i, 75). E. H.

**New Method of Representing van't Hoff's Investigations on Oceanic Salt Deposits.** III. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1907, 53, 319—326. Compare *Abstr.*, 1906, ii, 833; this vol., ii, 278).—With the present paper, which is illustrated by several diagrams, the author concludes his discussion of the problem in question; he mentions that van't Hoff considers his method a welcome simplification. G. S.

**Composition of Molybdic Ochre.** WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1907, [iv], 23, 297—303).—The mineral molybdite, or molybdic ochre, which has hitherto been supposed to be molybdenum trioxide, is proved to be a hydrous ferric molybdate,  $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ . The mineral has a fibrous structure and sometimes occurs in radiating groups; its colour is yellow, and the lustre is often silky. The fibres are strongly birefringent with straight extinction; the pleochroism is strong with marked absorption (pale yellow for vibrations across the fibres, and deep yellow to almost black for vibrations parallel to the fibres). The following analyses are given of material free from admixed limonite: I, from Westmoreland, New Hampshire (the mean of three analyses made on the largest amount of the more pure material); II, from Telluride, Colorado; III, probably from California; IV, from Renfrew, Ontario. At  $110^\circ$  there is a loss of  $6\text{H}_2\text{O}$ , and the remainder is expelled below  $200^\circ$ . When heated, the mineral exhibits a remarkable series of changes in colour (grey, light yellow, dark orange, green).

	$\text{MoO}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{H}_2\text{O}$ .	Insol.	Total.
I.	57.69	21.08	17.62	4.66	101.05
II.	59.3	19.0	15.8	[5.9]	100.0
III.	47.7	15.8	15.4	24.0	102.9
IV.	55.7	17.3	15.5	9.4	97.9

Artificial molybdenum trioxide has a platy structure, and is colourless and non-pleochroic; it is thus quite distinct from the natural molybdic ochre. Attempts to prepare hydrous ferric molybdate in a crystallised condition were not altogether successful, but some yellow pleochroic needles, apparently identical with the natural mineral, were obtained, together with other crystallised products. The precipitate formed when a solution of a ferric salt is added to ammonium molybdate appears to consist of mixtures of  $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot n(3\text{H}_2\text{O})$  with molybdic acid and water. L. J. S.

**Origin of Dolomite.** F. W. PFAFF (*Jahrb. Min., Beil.-Bd.*, 23, 529—580).—A detailed review of the literature is given, with many analyses of dolomitic limestones, &c. Dolomite is formed artificially

by the action of a solution of a magnesium salt on calcium carbonate and anhydrite in the presence of sodium chloride at pressures of 40—200 atmospheres; with a dilute solution, magnesian limestone results, whilst with a concentrated solution, normal dolomite is formed.

L. J. S.

**Apatite from Epprechtstein in Bavaria and Luxullian in Cornwall.** KARL WALTER (*Jahrb. Min.*, 1907, *Beil.-Bd.*, 23, 581—643).—A detailed description is given of material from these two localities, at both of which the mode of occurrence is very similar. The mineral occurs as brilliant, transparent crystals, rich in faces, associated with tourmaline, lithia-mica, &c., in cavities in granite, and is of pneumatolytic origin. Analysis I is of bluish-grey crystals with green and blue zoning from Epprechtstein; II—IV of blue and yellow-zoned crystals from Luxullian; II of blue material, and III and IV of yellow. All these analyses of fluor-apatite correspond closely with the formula  $\text{Ca}_5\text{P}_3(\text{F}, \text{Cl}, \text{OH})\text{O}_{12}$ .

	$\text{P}_2\text{O}_5$ .	CaO.	MgO.	$\text{Al}_2\text{O}_3$ .	FeO.	MnO.	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	F.	Cl.	$\text{H}_2\text{O}$ .	Insol. F & Cl.	Total (less O for Insol. F & Cl.)
I.	41.18	53.63	0.16	0.22	0.45	0.79	1.03	0.95	2.41	0.04	0.37	0.29	100.49
II.	41.16	54.03	0.15	0.19	0.21	0.39	1.07	1.11	2.60	0.07	0.35	0.27	100.49
III.	40.78	52.40	0.27	0.15	0.27	1.74	1.05	1.09	2.63	0.10	0.36	0.30	100.01
IV.	40.58	50.53	0.43	0.20	0.33	4.10	0.92	0.96	2.53	0.13	0.40	0.34	100.35

Detailed crystallographic and optical determinations are given; the values obtained for the material analysed are:

	$\omega(\text{Na})$ .	$\epsilon(\text{Na})$ .	$\omega - \epsilon$ .	$\alpha : c$ .
I.	1.6338	1.6323	0.0015	} 1 : 0.73381
II.	1.6337	1.6322	0.0015	
III.	1.6375	1.6359	0.0016	
IV.	1.6426	1.6409	0.0017	

The optical constants are compared with those of other apatites (compare *Abstr.*, 1902, ii, 330); they appear to vary with the amount of manganese present.

L. J. S.

**Podolite, a New Mineral.** WLADIMIR TSCHIRWINSKY (*Centr. Min.*, 1907, 279—283).—The phosphorite nodules, which are of wide distribution in the glauconitic sands of the Cretaceous formation in govt. Podolia, South Russia, contain in their cavities minute hexagonal crystals of prismatic habit with the composition given under I. Analysis of one of the phosphorite nodules gave II.:

	CaO.	$\text{P}_2\text{O}_5$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{CO}_2$ .	F.	$\text{SiO}_2$ .	Organic matter.	Total.
I.	51.15	39.04	—	3.04	—	—	3.90	nil	—	—	97.13
II.	51.31	36.44	0.46	1.73	0.45	0.66	4.18	0.26	4.87	0.56	100.92

The water-clear crystals are optically anomalous like apatite; they have a mean refractive index of 1.635, and birefringence  $\gamma - \alpha = 0.0075$ ;  $D_{3077}$ . The mineral also occurs in a spherulitic form. The above analyses correspond with the formula  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$ , which resembles that of apatite, but has  $\text{CaCO}_3$  in place of  $\text{Ca}(\text{F}, \text{Cl})_2$ . Like

staffelite (Abstr., 1906, ii, 35), podolite has probably been formed by the action of carbonated waters on fluor-bearing phosphorite.

The same crystallised mineral had previously been described by PETER TSCHIRWINSKY (*Ann. géol. min. Russ.*, 1906, 8, pts. 8-9) from the phosphorites of govt. Kursk, and named *carbapatite*, which name is now withdrawn and preference given to *podolite*. L. J. S.

**Constitution and Genesis of Iron Sulphates. VI. Coquimbite, Römerite, Copiapite.** RUDOLF SCHARIZER (*Zeitsch. Kryst. Min.*, 1907, 43, 113-129).—A solution of ferric hydroxide in excess of sulphuric acid ( $\text{SO}_3 : \text{Fe}_2\text{O}_3 > 3 < 4$ ), when evaporated and allowed to dry, gives a mixture of coquimbite,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , and the acid ferric sulphate,  $\text{Fe}_2\text{S}_4\text{O}_{15} \cdot 9\text{H}_2\text{O}$ , D 2.172 (Abstr., 1902, ii, 143). On exposing this mixture to moist air and washing with alcohol, the bluish-violet coquimbite was isolated as hexagonal plates, D 2.116. The artificial coquimbite loses  $6\text{H}_2\text{O}$  at  $100^\circ$ ,  $1\text{H}_2\text{O}$  at  $124^\circ$ , and  $2\text{H}_2\text{O}$  at about  $130^\circ$ ; during the process of heating, the temperature remains stationary for a time at  $100^\circ$  and  $124^\circ$  (compare F. Rinne, Abstr., 1900, ii, 202). Natural coquimbite from Chili loses its water at slightly different temperatures, although here also  $7\text{H}_2\text{O}$  is lost up to  $124^\circ$ ; the formula of coquimbite is therefore written as  $\text{SO}_4[\text{Fe}(\text{OH}) \cdot \text{SO}_4\text{H}]_2 \cdot 7\text{H}_2\text{O}$ .

A neutral solution of ferric sulphate, or of coquimbite, does not deposit coquimbite, but a mixture of yellowish-green copiapite,  $\text{Fe}_4\text{S}_5\text{O}_{21} \cdot 18(\text{or } 16)\text{H}_2\text{O}$ , and white spherulites of the acid ferric sulphate,  $\text{Fe}_2(\text{OH})_2(\text{SO}_4\text{H})_4 \cdot 6\text{H}_2\text{O}$ . Römerite (Abstr., 1903, ii, 555) decomposes in moist air to ferrous and ferric sulphates, the latter giving copiapite and acid sulphate. L. J. S.

**Tungsten Minerals at Genna Gurèu, between Nurri and Orroli (Cagliari).** DOMENICO LOVISATO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 632-638).—The author describes specimens of scheelite found in the mineral beds at Genna Gurèu. Its hardness is less than 5,  $D^{445} 5.987$ , and its composition :

$\text{WO}_3$ .	$\text{CaO}$ .	$\text{Fe}_2\text{O}_3$ .	$\text{SiO}_2$ .	$\text{MgO}$ .	Total.
80.42	19.60	0.07	traces	faint traces	100.09

The most remarkable feature of the mineral is the absence of molybdenum, which has been found in all samples of scheelite previously examined. Cerium, didymium, and lanthanum are also absent, although they seem to occur in the scheelite of Traversella. At Genna Gurèu, the scheelite is accompanied by meymacite.

T. H. P.

**Marignacite, a New Variety of Pyrochlore from Wisconsin.** SAMUEL WEIDMAN and VICTOR LENHER (*Amer. J. Sci.*, 1907, [iv], 23, 287-292).—The mineral occurs as small, light to dark brown octahedra in a pegmatite composed of quartz, felspar, and aegirite

near Wausau in Wisconsin. The crystals are optically anomalous ; D 4·13. Analyses gave :

Ch <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	Ce <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	ThO <sub>2</sub> .
55·22	5·86	3·10	2·88	0·50	0·02	13·33	5·07	0·20

CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	F.	H <sub>2</sub> O (above 110°).	H <sub>2</sub> O (below 110°).	Total.
4·10	0·16	2·52	0·57	nil	5·95	0·45	99·93

Also traces of Al<sub>2</sub>O<sub>3</sub>, MnO, SnO<sub>2</sub>, WO<sub>3</sub>, Di<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>.

Marignacite thus differs from other members of the pyrochlore group in containing more cerium and yttrium and less calcium and iron ; also in the presence of a little silica, suggesting a relation to the titano-silicates. The water, no doubt, represents hydroxyl isomorphously replacing fluorine, which is here absent. L. J. S.

**Minerals of the "Micaceous Zeolite" Group.** FELIX CORNU (*Tsch. Min. Mitt.*, 1907, 25, 513—521).—The author has previously suggested that gyrolite and zeophyllite might be identical, since in both the thin plates with pearly cleavage are rhombohedral and form very similar radial aggregates ; he now finds, however, from the following approximate analyses and determinations of the D and refractive index ( $\omega$ ) that they are distinct minerals. Analyses I—III (I, of material from Skye ; II, from Poonah ; III, from Böhmisch-Leipa) are of gyrolite, and IV, of zeophyllite from Radzein, Bohemia :

	SiO <sub>2</sub> .	CaO.	Al <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub>	Total.	Sp. gr.	$\omega$ .
I.	51·99	32·02	—	12·0	96·81	2·420	1·54—1·55
II.	52·63	32·23	—	12·0	97·83	2·342—2·410	1·546
III.	52·89	32·35	—	13·0	98·30	2·397	1·542
IV.*	38·82	43·44	2·16	8·0	98·51	—	—
V.	53·31	32·22	3·27	6·0	95·98	2·499—2·578	1·564

\* Also : MgO, 0·26 ; F, 48 % ; total, less O for F.

Two other minerals, indistinguishable in external appearance from gyrolite and zeophyllite, are added to this group of "micaceous zeolites." One of these, for which the name *reyerite* is proposed, has the composition given under V ; the specimens examined were collected in Greenland by C. L. Giesecke in 1807—1813, and the mineral is probably identical with that referred to by him as "Glimmerzeolith." The fourth member of the group, as yet incompletely determined, was observed as rosettes of six-sided plates with perfect cleavage and  $\omega = 1·536$  in crevices in a shonkinite in Baden. L. J. S.

**Albite from Nurra, Sardinia.** CARLO M. VIOLA (*Zeitsch. Kryst. Min.*, 1907, 43, 202—209).—Crystals of albite occur in the cavities and crevices of a hornblende-dabase between Porto-Torres and Capo Argenteria in the Nurra district. Analysis by H. Steinmetz gave :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Total.	Sp. gr.
67·16	17·57	4·52	1·07	9·51	99·83	2·623



corresponding with  $10\text{NaAlSi}_3\text{O}_8$  (albite) +  $1\cdot3\text{KAlSi}_3\text{O}_8$  (orthoclase) +  $5\text{CaSiO}_3$ . The calcium is therefore not present as anorthite, and it is considered to be an impurity; when the powdered mineral is digested with hydrochloric acid, 3·5% CaO goes into solution and a little gelatinous silica separates. A few earlier analyses of feldspars exhibiting this peculiarity are cited.

Optical and crystallographic determinations are given: the refractive indices for sodium-light are  $\alpha = 1\cdot5281$ ,  $\beta = 1\cdot5320$ ,  $\gamma = 1\cdot5383$ .

L. J. S.

**Tschernichewite, a New Amphibole.** LOUIS DUPARC and FRANCIS PEARCE (*Compt. rend.*, 1907, 144, 763—764).—This mineral occurs as small, acicular crystals, together with octahedra of magnetite and a little hæmatite, in a quartzite near Verkne-Tschouwal in the northern Urals. It is defined by its optical characters: the plane of the optic axes is perpendicular to the plane of symmetry and the axial angle is near  $90^\circ$ ;  $\gamma : c' = 4^\circ$ ; the pleochroism is very strong. These characters point to an amphibole rich in iron and sodium.

L. J. S.

**Lawsonite.** ARTHUR S. EAKLE (*Bull. Dept. Geol. Univ. California*, 1907, 5, 81—94).—Lawsonite from the original locality, namely, Tiburon Peninsula, California (Abstr., 1896, ii, 370), was described as occurring embedded in margarite veins in amphibole-schist; the following analysis (I, by E. S. Larsen) of this supposed margarite proves it, however, to be muscovite. Lawsonite is recorded as a rock-forming mineral, occurring especially in connexion with glaucophane-schists, from several localities in California. Analysis II is of thin tabular crystals occurring with muscovite in a chloritic boulder on the Berkeley Hills; the analysis is incomplete, since the colourless mineral is strongly impregnated with chlorite:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total
I.	48·42	28·41	—	2·10	0·48	3·81	10·36	1·95	4·72	100·25
II.	38·43	33·39	—	—	16·85	—	—	—	9·83	98·50

Lawsonite appears to be a product of metamorphism of the soda-lime-feldspars of basic rocks, the soda going to form glaucophane and the lime to form lawsonite.

The paper also contains crystallographic notes on some other Californian minerals and of calcite from Terlingua, Texas. L. J. S.

**Meteorite from Rich Mountain, North Carolina.** GEORGE P. MERRILL, with analyses by WIRT TASSIN (*Proc. U.S. National Mus.*, 1907, 32, 241—244).—This meteoric stone, weighing 668 grams, was seen to fall in Jackson Co., N.C., in 1903. It has an indistinct chondritic structure, and, besides olivine, enstatite, and a little monoclinic pyroxene, it contains a colourless silicate which is probably

identical with maskelynite. Analysis of the metallic portion (I) and of the soluble (II) and insoluble (III) silicates gave :

I.			II.						
Fe.	Ni.	Co.	S.	F.	SiO <sub>2</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.
7.07	0.73	0.031	1.42	0.03	18.28	9.06	0.50	0.99	18.16

III.								
SiO <sub>2</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Fe <sub>3</sub> O <sub>4</sub> . (magnetite).	C (graphite).	K <sub>2</sub> O.	Na <sub>2</sub> O.
23.00	4.92	2.10	1.51	8.27	0.15	0.015	0.16	0.68

These numbers correspond with the following mineralogical composition : nickel-iron, 7.831 ; troilite, 3.89 ; schreibersite, 0.20 ; olivine, 46.99 ; insoluble silicates (enstatite, &c.), 40.67 ; magnetite, 0.15 ; graphite, 0.15 = 99.736.

L. J. S.

**Amount of Arsenic in the Max Spring at Bad Dürkheim a. d. Haardt.** ERICH EBLER (*Ber.*, 1907, 40, 1804—1807).—The sediment obtained when the clear water from the Max Spring is exposed to the air contains 10.7% of arsenious oxide. One litre of the fresh, clear water contains some 17.4 mg. of arsenious oxide in solution, and yields a decided precipitate with hydrogen sulphide. One gram of sediment is obtained from 5 litres of water, and in the course of a day 20 kilos. of sediment containing 2 kilos. of arsenic are deposited.

J. J. S.

## Physiological Chemistry.

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**Hæmolysis by Substances in Homologous Series.** HERMANN FÜHNER and ERNST NEUBAUER (*Arch. exp. Path. Pharm.*, 1907, 56, 333—345).—The experiments were performed with alcohols, urethanes, amines, fatty acids, and other substances in homologous series. A parallelism was found between their hæmolytic action and their physico-chemical properties, such as similar work by H. Meyer and E. Overton has shown to exist between these properties and their narcotic action. The action depends on the concentration of hydroxyl and hydrogen ions in the solutions used. W. D. H.

**Physico-chemical Variations of Serum during the Action of Alcohol and of Anæsthetics.** GIUSEPPE BUGLIA and I. SIMON (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 418—435).—The authors have investigated the physico-chemical changes produced (1) by the addition of alcohol to blood serum *in vitro* and (2) in the blood of dogs to which alcohol, ether, or chloroform has been administered.

Both *in vitro* and *in vivo*, alcohol causes diminution of the density,

considerable increase in the molecular concentration, and marked diminution in the electrical conductivity of the blood serum of dogs.

The physico-chemical changes produced in blood serum are small in the case of ether and smaller still with chloroform, so that the latter is, from this point of view, the less harmful of the two anæsthetics.

T. H. P.

**The Fission of Certain Polypeptides by the Blood Corpuscles of the Horse.** EMIL ABDERHALDEN and H. DEETJEN. (*Zeitsch. physiol. Chem.*, 1907, 51, 334—341).—A distinction is drawn between proteolytic and peptolytic ferments, the latter term being reserved for enzymes that decompose peptones and polypeptides into their ultimate cleavage products; such are present in many tissue extracts; the present work relates only to one tissue, namely, the blood. Horse's blood was oxalated and centrifuged; the plasma and the corpuscles (after washing) were then examined separately. The upper layers of the corpuscles would contain most white corpuscles and platelets, the lower layers least; no differentiation beyond this was attempted. The corpuscular mass was found capable of hydrolysing *dl*-alanylglycine, glycyl-*l*-tyrosine, *dl*-alanylglycylglycine, and glycyl-*dl*-leucine; the plasma hydrolyses some of these, but not others; for instance, it does not hydrolyse glycyl-*l*-tyrosine, but it does *dl*-leucylglycylglycine. The ferments in the corpuscles are considered to be chiefly in the red ones. Organ extracts are more powerful than the blood; therefore contamination with blood will not explain their activity.

W. D. H.

**Metabolic and Energy Value of Different Foods.** W. FALTA, F. GROTE, and RUD. STAEHELIN (*Beitr. chem. Physiol. Path.*, 1907, 9, 333—385).—The research was carried out on dogs with different diets (horse-flesh, casein, hydrolysed casein, horse-flesh with lævulose, &c.), and a very complete metabolic study made, the results of which are fully given, mainly in tabular form. Among the questions investigated was the specific dynamic value of individual proteins as sources of heat and energy. The differences found were, however, very small. The abiuretic products of protein cleavage have the same specific dynamic value and nutritive value as the native proteins; the effect on heat production was smaller than anticipated. This is possibly due to the influence of carbohydrates, and led to the addition of lævulose in some experiments; these, however, are at present incomplete.

W. D. H.

**Metabolism in a Healthy Vegetarian.** WILLIAM GORDON LITTLE and CHARLES E. HARRIS (*Biochem. J.*, 1907, 2, 230—239).—A metabolic study in a genuine case of small nitrogen intake. The protein utilised in vegetables and milk was less than 50 grams *per diem*, which would be equivalent to 70 grams in a person of average weight. The regime caused no loss of weight or ill-health, and was followed by the disappearance of gouty deposits in the fingers; the arthritic symptoms temporarily returned during residence in a locality with a hard water supply.

W. D. H.

**Glycogen Metabolism in the Rabbit's Liver.** IVAR BANG, MALTE LJUNGDAHL, and VERNER BOHM (*Beitr. chem. Physiol. Path.*, 1907, 9, 408—430).—In normal animals the amount of the ferment which hydrolyses glycogen is small, and the amount of glycogen metabolism is very constant. In inanition, the total glycogen sinks, but the amount changed is relatively large. Loss of blood leads to an increased transformation of glycogen, and so does loss of oxygen; in these cases the nerve centre concerned is probably stimulated by the asphyxia produced; injection of salt solution, if it is cold, or hypotonic produces a similar result. These statements are supported by analyses.

W. D. H.

**Protein Digestion. II.** OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1907, 51, 415—424. Compare Abstr., 1906, ii, 871).—In this research, natural digestion is contrasted with digestion *in vitro*. In the latter experiments, the ferments were used in the sequence and combinations in which they occur naturally, and complete cleavage of protein is the result. The yield of arginine, for instance, is the same as in acid-hydrolysis.

W. D. H.

**Behaviour of Certain Polypeptides to Pancreatic Juice.** EMIL FISCHER and EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1907, 51, 264—268. Compare Abstr., 1906, ii, 99).—Of the peptides examined, the following were found to be hydrolysable by pancreatic juice: *d*-alanyl-*d*-alanine, *d*-alanyl-*l*-leucine, *l*-leucyl-*l*-leucine, and *l*-leucyl-*d*-glutamic acid. The following were not hydrolysable: *d*-alanyl-*l*-alanine, *l*-alanyl-*d*-alanine, *l*-leucylglycine, *l*-leucyl-*d*-leucine, and *d*-leucyl-*l*-leucine. The hydrolysable dipeptides are exclusively those composed of amino-acids which occur in nature. The results confirm the authors' previous conclusions concerning the part played by the configuration of the molecule, the nature of the amino-acids, the method of linking, and other factors.

W. D. H.

**Assimilation of Protein in Animals.** EMIL ABDERHALDEN, CASIMIR FUNK, and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 51, 269—293. Compare Abstr., 1905, ii, 840).—It is now held that the cleavage proteins undergo during digestion is very complete, and so an animal is able to construct its own protein matter in spite of the fact that the cleavage products in the food-protein may be very different quantitatively. The administrations of gliadin (a protein very rich in glutamic acid) does not increase the glutamic acid yield of the blood-proteins in the animals to which it is given. With the view of discovering where the synthesis of the blood-protein occurs, the present experiments were made on dogs in which an Eck's fistula had been performed; this operation throws the liver largely out of gear. The blood of the animal was then removed in large quantity, and the new blood formed as the result of feeding was examined. The amount of glutamic acid was the main feature examined in the proteins. One dog was fed on meat; another on egg-white, and a third on gliadin. The biological reaction was in all cases negative, showing that no unchanged food-protein has been absorbed. (If the protein is given subcutaneously it can be detected by the biological reaction.) The blood was also

entirely free from proteoses. The mixed proteins of the blood-plasma were separated as a heat coagulum, but the yield of glutamic acid was practically the same in all cases in spite of the differences in the food. The same is true for the protein matter of the blood-corpuscles. The animals fed on gliadin did yield a rather larger amount of glutamic acid, but the difference is too small to militate against the general conclusion just given. The actual figures are as follows. The plasma proteid contained in the dog fed on flesh, 14·8% of glutamic acid; in the dog fed on egg-white, 14·7% to 15·1%; in that fed on gliadin, 15·5%. The numbers for the corpuscle proteins were 14·5%, 14·8%, and 15·9% respectively. The increase, such as it is, is rather larger in the corpuscles, and this suggests that the corpuscles may be concerned in transport.

W. D. H.

**The Use of Optically Active Polypeptides for Estimating the Activity of Proteolytic Enzymes.** EMIL ABDERHALDEN and ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1907, 51, 294—310).—Previous researches have shown that certain polypeptides which are not hydrolysable by pancreatic juice are nevertheless split by other enzymes, such as those in the intestinal juice or tissue extracts. The optically active polypeptides lend themselves well to such work, as the amount of change can be judged by the polarimetric method. The two investigated in the present research were *d*-alanyl-*d*-alanine and *d*-alanyl-*l*-leucine. The former is attacked very slowly by pancreatic juice; after forty-eight hours' action, the rotation is almost unchanged; intestinal juice acts more rapidly, and expressed yeast juice more quickly still. So far as the law of ferment action is concerned, the results are at present insufficient for accurate conclusions to be drawn. With regard to the second dipeptide mentioned, only two experiments with pancreatic juice are given; it is not so useful from the point of view of the present work as the other, for one of its cleavage products, *l*-leucine, has itself a strong rotatory action.

W. D. H.

**The Part Played by Certain Amino-acids in Different Animals.** EMIL ABDERHALDEN, ALFRED GIGON, and EDUARD STRAUSS. (*Zeitsch. physiol. Chem.*, 1907, 51, 311—322).—Some of the most difficult questions in intermediary metabolism relate to the rôle played by, and the relative importance of, the protein cleavage products. Among the points alluded to, are the inferior value of gelatin as a food, the possible origin of carbohydrate after the deamidising of the cleavage products, and the part taken by glycine in hippuric acid synthesis. The present research deals with only a small part of the larger questions, and particularly with glycine and glutamic acid. Three animals (cat, rabbit, and hen) of different dietary habits were analysed (minus their skin and intestinal contents), and the total yield of the two amino-acids per 100 grams of protein did not differ materially; the numbers for glycine are 2·9—3·3 in the cat, 2·3—3·3 in the rabbit, and 3·15 in the hen; the numbers for glutamic acid were 12·4—13·4, 13·9—14·4, and 12·02 respectively. The expectation that the rabbit, a vegetable feeder, would yield more glycine was not fulfilled. It is suggested that the ease with which mammals form

glycine is a phylogenetic vestige from birds and reptiles, which animals are able to synthesise uric acid.

W. D. H.

**The Decomposition of Racemic Amino-acids in the Dog's Organism.** EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1907, 51, 323—333).—Normal urine is practically free from amino-acids, glycine being the only one hitherto detected, and that in quite small quantity. It is interesting to discover whether amino-acids of a kind not occurring naturally in the body can be completely broken down also, and the way selected to study this was to administer different kinds of alanine, namely, *dl*-alanine, *d*-alanine, *l*-alanine, and  $\beta$ -alanine. After one or other of these acids was given, a prompt rise in urinary nitrogen followed, most of the extra nitrogen given being excreted on the same day.  $\beta$ -Alanine, however, which does not occur naturally in the body, is apparently burnt with more difficulty, the increase of nitrogen being very largely seen on the second day. One experiment was made with racemic leucine, this followed the usual rule. Further examination of the urine showed that *l*-alanine is burnt with greater difficulty than *d*-alanine; the former acid is not contained in proteins, and none of it passes as such into the urine. This is the case whether the acids are given separately or together as racemic alanine. In some experiments, thyroid tablets were given at the same time, but this produced little or no effect. The paper contains a general discussion of the use of the word assimilation, and as to whether amino-acids such as alanine are really assimilated.

W. D. H.

**Normal Protein-digestion in the Dog's Alimentary Canal.** EMIL ABDERHALDEN, LOUIS BAUMANN, and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 51, 384—393. Compare Abstr., 1906, ii, 778).—Egg-white was given to dogs, each of which had a fistula in a different part of the intestine. Each received daily 200 grams or more of protein; the material issuing from the fistula was collected, and the nitrogen determined in the heat-coagulum and the filtrate. The following numbers were obtained:

	Position of fistula.	Nitrogen in protein given.	Nitrogen in digested material.	
			In heat-coagulable protein.	In filtrate.
Dog 1.	4 cm. from pylorus ...	36.92 grams	21.73 grams	16.72 grams
Dog 2.	20 cm. „ „ .....	29.54 „	19.41 „	10.71 „
Dog 3.	175 cm. „ „ .....	36.92 „	16.03 „	14.01 „
Dog 4.	100 cm. from cæcum.....	41.13 „	5.17 „	7.39 „
Dog 5.	2 cm. „ „ .....	39.41 „	0.62 „	3.66 „

The lower down the intestine the fistula is, the less is the total nitrogen in the digested products, and the amount of heat-coagulable protein becomes especially small.

The material obtained from the first animal was that which had just left the stomach; only traces of amino-acids were present, and these possibly came by regurgitation from the intestine. The second stage of digestion is in the duodenum under the influence of the pancreatic and intestinal juices, and the third stage occurs in the

lower part of the intestine where the more complete cleavage due to intestinal juice occurs.

W. D. H.

**The Value of Amide Mixtures in Molasses in Ruminants.** W. VÖLTZ (*Pflüger's Archiv*, 1907, 117, 541—563).—The amide substances in molasses can within wide limits completely take the place of protein in adult ruminants.

W. D. H.

**Internal Function of the Pancreas in Reference to Fat-metabolism.** UGO LOMBROSO (*Arch. exp. Path. Pharm.*, 1907, 56, 357—369).—The experiments recorded show that the pancreas is not only concerned in the digestion of fat, but in virtue of its "internal function" exercises an action on the metabolism of fat as well as of carbohydrate in the body.

W. D. H.

**Oxidation of Simple Aliphatic Substances in the Animal Organism.** HENRY D. DAKIN (*J. Biol. Chem.*, 1907, 3, 57—80).—This is very largely a theoretical discussion of the mode of oxidation which occurs in the body. If glyoxylic acid is given, it is in part oxidised to oxalic acid which appears in the urine; the amount of oxalic acid is least when glyoxylic acid is given by the mouth. There was no increase of formic acid, although formic acid may occur as an intermediate product. No glyoxylic acid was found in the urine, nor was there any formation of allantoin. The view is advanced that glycollic, glyoxylic, and oxalic acids are intermediate products of the oxidation of acetic acid, but no oxalic acid was found in the urine as the result of giving acetates. If glycollates are given, there is a decided rise in oxalic acid excretion. Moderate amounts of oxalic acid are almost completely burnt in the body. Glycol administration leads to marked oxaluria, and slight oxaluria follows the consumption of large quantities of gelatin in man.

W. D. H.

**Formation of Glycogen in Muscle.** ROBERT A. HATCHER and CHARLES G. L. WOLF (*J. Biol. Chem.*, 1907, 3, 25—34).—Glycogen is not formed in the perfusion of muscle by blood which contains sucrose. Muscles rendered free from glycogen by starvation and strychnine do not form glycogen from either glucose or sucrose. The amount of glycogen in symmetrical muscles is approximately the same.

W. D. H.

**Formation of Creatinine.** JOHN SEEMANN (*Zeitsch. Biol.*, 1907, 49, 333—344).—A study of the oxidation of gelatin leads to the view that the atomic grouping of creatinine is preformed in the protein molecule. If arginine or a similar guanidine derivative is united to another amino-acid, then by imide formation between the two neighbouring amino-groups, creatinine will be formed. Hitherto, creatinine has not been obtained as the result of hydrolysis produced by acids or by enzymes; it is known in the body as a characteristic break-down product of muscular activity. On autolysis of muscle for three months, the amount of creatinine increases, especially if a protein rich in arginine (such as gelatin) is added also. If a protein



poor in arginine (such as casein) is added, the yield is not so great. Arginine injection alone does not increase the excretion of creatinine in the urine.

W. D. H.

**Further Investigations on the Action of Asparagine on the Nitrogenous Exchange of the Animal Body.** MAX MÜLLER (*Pflüger's Archiv*, 1907, 117, 497—537). CURT LEHMANN (*ibid.*, 538—540. Compare Abstr., 1906, ii, 465, 560, 690).—The first paper presents new experiments in support of views previously expressed. The second is polemical, criticising the opinions of both Müller and Kellner.

W. D. H.

**Crab Extract. II. and III.** D. ACKERMANN AND FRIEDRICH KUTSCHER (*Zeitsch. Nahr. Genussm.*, 1907, 13, 610—613, 613—614).—Crab extract is found to contain hypoxanthine, betaine, and *d*-lactic acid in addition to the substances recorded in the previous paper (this vol., ii, 283). Succinic acid is not present in the fresh extract, but is formed by decomposition of the crab flesh. Betaine, which occurs commonly in plant extracts, has been found previously in only one animal extract, that of the edible mussel.

G. Y.

**The Distribution of Iodine in the Animal Body after the Administration of its Compound.** OSWALD LOEB (*Arch. exp. Path. Pharm.*, 1907, 56, 320—332).—The amount of iodine in the various tissues and organs of rabbits was estimated after the administration of potassium iodide, iodoform, ethyl iodide, and iodoaniline. In the case of potassium iodide, no iodine was found in nervous tissues, fat, or bone; it was found in varying quantities in other places, and the largest amount in the thyroid and in the blood. The results are given in tables. With the other three compounds iodine was found in large measure in fat, but variations on the distribution are noted, for instance, in the case of ethyl iodide, a great deal of iodine was found in the lungs, whereas this was not so for iodoaniline.

W. D. H.

**The Structure and Secretion of the Parathyroids in Man.** DAVID FORSYTH. (*Brit. Med. J.*, 1907, ii, 1177—1181).—The paper is largely histological; the microscopic appearances indicate phases of rest and action. The secretion begins to be formed about the third month of life and is indistinguishable from the colloid of the thyroid.

W. D. H.

**Absorption of Anti-substances from the Subcutaneous Tissues and Peritoneal Cavity.** J. HENDERSON SMITH (*J. Hygiene*, 1907, 7, 205—215).—Absorption of anti-substances from the subcutaneous tissues and peritoneal cavity is slow. In urgent cases, time amounting to two or three days may thus be lost. Intravenous injection is therefore advisable.

W. D. H.

**Influence of Asparagine on the Production of Milk and its Constituents.** THEODOR PFEIFFER, W. SCHNEIDER, and ALBERT HEPNER (*Bied.-Zentr.*, 1907, 36, 250—256; from *Mitt. landw. Inst. Univ. Breslau*, 3, 747. Compare Abstr., 1905, ii, 757).—Experiments

with goats showed that asparagine increased the amount of dry matter in milk and also slightly increased the production of milk fat. The results were similar to those obtained with aleuronate. Whilst, however, the latter was utilised as food, asparagine acted as a stimulant, the increased milk production being coincident with a loss of live weight.

N. H. J. M.

**Bitter Milk.** J. AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1907, 144, 926—929. Compare Abstr., 1905, ii, 490).—The authors find that (1) bitter milk contains aldehydes and ammonia. (2) Milk can be made bitter by treatment with both aldehydes and ammonia. (3) Milk when inoculated both with a yeast (producing aldehydes) and an ammonia-forming bacillus (*B. Flügge*, V), but not with either separately, becomes bitter and at the same time develops 35—45 mg. aldehyde and 22—25 mg. ammonia per litre.

E. H.

**Acid Coagulation of Milk.** CECIL REVIS and GEORGE ARTHUR PAYNE (*J. Hygiene*, 1907, 7, 216—231).—Rise in acidity is less rapid than increase of acid-forming organisms in milk. No chemical basis for this delay is found, and the hypothesis that the acid formed is neutralised by some constituent of the milk is not confirmed. Details are given of the relationships between the calcium compounds of caseinogen and of lactic acid. At the moment when the former is precipitated, the calcium triphosphate has been eliminated, and the compound with lactic acid has reached a maximum.

W. D. H.

**The Acid Reaction of Urine.** B. WAGNER (*Chem. Zeit.*, 1907, 31, 485).—Experiments showing that the acidity of normal urine is not caused by phosphates, but is due mainly to organic acids. The author succeeded in isolating, by means of ether, a compound of urea and hippuric acid to which the acid reaction is partly due.

L. DE K.

**Urine in Starvation.** FRANCIS G. BENEDICT and A. R. DIEFENDORF. **Elimination and Estimation of Creatine and Creatinine.** FRANCIS G. BENEDICT and VICTOR CARYL MYERS (*Amer. J. Physiol.*, 1907, 18, 362—376, 377—396, 397—405, 406—412).—The first observations were made on a woman who from religious delusions reduced her diet, and part of the time fasted absolutely, not even taking water for three days. The volume of the urine sank to 237 c.c. in the day; its sp. gr. was 1.035. The nitrogen output increased for the first three days and then sank; on one day the output was only 3.17 grams. The total potential energy of the urine was less than in fasting men. There were indications of acidosis. The preformed creatinine excretion was low, being only 11 mg. per kilo. of body-weight; the preformed creatine increased markedly during fasting and disappeared at the conclusion of the fast. The faeces showed an abnormally high percentage of ash and fatty acids.

The creatinine excretion in women is usually lower than in men, and elderly people excrete less than younger people of the same weight; still there is a rough proportionality to the bodyweight and not to the active mass of protoplasmic tissues.

The method used for estimating creatinine and creatine was Folin's colorimetric method; the conversion of creatine into creatinine can be accomplished by heating at  $117^{\circ}$  for fifteen minutes; at the boiling temperature, as in Folin's work, it takes some hours. If the urine is kept for some time, creatinine is partly converted into creatine, probably by bacterial agencies; the antiseptic recommended to prevent this is a solution of thymol in chloroform, 1 in 10.

The creatine in urine is probably independent of creatinine; its presence is pathological, and it occurs in wasting diseases when flesh is broken down. It is an index of the flesh katabolised during fasting.

W. D. H.

**Excretion of Boric Acid from the Human Body.** HARVEY W. WILEY (*J. Biol. Chem.*, 1907, 3, 11—20).—More than 80% of boric acid, administered either as such or as borax, is excreted by the kidneys. The poison is a cumulative one; even ten days after the cessation of its administration an appreciable amount is found in the urine. Boric acid increases the acidity of the urine; borax diminishes it. No volatile compounds of boron are found in the expired air. The faeces contain about 1% of the amount given. The quantity in the sweat brings up the total recovered to 85% of that given. A variable amount passes out by the milk in nursing women.

W. D. H.

**Separation of Fat in Normal Dog's Urine.** BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1907, 117, 291—294. Compare Hammerbacher, *ibid.*, 1883, 33, 93).—The urine of a dog fed on lard (300 grams) and horse-flesh (100 grams per day) contains appreciable amounts of fat which can be extracted by ether. The amount of fatty acid obtained by hydrolysing the fat was 0.12 gram per day or 0.126 gram of fat.

J. J. S.

**Action of Sodium Salicylate on the Uric Excretion.** PIERRE FAUVEL (*Compt. rend.*, 1907, 144, 932—934).—If a dose of 3—4 grams of sodium salicylate is administered to an adult subject, the amounts of xanthine bases and uric acid excreted on the day of treatment rise considerably above the normal, but fall considerably below it on the following day. On the other hand, small doses (1—2 grams) of the salicylate reduce the amounts of xanthine bases and uric acid excreted. From experiments on a subject who had been fed on a diet containing a minimum quantity of purine, the author concludes that sodium salicylate does not increase the production of uric acid and xanthine bases, but by accelerating their excretion, eliminates part of the acid normally contained in the tissues, so that when its action ceases, excretion diminishes until the organism has regained its normal amount of uric acid.

E. H.

**The Distribution of Nitrogen in Urine under the Influence of Different Types of Food.** BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1907, 117, 257—274. Compare Bleibtreu, *Abstr.*, 1890, 279; Schultze, *ibid.*, 280; Folin, *Abstr.*, 1905, ii, 183).—It has been found that when dogs are fed entirely with meat the amount of

nitrogen as urea compared with the total nitrogen increases considerably and may reach a maximum value of 97·98% of the total. If food is then dispensed with, the proportion of urea nitrogen can fall as low as 75·44% of the total. With food of an entirely carbohydrate and fatty nature, the mean value is 85—86% of the total. J. J. S.

**Alkylureas [Alkylcarbamides] and Alkylamines.** OTTO FOLIN (*J. Biol. Chem.*, 1907, 3, 83—86).—In feeding experiments with creatine, search was made in the urine for methylcarbamide or methylamine to account for some of the missing creatine; the result was negative. Still, all human urines contain small amounts of methylcarbamide, and some urines, especially in typhoid fever, also contain appreciable amounts of methylamine, and ammonia elimination is here also high. These substances can be detected by Hoffmann's carbylamine reaction. On nitrogen-rich diets, 4% to 6% of the urea is in the form of methylcarbamide; on low nitrogen diets the methylcarbamide excretion diminishes, but it is never entirely absent.

Methylamine (or other alkylamines) can be formed by the hydrolysis of ordinary amino-acids, and there is no necessity for assuming any genetic relationship between the methylamine groups of the food and those of the urine where experimental evidence in favour of such a relationship is wanting. W. D. H.

**Indoxyl Sulphate in the Urine of the Insane.** J. HARVEY BORDEN (*J. Biol. Chem.*, 1907, 2, 575—602).—Indole is not a factor of importance; it may be present in excess in insanity, or it may not. Its amount bears no relation to any mental condition or form of insanity. W. D. H.

**Excretion of Quinine in Human Urine.** RICHARD SCHMITZ (*Arch. exp. Path. Pharm.*, 1907, 56, 301—313).—When given by the mouth, quinine is excreted by the urine to the extent of 27% on the average; when given subcutaneously, this figure sinks to 16. The remainder is destroyed in the organism. The capacity to destroy quinine does not increase by prolonged medication. Some improvements are suggested in Kleine's method for the estimation of quinine. The quinine in the urine is unchanged; derivatives such as Kerner's dihydroxyquinine were not found. W. D. H.

**The Non-dialysable Material of the Urine.** KUMUJI SASAKI. **Excretion of Chondroitin-sulphuric Acid in Urine.** CH. PONS. **The Amount of Non-dialysable Material in the Urine of Women in Health and Disease.** M. SAVARÈ (*Beitr. chem. Physiol. Path.*, 1907, 9, 386—392, 393—400, 401—407).—The non-dialysable material of the urine consists of chondroitin-sulphuric acid, nucleic acid, and traces of protein. The amount varies from 0·2 to 0·68 gram per litre. When injected into rabbits, it causes no toxic effects.

The amount of chondroitin-sulphuric acid was estimated from the yield of sulphur, and in human urine amounts to 0·08 to 0·09 gram in the twenty-four hours. In dogs and rabbits the amount is absolutely smaller, but relatively to their body-weight greater.

In twenty normal non-pregnant women, the total non-dialysable

material averaged 0.44 gram per litre; in pregnancy (average of 25 cases) this rose to 0.6 gram, but this small rise is not considered noteworthy. In nephritis the average (7 cases) was 0.7, and in eclampsia, 2.2—6.97 (4 cases). Whether the material from cases of eclampsia is toxic was not investigated.

W. D. H.

**Alcaptonuria.** ARCHIBALD E. GARROD and J. WOOD CLARKE (*Bio-Chem. J.*, 1907, 2, 217—220).—Another case of alcaptonuria is recorded in which the ratio homogentisic acid: nitrogen was in accord with that obtained in other cases. Full details are given, and the case is noteworthy as occurring in a female. There was no evidence of the same condition having occurred in the family, and there was no blood relationship between the parents as is commonly the case. A second alcapton acid (uroleucic acid) was not detected.

W. D. H.

**Action of the Benzidine Dyes on Mice Infected with Trypanosoma.** C. M. WENYON (*J. Hygiene*, 1907, 7, 273—290).—The relative action of various benzidine dyes and the relative resistance of different forms of trypanosoma to the action of the pigments are detailed. *T. dimorphon* is the most resistant to all forms of medication, and the drug which promises success is the azo-dye from 2:7-diaminonaphthalene-3:6-disulphonic acid + benzidine, but this has to be given in repeated doses. It is hoped more successful results will be obtained in larger animals.

W. D. H.

**Treatment of Trypanosomiasis.** BENJAMIN MOORE, MAXIMILIAN NIERENSTEIN, and JOHN L. TODD (*Bio-Chem. J.*, 1907, 2, 300—324).—Parasitic protozoa are differently susceptible to drug treatment in different phases of their life-history, and therefore treatment with successive drugs is necessary. In rats affected with *Trypanosoma brucei*, combined treatment with atoxyl and mercuric chloride gave better results than treatment with the former alone, and it is suggested this should be tried in men. Ehrlich and Bertheim state that atoxyl is the sodium salt of *p*-aminophenylarsonic acid with 4H<sub>2</sub>O. The present analyses support this view, but the amount of water found was rather less.

W. D. H.

**Action of Metals of the Nickel Group.** FRIEDRICH WOHLWILL (*Arch. exp. Path. Pharm.*, 1907, 56, 403—409).—The four metals, iron, manganese, nickel, and cobalt, have an identical action in causing capillary hyperæmia of the alimentary tract. Accompanying this there are nervous symptoms, and it is possible these may be due to direct action on the central nervous system. The metals mentioned differ from arsenic in the difficulty with which they are absorbed from the alimentary canal.

W. D. H.

**Pharmacological Action of Thorium.** TORALD SOLLMANN and E. D. BROWN (*Amer. J. Physiol.*, 1907, 18, 426—456).—Thorium nitrate is an astringent irritant; it precipitates proteins and blood, and its effects are due to this. Its toxicity is low, and if dissolved in sodium citrate solution, its astringent effects are abolished. It is

neither absorbed nor excreted by the alimentary canal. If given subcutaneously, it is rapidly excreted in the urine. Trustworthy methods of estimation in the tissues and fluids were not found. In general, it resembles aluminium.

W. D. H.

**Poisonous Action of Thorium.** ARTHUR F. CHACE and WILLIAM J. GIES (*Amer. J. Physiol.*, 1907, 18, 457—475).—The experiments were made with thorium chloride. An intravenous dose of 7 mg. per kilo. of body-weight in a dog caused death; other dogs stood larger doses. Subcutaneous injection caused local irritation and sloughing (due to its astringent action), muscular twitchings, and weakness. If given by the mouth, the main symptoms were impaired appetite and vomiting.

W. D. H.

**Action of Mesityl Oxide, Phorone, and Acetone on the Animal Body.** LOUIS LEWIN (*Arch. exp. Path. Pharm.*, 1907, 56, 346—356).—Acetone, when heated with strong mineral acids, yield water and 1 mol. of mesityl oxide for every 2 molecules of acetone. Mesityl oxide causes narcosis and paralysis in frogs and mammals, and repeated doses produce death. The fæces, urine, and breath have a strong unpleasant odour. When acetone is condensed by hydrogen chloride, 3 molecules yield 2 of water and 1 of phorone; this produces similar symptoms. The greater part of the substances given, leave the body as a substance rich in sulphur. The identity of the compound formed is discussed at length; it is probably combined with a sulphhydryl group. Acetone does not lead to the production of this substance.

W. D. H.

**The Biological Behaviour of Phenylalkylamines and Phenylalkylammonium Bases.** HERMANN HILDEBRANDT (*Beitr. chem. physiol. Path.*, 1907, 9, 470—480. Compare Abstr., 1906, ii, 110).—When dimethyl-*o*-toluidine is administered to dogs, the methyl group undergoes oxidation in the organism, although dimethyl-*o*-aminobenzoic acid has not been isolated from the urine. Dimethylantranilic acid itself has a much more pronounced toxic effect than the isomeric para-compound, and in the urine a readily soluble compound with glycuronic acid is present.

The urine of a dog to which dimethyl-*o*-toluidine has been administered, yields dimethyl-*p*-aminophenol after precipitating with lead acetate and hydrolysing with sulphuric acid. This indicates that not merely is the methyl group oxidised, but that also a phenolic hydroxyl is introduced in the para-position with respect to the nitrogen. The urine in this case is coloured deep red, and shows the spectrum of oxy-hæmoglobin, just as when arsine, phthallin, or helvellic acid is administered. Dimethylaniline causes the elimination of considerable amounts of albumin in the urine, and dimethyl-*p*-aminophenol can be obtained from the lead precipitate and also small amounts of the isomeric ortho-compound.

Dimethylaniline oxide has not the same physiological action as dimethylaniline, but is transformed into the two isomeric aminophenols.

*p*-Bromodimethylaniline yields *p*-bromo-*o*-dimethylaminophenol in the organism. The phenol has pronounced physiological action and couples with glycuronic acid.

It is probable that the urine obtained from dogs fed with dimethylaniline contains Griess' *p*-trimethylphenolammonium, which can pass through the organism unaltered.

Phenyltrimethylammonium hydroxide is a strong poison. This quaternary base and also the corresponding bases from *o*- and *p*-dimethyltoluidine do not resemble muscarine, whereas *benzyltrimethylammonium bromide*, m. p. 215°, does. The quaternary bases do not appear to undergo molecular transformation in the organism.

Auwers and Dombrowski's base from formaldehyde, dimethylaniline, and  $\beta$ -naphthol (Abstr., 1906, i, 380) has the characteristic amine action. The corresponding ammonium salts are poisonous. J. J. S.

**Lysol and Cresol Poisoning.** MANFRED BIAL (*Arch. exp. Path. Pharm.*, 1907, 56, 416—419), OSKAR WANDEL (*ibid.*, 420—421. Compare this vol., ii, 380).—Polemical on the question as to the relative amount of free cresol and its glycuronate excreted by the bile. W. D. H.

**Toxic Action of Saponin.** RAYMOND FOSS BACON and HARRY T. MARSHALL (*Philippine J. Sci.*, 1906, 1, 1037—1043).—The saponin from *Entada scandens* is highly toxic for rabbits and guinea-pigs; it is also powerfully hæmolytic, but loses this power after the addition of horse's serum. No immunity could be demonstrated in rabbits or guinea-pigs previously treated by intraperitoneal doses of saponin or of a saponin serum mixture. Amœbæ from dysenteric patients and from tap-water are destroyed by saponin, the cells bursting with explosive violence, whereas atmospheric bacteria grow abundantly in a solution of crude saponin. J. J. S.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Cleavage of Gliadin by *Bacillus mesentericus vulgatus*.**  
EMIL ABDERHALDEN and OSKAR EMMERLING (*Zeitsch. physiol. Chem.*, 1907, 51, 394—396).—The *Bacillus mesentericus vulgatus* was allowed to act on gliadin for six weeks; among the products isolated were glycine, leucine, alanine, proline, aminovaleric acid, and glutamic acid. The ferments of the micro-organism are thus able to split the protein down to amino-acids, the small yield of which, however, is attributed to the comparatively short time the action lasted. W. D. H.

**Influence of Lactose and Lactic Acid on the Decomposition of Caseinogen by Micro-organisms.** OTAKAR LAXA (*Milchw. Zentr.*, 1907, 3, 200—207).—Sterile artificial media  
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containing mineral salts, 3% of caseinogen, and in some cases either 1% of lactose or 0.8% of lactic acid were inoculated with certain organisms isolated from hard cheese. The organisms were lactic acid producers of the type *Bacillus lactis acidii*, two gelatin liquefying bacilli, *Oidium lactis*, two moulds, and *Pencillium*. It was found that the proteolytic action of the gelatin liquefying bacilli was stimulated to a certain extent by lactose and inhibited by lactic acid to a degree which varied with the organism in question. Hence only a very limited proteolysis of the caseinogen of a caseinogen-lactose medium took place when it was inoculated both with a gelatin liquefying organism and a lactic acid producing one. So also, was the proteolysis very limited when a caseinogen-lactic acid medium was inoculated with a gelatin liquefying organism alone. The addition of *Oidium lactis* in either case brought about a greatly increased digestion of the caseinogen. The disappearance of lactic acid shown by other experiments to be concomitant with the growth of this mould, indicated the mechanism of the symbiosis. The known phenomena of cheese ripening are discussed in the light of these results. G. S. W

**The Kinds of Lactic Acid Produced by Lactic Acid Bacteria.** P. G. HEINEMANN (*J. Biol. Chem.*, 1907, 2, 603—612).—Milk naturally soured at the room temperature contains chiefly *d*-lactic acid, whilst, at 37°, it contains chiefly the *r*-acid, with *l*-acid in excess if kept for several days. *Streptococcus lacticus* and *S. pyogenes* produce *d*-acid; *B. aërogenes* produces *l*-acid. The *r*-acid is not known to be the product of one species only, but is the result of the formation of *d*- and *l*-acids by at least two kinds of micro-organism. The presence of the *d*-acid alone is a more favourable condition in dairy work, the absence of the *l*-acid indicating the absence also of other volatile acids, gas, and ethyl alcohol which the *B. aërogenes* gives rise to.

W. D. H.

**Fixation of Nitrogen by the Nodule-former.** R. GREIG SMITH (*J. Soc. Chem. Ind.*, 1907, 26, 304—307).—When nodule bacteria are cultivated in saccharin media they usually at once produce slime as in the majority of leguminous root nodules. In the nodules themselves there is probably a continuous production of slime which, as it is not exuded, must be utilised by the plant.

Quantitative experiments on nitrogen fixation by nodule-bacteria showed that fixation depended on the production of slime and that the greater the amount of slime produced the greater was the amount of nitrogen fixed. The media on which fixation occurred were permanently alkaline.

The slime is nitrogenous and the essential constituent is a gum which is sometimes dextro- and sometimes lævo-rotatory. When hydrolysed, the gum yields dextrcse and galactose.

Nodule-bacteria are found in the stems of lupins; these bacteria, which exist under conditions of acidity, are unable at once to produce slime. They acquire this power after a time under suitable treatment. The carbon necessary for the production of slime may be in the form of dextrose, lævulose, sucrose, maltose, or mannitol; glycerol may be

used, but lactose is very unsuitable. Nitrogen is not essential, but the production of slime is accelerated by the presence of asparagine or nitrates; inorganic ammonium salts are unsuitable.

Field peas in different months yielded similar bacteria, whilst blue lupin nodules yielded several races. In one case a single lupin nodule yielded three distinct races. It is suggested that a universal nitrugin consisting of a mixed culture of active slime-forming bacteria should be used for all leguminous crops.

N. H. J. M.

**The Size of the Cells of *Pleurococcus* and *Saccharomyces* in Neutral Salt Solutions.** ERIC DRABBLE, HILDA DRABBLE, and DAISY G. SCOTT (*Bio-Chem. J.*, 1907, 2, 221—229).—The cells decrease in size with increase in the external osmotic pressure of the salt solution in which they lie. The decrease commences when the pressure is lower than that of the cell sap. The plasmolytic method of determining the osmotic pressure of the cell sap in these organisms is therefore untrustworthy, although in the mature cells of multicellular plants it gives correct results.

W. D. H.

**Production of Glycerol in Alcoholic Fermentation.** RUDOLPH REISCH (*Centr. Bakt. Par.*, ii, 1907, 18, 396—398).—The production of glycerol in musts occurs chiefly during the early stages of fermentation and diminishes rapidly towards the end. It has no relation to alcohol production; glycerol is not therefore a direct product of fermentation, but a metabolic product of the yeast. The more nitrogenous must ( $N=0.098\%$ ) yielded somewhat more glycerol than a less nitrogenous one ( $N=0.039\%$ ); the amount of nitrogen does not, however, seem to be of importance.

N. H. J. M.

**Invertase in Apple Must and Cider.** G. WARCOLLIER (*Compt. rend.*, 1907, 144, 987—990).—No change in the amounts of sucrose or of reducing sugars naturally present in apple must takes place when this material is partially neutralised with sodium hydroxide and kept at  $56^{\circ}$  during one hour, whence it is concluded that invertase does not occur in apple must and that the preliminary inversion of sucrose, which occurs in the change of apple must into cider, must be due to the action of invertase secreted by the yeast cells and that the ferment diffuses from the latter into the must where it is capable of existing for considerable periods. Invertase must occur naturally in apples, since sucrose is inverted during the ripening of the fruit and it is suggested that the ferment is destroyed during the pressing of the apples, perhaps as the result of precipitation by tannin.

T. A. H.

**Occurrence of Coumarin in *Achlys triphylla*.** C. E. BRADLEY (*J. Amer. Chem. Soc.*, 1907, 29, 606—607).—The odour of *Achlys triphylla* is not due to a volatile oil, but to the presence of about 0.2% of coumarin, a large proportion of which occurs in the leaf stalks. Mature plants give the best yield.

E. G.

**The Physiologically Active Constituents of Certain Philippine Medicinal Plants.** RAYMOND FOSS BACON (*Philippine J. Sci.*, 1906, 1, 1007—1036).—The alkaloids obtained from the bark of *Alstonia scholaris*, commonly known as *dita*, have been investigated (compare Hesse, this Journ., 1876, i, 276; Abstr., 1881, 448; Harnack, Abstr., 1879, 332). The amount of ditamine obtained is only some 0.3 gram per 5 kilos. of bark. A few qualitative reactions only have been conducted with the alkaloid. Echitamine is soluble in ether when freshly precipitated, but the crystals appear to be insoluble. The base liberates ammonia from ammonium salts and with calcium or sodium chlorides yield the corresponding hydroxide and echitammonium chloride which crystallises readily. The base melts and decomposes at 200—208° when rapidly heated, and when boiled with hydrochloric acid does not yield a reducing sugar. Alkali hydroxides precipitate the base from concentrated solutions of the chloride. Electrical conductivity determinations of aqueous solutions of the alkaloid indicate that it is a much stronger base than piperidine. The minimum fatal dose for a guinea-pig appears to be about 0.025 gram per kilogram of body-weight.

*Datura alba* contains hyoscyne, hyoscyamine, and atropine; in the air-dried leaves the total amount of alkaloids is 0.21%, in the seeds 0.465, and in the wood and roots 0.17, and 90% of the totals consists of hyoscyne. Hesse's description of the properties of this alkaloid is confirmed.

Brazilin has been isolated from Sappan wood (*Cæsalpinia sappan*). A saponin has been isolated from the wood of *Entada scandens* (locally known as *gogo*) in the form of a white, amorphous powder, or in some cases in crystalline needles. It dissolves in water, yielding a faintly acid solution which readily froths. When heated, it begins to turn brown at 180° and at higher temperatures chars. It is not precipitated by saturating its aqueous solution with ammonium sulphate, but readily holds many solids in suspension; it emulsifies oils and prevents the crystallisation of various compounds. It does not reduce Fehling's solution, but when boiled with dilute acids yields a sapogenin,  $C_{26}H_{42}O_8$ , and galactose. Sapogenin is also obtained by the action of species of *Pericillium* on saponin, carbon dioxide being evolved. It forms colourless needles, insoluble in water, acids, or alkalis, but soluble in most organic solvents. It does not change when heated to 270°.

A number of fish poisons obtained from vegetable sources have been examined. The fruit of *Croton tiglium* contains croton. *Anamirta cocculus* contains picrotoxin (Abstr., 1888, 845, 846). *Albizia saponaria*, *Pithecolobium acle*, *Barringtonia luzoniensis*, *Ganophyllum obliquum*, and *Maesa denticulata* all contain saponine.

The stem of *Tinospora crispa* does not contain any physiologically active compounds. *Argemone mexicana* does not contain morphine, but some other alkaloid. *Erythroxylon burmanicum* does not contain cocaine.

From the seeds of *Cæsalpinia bonducella* a mixture of resins termed *bonducin* has been isolated, this has no action on guinea-pigs, but possesses a strong, astringent taste.

The purging oils from *Aleurites moluccana*, *A. trisperma*, and *Jatropha curcas* have been examined. J. J. S.

**Presence of Mannitol in the Jasminaceæ.** J. VINTILESCO (*J. Pharm. Chim.*, 1907, [vi], 25, 373—377. Compare this vol., ii, 123).—*D*-Mannitol has been obtained from the leaves and branches of *Jasminum officinale* and *J. nudiflorum*, and is probably also present in *J. fruticans*. T. A. H.

**English and French Rhubarb.** ALEXANDER TSCHIRCH and J. EDNER (*Arch. Pharm.*, 1907, 245, 139—149. Compare Abstr., 1906, ii, 851, and Hesse, Abstr., 1900, i, 41).—From a sample of English rhubarb root there were isolated, in part after hydrolysis: chrysophanic acid, emodin, *iso*emodin (rhabarberone), rheum-red, rheonigrins, and dextrose; rhein could not be identified with certainty, and rhaponticin was absent. The source of the drug was evidently *Rheum officinale*.

From a sample of French rhubarb root there were isolated: rhaponticin (yielding rhapontigenin and dextrose on hydrolysis), chrysophanic acid, and chrysopontin; emodin and rhein were absent. The source of the drug was evidently *Rheum rhaponticum*.

C. F. B.

**Fruit of Smilacina Racemosa and S. Bifolia.** C. G. ELDRIDGE and L. M. LIDDLE (*Chem. News*, 1907, 95, 182—183).—An investigation of the berries of these two species shows that they both seem to possess the same general properties. Potassium hydrogen tartrate, potassium hydrogen oxalate, tannic acid, and a small amount of gum are found in the ripened fruit of both species. The husks contain a small quantity of calcium oxalate, also lævulose with possibly a little dextrose; these two sugars are also present in the fleshy part of the berry. Olein, palmitin, and pure lævulose are found in the nutlets.

W. H. G.

**Cultivation of Leguminous Fodders.** J. DUMONT and CH. DUPONT (*Compt. rend.*, 1907, 144, 985—987).—It is found that of two soils of similar composition as regards content of carbon, hydrogen, nitrogen, and total organic matter, the one, which has previously borne vines, yields a much better crop of lucerne, sainfoin, or clover than that which has previously produced a crop of lucerne. The yield of a leguminous crop from soil, which has produced a crop of lucerne, may be somewhat increased by aëration, by the addition of humus, or, better, by admixture of 10% of vineyard soil, but is scarcely affected by adding mineral manures.

T. A. H.

**Quantity of Plus-Sugar Calculated as Anhydrous Raffinose contained in Beetroot.** HENRI PELLET and LÉON PELLET (*Chem. Zentr.*, 1907, i, 484; from *Bull. Assoc. chim. Sucr. Dist.*, 24, 454—460).—The researches of Herzfeld (*Zeitsch. Ver. Rubenzuck.-Ind.*, 1906, 751) and Neumann (*Zeitsch. Zuckerind. Böhm.*, 30, 536) are discussed in the original paper. Six samples of French sugar juices of 1906 have been found to have practically the same polarising powers.

both before (+62.23°) and after (about -19°) inversion, but 2.04% of raffinose was detected in a German sample of molasses of 1905.

E. W. W.

**Treatment of Soils by Carbon Disulphide.** BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1907, ii, 18, 462—470. Compare this vol., ii, 388).—Carbon disulphide retards nitrification generally, but especially the nitrification of ammonium sulphate. Indications were obtained that not only mustard oil but the green substance of mustard has a retarding effect on nitrification, at any rate for a time. Thio-carbonates, thiosulphates, sulphides, and sulphur failed to yield definite results, and further experiments will be necessary.

N. H. J. M.

**Action of Fresh Green Manure (Peas, Beans, and Vetches mixed) and Beet Leaves, Compared with Sodium Nitrate.** WILHELM SCHNEIDEWIND, DIEDRICH MEYER, and H. FRESE (*Chem. Centr.*, 1907, i, 748; from *Landw. Jahrb.*, 35, 923—926).—Results obtained with two different soils showed that the average utilisation of nitrogen as nitrate (including after effect in the second year) was 82.6%; that of the mixed green manure, 42.8%, and that of beet leaves, 36.2%.

N. H. J. M.

**Experiments with Phosphoric Acid on Different Kinds of Soils.** WILHELM SCHNEIDEWIND, DIEDRICH MEYER, and H. FRESE (*Chem. Centr.*, 1907, i, 748—749; from *Landw. Jahrb.*, 35, 927—936).—Pot experiments with barley in ten different soils showed that in some cases the amount of soil phosphoric acid soluble in 2% citric acid gives indications as to the requirements of the soil. Sandy soils, deficient in calcium, magnesium, and iron, containing appreciable amounts of citric acid-soluble phosphoric acid do not respond to phosphoric acid manure even when the total phosphoric acid content is low. Heavy soils containing fair amounts of calcium, &c., only fail to respond to phosphate manuring when they contain considerable amounts of phosphoric acid soluble in citric acid.

In the case of light soils benefited by phosphoric acid, basic slag was equal to superphosphate, whilst bone-meal also gave very good results. On heavy soils, basic slag was less satisfactory, and bone-meal had practically no effect.

N. H. J. M.

**Action of the Phosphoric Acid of High and Low per cent. Basic Slag.** WILHELM SCHNEIDEWIND, DIEDRICH MEYER, and H. FRESE (*Chem. Centr.*, 1907, i, 749; from *Landw. Jahrb.*, 35, 937—940).—The same amounts of citric acid-soluble phosphoric acid produced the same effects (with oats and winter rye) whether the basic slag contained high or low percentages. One slag with a very low percentage, but with a high percentage of fine meal, acted far better than the others. Superphosphate, precipitated phosphate, and Wolter's phosphate were found to be far more efficient than basic slag, whilst calcium triphosphate and Florida phosphate had no effect. Steamed basic slag gave much more unsatisfactory results than ordinary slag.

N. H. J. M.

## Analytical Chemistry.

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**Modification of Volhard's Method for the Estimation of Chlorides.** M. A. ROSANOFF and ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1907, 29, 269—275).—Volhard's process for the estimation of halogens consists, as is well known, in adding excess of standard silver solution and titrating the non-precipitated silver with potassium thiocyanate with ferric alum as indicator.

The authors have found that when estimating chlorides it is absolutely necessary that the silver chloride should be removed by filtration before titrating with thiocyanate. With bromides or iodides, this is unnecessary.  
L. DE K.

**Direct Separation of Chlorides and Bromides.** LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1907, 29, 275—283).—If the amount of potassium chloride in commercial potassium bromide is supposed to be 5—10%, 0.6 gram of the sample is boiled in a large flask with 250 c.c. of water, 36 c.c. of *N/5* potassium iodate, and 20 c.c. of 2*N* nitric acid. If the chloride is below 5%, more iodate and acid should be used. The liquid is now boiled down to 90 c.c., and after testing the escaping steam for bromine by means of fluorescein paper, the final test for bromine is made by passing it through a solution of potassium iodide faintly acidified with hydrochloric acid. When this remains colourless, the bromine has completely disappeared and the iodine is now removed by adding 1—1.5 c.c. of 20% solution of phosphorous acid and boiling for another ten minutes. The chloride remaining in the solution is then titrated as usual by Volhard's silver thiocyanate method. When free chlorine has to be determined in commercial bromine, 3 grams of the sample are treated with 2 grams of potassium iodide and 50 c.c. of water, which fixes all the chlorine and part of the bromine. The mixture is then transferred to a Kjeldahl flask, 60 c.c. of *N/5* potassium iodate and 24 c.c. of 2*N* nitric acid are added, and then water up to 250 c.c. The whole is now boiled to expel bromine and iodine vapours and again boiled with phosphorous acid. The residual chlorine is then titrated as just directed. A special pipette for measuring bromine is described. A Lunge-Rey weighing pipette may also be used.  
L. DE K.

**Reduction of Barium Sulphate in Ordinary Gravimetric Estimations.** OTTO FOLIN (*J. Biol. Chem.*, 1907, 3, 83—86).—A reply to Acree's criticism (*Abstr.*, 1906, ii, 897). Fresh experiments are brought forward in support of the author's contention (*ibid.*, ii, 123) that barium sulphate precipitates are not reduced ordinarily when ignited together with filter paper.  
W. D. H.

**Detection and Estimation of Ammonia in Methylamine and Volatile Fatty Amines.** MAURICE FRANÇOIS (*Compt. rend.*, 1907, 144, 857—859. Compare this vol., i, 391).—The method of separat-

ing methylamine and ammonia, already described, may be applied quantitatively by taking a weighed quantity, near to, but not exceeding, 0.5 gram of the carefully dried amine hydrochloride, placing this in a 250 c.c. flask, adding 7 c.c. of a 30% solution of sodium hydroxide, 10 c.c. of a 20% solution of sodium carbonate, and 5 grams of yellow mercuric oxide, filling up to the mark with water and agitating the whole for one hour. The freedom of the supernatant liquid from ammonia may then be ascertained by adding a few c.c. of it to a Nessler solution made by dissolving mercuric iodide (22.7 grams), potassium iodide (33 grams), and sodium hydroxide (35 grams) in sufficient water to form a litre of solution.

This Nessler solution when heated to boiling will furnish a reddish-brown precipitate if a liquid containing as little as 0.002% of ammonium chloride is added, but furnishes no precipitate with methylamine hydrochloride.

The amount of methylamine contained in the supernatant liquid may be estimated by Schloesing's method, using litmus as an indicator and baryta water as a standard alkali. The ammonia remains in combination with the mercuric oxide and may be obtained by washing the latter with water containing sodium hydroxide and sodium carbonate, placing it in a Schloesing's apparatus, and adding potassium iodide which liberates the ammonia, which may then be estimated in the usual manner.

This method of estimation is equally applicable to di- and tri-methylamine and to mono-, di-, and tri-ethylamine, but in detecting ammonia in presence of di- and tri-methylamine the bases must be liberated from the hydrochlorides by the addition of a solution of sodium hydroxide.

T. A. H.

**Berthier's Method for Estimating Calorific Power, and Welter's Hypothesis.** MAX STOECKER (*Zeitsch. angew. Chem.*, 1907, 20, 653—655).—A review of papers published on this subject. Although Langbein (*Chem. Zeit.*, 1906, 31, 1115) has shown that Berthier's method for estimating the calorific power of fuels is untrustworthy, Welter's law nevertheless holds true, provided the combustible be in the gaseous state; in the case of solids, the heat rendered latent on the passage of the combustible from the solid to the gaseous state must be taken into account.

W. H. G.

**Laboratory Apparatus.** [Estimation of Carbon Dioxide. Evolution of Gases under Pressure.] NICOLAE TECLU (*J. pr. Chem.*, 1907, [ii], 75, 234—237).—A new form of apparatus for the estimation of carbon dioxide and an apparatus for the evolution of gases under high pressures are described with illustrations.

G. Y.

**The Estimation of Potassium by the Platinum Chloride Method.** HENRI J. F. DE VRIES (*Chem. Weekblad*, 1907, 4, 231—242).—The causes of error in the estimation of potassium by the platinum chloride method are discussed, and the author's views as to the best means of avoiding them are stated. A summary of work on this subject is given.

A. J. W.

**Volumetric Estimation of Dilute Solutions of Alkali Hydroxides containing Carbonate by Winkler's Method.** MAX LE BLANC (*Zeitsch. anorg. Chem.*, 1907, 53, 344—348).—In a previous paper (Le Blanc and Novotný, this vol., ii, 22) it was pointed out that, although Winkler's method for the volumetric estimation of mixed alkali carbonate and hydroxide gives trustworthy results in strong solutions, errors arise with dilute solutions owing to the fact that when alkali carbonate is added to a solution of barium chloride, the solution becomes slightly acid. Similarly, it is now shown that when gradually increasing amounts of alkali carbonate are added to mixed solutions of barium chloride and hydroxide, the amount of dilute hydrochloric acid required for neutralisation gradually diminishes. The acidity increases with, but is not proportional to, the amount of carbonate added. The phenomenon is analogous to the carrying down of a certain amount of barium hydroxide from barium chloride solutions by colloidal arsenic sulphide. The error is not diminished by carrying out the precipitation at a high temperature, but may be to some extent corrected for by control experiments.

Owing to a slight error in deducing the formulæ, the degree of hydrolysis of calcium carbonate in aqueous solution was given incorrectly in the former paper; from conductivity measurements, 95%, and from direct solubility measurements, 89% of the salt is hydrolysed at 18°. G. S.

**The Arsenate Process for the Separation of Magnesium and the Alkalis.** PHILIP E. BROWNING and W. A. DRUSHEL (*Amer. J. Sci.*, 1907, [iv], 23, 293—296).—The magnesium is precipitated by adding to the distinctly ammoniacal solution an excess (40—80%) of ammonium arsenate. The precipitation may be hastened by cooling in a freezing mixture, or more conveniently by adding one-fifth of the volume of alcohol. The precipitate is collected in a weighed, perforated, platinum crucible containing an asbestos felt, and finally converted by ignition into pyroarsenate.

The filtrate is transferred to a platinum dish, 10 c.c. of fuming hydrochloric and 10 c.c. of hydrobromic acid are added, and the whole is evaporated to dryness. Instead of hydrobromic acid, 1—3 grams of ammonium bromide may be employed. The residue after being gently ignited is free from arsenic, and contains the alkalis as chlorides. These are dissolved in a little water, transferred to a weighed platinum crucible, evaporated with addition of a little sulphuric acid (1 : 1), gradually heated to redness, and finally weighed as sulphates. L. DE K.

**Report of the [American] Sub-committee on Zinc Ore Analysis.** GEORGE C. STONE and W. GEORGE WARING (*J. Amer. Chem. Soc.*, 1907, 29, 262—269).—The assay of zinc ores is in a most unsatisfactory state. The following process is therefore recommended.

The ore (if necessary after a preliminary fusion) is dissolved in nitric, or hydrochloric, acid and finally evaporated with excess of sulphuric acid. The mass is dissolved in water, and boiled for ten minutes with a heavy sheet of aluminium. To prevent oxidation, both



the filter and the beaker should contain a strip of aluminium. The filtrate is neutralised with sodium hydrogen carbonate, using methyl-orange as indicator, and a few drops of formic acid are added. If much iron is present, 2—4 grams of ammonium thiocyanate are added, the aluminium is removed, and the liquid is heated to boiling and saturated with hydrogen sulphide. The zinc sulphide is collected, washed with hot water, and then redissolved in 30—40 c.c. of water and 8—10 c.c. of hydrochloric acid. After expelling the hydrogen sulphide the zinc is estimated gravimetrically as pyrophosphate or, in experienced hands, it may also be titrated with potassium ferrocyanide with ammonium heptamolybdate as indicator. L. DE K.

**Electrolytic Estimation of Lead in Tin Alloys and Tinned Iron.** ARTHUR WESTERKAMP (*Arch. Pharm.*, 1907, 245, 132—139).—About 0.5 gram of the alloy in fine filings is treated with 2—3 c.c. of red, fuming nitric acid of sp. gr. 1.52; after a quarter of an hour, 10—15 c.c. of dilute nitric acid are added, and the whole is digested on the water-bath for a quarter of an hour; it is then allowed to cool and filtered, and from the filtrate the lead is precipitated electrolytically as the dioxide on an anode of platinum gauze by means of a current of 0.2 ampere at 2—3 volts, the operation requiring twelve hours.

The use of anhydrous nitric acid is essential; in an alloy of 2.5% of lead with tin the amounts of lead found were 2.365% and 2.205% respectively when acid of sp. gr. 1.4 and of 25% strength were used, as against 2.42% when acid of sp. gr. 1.52 was used. C. F. B.

**Estimation of Lead as Sulphate.** LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1907, 21, 141—149).—The lead is precipitated with sulphuric acid, avoiding large excess, and washed with water containing 0.7% of ammonium sulphate. The precipitate is then dried and ignited, the filter being burnt separately. L. DE K.

[**Estimation of**] **Thallium.** L. F. HAWLEY (*J. Amer. Chem. Soc.*, 1907, 29, 300—304).—See this vol., ii, 460.

**Estimation of Alumina in Silicates** F. WILLY HINRICHSSEN [and, in part, E. KEDESZY, V. RODT, and F. THOMAS] (*Ber.*, 1907, 40, 1497—1501).—It has been observed in the analysis of silicates, that much smaller amounts of alumina are found if the silicate is dissolved in a mixture of hydrofluoric and sulphuric acids than if it is fused with sodium potassium carbonate, the loss amounting in some cases to 30% of the total aluminium oxide present. This work was undertaken with the object of determining the source of the error. It is found that the hydrogen fluoride is not driven off completely even when the acid mixture evolves sulphur trioxide copiously; on addition of ammonia, the hydrofluoric acid remaining in the solution forms *ammonium aluminium fluoride*,  $(\text{NH}_4)_3\text{AlF}_6$ , which separates as a crystalline precipitate only when the solution is cooled. The results of a number of experiments, which are tabulated and expressed by a curve, show that the amount of aluminium hydroxide precipitated from the boiling solution by

ammonia diminishes as the proportion of ammonium fluoride present is increased, until no precipitation takes place from a solution containing 0.1398 gram of aluminium oxide and 0.600 gram of ammonium fluoride. The curve has a break at the point representing a mixture of 0.33 gram of ammonium fluoride and 0.1398 gram of aluminium oxide, which suggests that aluminium fluoride is formed in presence of small proportions, but ammonium aluminium fluoride in presence of greater proportions, of ammonium fluoride.

The results of a series of determinations of the amount of hydrogen fluoride remaining after mixtures of alumina and sulphuric and hydrofluoric acids, in known proportions, have been heated, show that even under the most favourable conditions of heating the residue readily contains sufficient hydrogen fluoride to account for the errors observed in the silicate analyses. When, as in the determination of the alkali metals in a silicate, the hydrofluoric-sulphuric acid method of solution must be used, the sulphuric acid should be evaporated completely and the residue ignited gently to insure expulsion of all fluorine.

G. Y.

**Estimation of Iron in Presence of Titanium.** FRANK A. GOOCH and H. D. NEWTON (*Amer. J. Sci.*, 1907, 28, 365—367).—Hitherto, the well-known process of reducing ferric salts with metallic zinc before titration with permanganate could not be applied in presence of titanium as this is also reduced. The authors find that this may be reoxidised without the ferrous compound being affected, by adding to the reduced solution a little copper sulphate or oxide or preferably some bismuth oxide. The liquid is then rapidly filtered and titrated.

The ferric solution is reduced most conveniently by passing it through a Blair reductor charged with amalgamated zinc.

L. DE K.

**Estimation of Tungstic Acid in Natural and Concentrated Tungsten Ores.** HUGH F. WATTS (*Chem. Zentr.*, 1907, i, 760—761; from *Western Chemist and Metallurgist*, July, 1906).—One gram of the carefully powdered material is heated with 50 c.c. of concentrated hydrochloric acid and 15 c.c. of concentrated nitric acid in a covered beaker at just below the boiling point for four hours; it is not advisable to evaporate to dryness as the residue is often very sparingly soluble in ammonia. Fifty c.c. of hot water are added to the 10—15 c.c. of liquid which is left, the clear solution is poured off after half an hour, and the residue washed twice with 50 c.c. of hot water to which 5 c.c. of hydrochloric acid have been added. The addition of hydrochloric acid to the wash-water causes the tungstic acid to settle. The tungstic acid is separated from the silicic acid by treatment with a dilute solution of ammonia containing a small quantity of ammonium chloride; the latter causes the filter paper to retain the silicic acid. If the precipitate after thoroughly washing with ammonia still contains undecomposed material, the process is repeated after treatment with aqua regia. The ammoniacal solution is evaporated in a porcelain crucible, the ammonium salts expelled, and the residual tungstic acid

calcined at the highest temperature of an ordinary Bunsen burner; a blow-pipe should not be used owing to the volatility of the acid. The tungstic acid contains only traces of silica. E. W. W.

**Composition and Analysis of Wolfram and Hübnerite.** PAUL NICOLARDOT (*Compt. rend.*, 1907, 144, 859—861).—This process is intended for the examination of the commercial minerals, which have been separated from excess of tinstone and siliceous matters by the usual electro-magnetic methods, and contain at least 60% of tungstic anhydride.

A weighed quantity of the mineral is placed in a silver crucible containing a thin layer of potassium or sodium hydroxide, and is covered with about three times its weight of the same alkali. The mixture is heated and in about a quarter of a minute after the alkali has been melted the reaction is complete. The alkaline liquid is filtered, oxidised with bromine, neutralised with nitric acid, rendered acid with tartaric acid, and the sulphates estimated by the addition of barium nitrate. The acid filtrate, after removal of excess of barium, is evaporated to dryness, and the residual silica collected and weighed unless it exhibits a yellow colour, when it should first be fused with potassium hydrogen sulphate, and the acid solution from this added to the main liquid, which is then treated with hydrogen sulphide to remove arsenic, molybdenum, and tin, and possibly copper or bismuth. Ammonia is added to the filtrate, which is again treated with hydrogen sulphide to transform the tungsten into sulphotungstate, which is carefully decomposed with hydrochloric acid, and the tungsten separated as the sulphide, which is filtered out, washed with dilute nitric acid, dried, calcined, and weighed. In the filtrate, iron and phosphorus are estimated in the usual manner. In the residue left from the alkaline fusion, iron, manganese, and tin are estimated by the usual processes. In all cases the barium sulphate precipitate should be examined for silica, tungstic, tantallic, and columbic acids, and the two last should also be sought for in the silica. All the samples of wolfram examined have been found to contain columbic and tantallic acids, which are estimated by the usual methods.

This method of analysis supports Ebelman's view that wolfram consists of ferrous tungstate, since tungsten dioxide is attacked very slowly by melted alkalis, whereas the mineral is readily acted on.

T. A. H.

**Quantitative Estimation of Antimony by Electrolysis of Solutions of its Sulpho-salts.** FRITZ FOERSTER and J. WOLF (*Zeitsch. Elektrochem.*, 1907, 13, 205—210).—When antimony is deposited from a solution of thioantimonate in presence of potassium cyanide the deposit is always too heavy by 1 or 2 per cent. The authors confirm this very fully and show that the excess weight is due to the presence of oxygen in the metal and also to traces of sulphur.

T. E.

**Employment of Cryoscopy in the Analysis of Spices and other Drugs.** ERNST BECKMANN (*Arch. Pharm.*, 1907, 245, 211—234). [With P. DANCKWORTT].—Of the powdered drug, 5 grams are

allowed to remain for a day with 30 grams of ethylene bromide, the solution is filtered into a freezing point apparatus, a few drops of water are added, and the freezing point is taken and compared with that obtained with moist ethylene bromide alone. Another 5 grams in a thimble of filter paper are then heated in a current, first of saturated steam until they are moistened throughout, then of superheated steam at  $130^{\circ}$  until the essential oil has been expelled; the (dry) residue is then treated as described above for the freezing point determination. Experiments with certain essential oils (those of anise, cardamom, coriander, dill, fennel, caraway, mace, cloves, peppermint, cassia, and cinnamon) showed that the specific lowering of freezing point produced by 1 gram of oil in 100 grams of moist ethylene bromide is  $0.77 \pm 0.06^{\circ}$ . Consequently an approximate estimation of the amount of essential oil in a spice or other drug can be made by taking the difference of the freezing points obtained with the original and with the steam-distilled drug, and reckoning 1 gram of essential oil to be present in 100 grams of the ethylene bromide for each  $0.77^{\circ}$  in this difference.

In aromatic waters containing only water and essential oil, the latter can be estimated by shaking 250 grams of the aromatic water with 30 grams of ethylene bromide, taking the freezing point of the latter, and comparing it with that of moist ethylene bromide,  $0.03^{\circ}$  being subtracted from the difference in order to correct for the loss of ethylene bromide by solution in the water, and then reckoning as above. If the aromatic water contains alcohol, the ethylene bromide extract must be shaken with 250 grams of water before its freezing point is taken; in this case no correction need be applied, as the errors counterbalance each other.

The cryoscopic method was used also to estimate the fatty oil in several seeds, the lowering of freezing point produced by the corresponding oils having been determined first; also to estimate the butter-fat in (watered) milk, in cheese, and in confectionery.

In many cases the results obtained were compared with results obtained by the usual methods, and the agreement was found to be good.

C. F. B.

**Quantitative Estimation of Hydroxyl Groups by Means of Organo-magnesium Compounds.** TH. ZEREWITINOFF (*Ber.*, 1907, 40, 2023—2031).—An extension of the method introduced by Hibbert and Sudborough (*Trans.*, 1904, 85, 933). When the substance is not soluble in amyl ether, anhydrous pyridine may be used. A definite compound with the amyl ether derivative of magnesium methyl iodide,  $(C_5H_5N)_2MgIMe(C_5H_{11})_2O$ , is formed, but this reacts with the hydroxyl derivative in the same manner as the free magnesium methyl iodide. When pyridine is used, the mixture must not be heated, and the measurement of the methane evolved should be made as quickly as possible, as pyridine itself reacts with magnesium methyl iodide when heated, evolving a gas. A slightly modified form of apparatus is used, and it is stated that the determination can be made without replacing the air in the apparatus by nitrogen, although oxygen is slowly absorbed by the Grignard compound.

Good results have been obtained with some thirty-six compounds, including acids, such as succinic, tartaric, benzenesulphonic, salicylic, and oximes, for instance, camphoroxime and benzildioxime.

J. J. S.

**Detection of Sucrose in Plants with the Aid of Invertase.** EMILE BOURQUELOT (*Arch. Pharm.*, 1907, 245, 164—171).—Into 90—95% alcohol, boiling in a flask, pieces of the part of the plant to be examined are dropped in one by one as they are cut off, 250 grams being added in all; the boiling is then continued for twenty minutes. The alcoholic solution is mixed with a slight excess of calcium carbonate in order to neutralise organic acids, the alcohol is distilled off in the water-bath, and the residue is extracted with water saturated with thymol, the extract being diluted to 250 c.c. with the same liquid. Of the diluted extract, 50 c.c. are allowed to remain in a corked flask at 25—30°, and side by side with them in another flask the remainder mixed with 1 gram of prepared yeast powder. After two days, 20 c.c. of each liquid are clarified with lead acetate solution (4 c.c. usually suffice), filtered, and examined in the 2-dcm. tube of a polarimeter; a smaller dextro-rotation in the extract treated with yeast, as compared with the other, indicates that sucrose was present and has undergone inversion. As a confirmatory experiment, the reducing power of the two liquids can be determined and the difference reckoned as invert-sugar produced from sucrose; if the two methods give different results, the sugar present cannot have been sucrose, or wholly sucrose (gentianose, raffinose, and stachyose are also hydrolysed by invertase).

The prepared yeast, containing invertase but freed from other enzymes, is obtained as follows. Fresh top-yeast ("bakers' yeast" will do) is stirred with a little water and drained with the pump; it is then stirred with eight to ten times its weight of 95% alcohol, and allowed to remain with the latter twelve to fifteen hours; finally it is drained with the pump, washed first with a little 95% alcohol and then with ether, and dried at 30—35°.

By this method, sucrose has been found to be present almost universally in all parts of those plants which contain chlorophyll.

C. F. B.

**Employment of the Biochemical Method for the Detection and Estimation of Sucrose and Glucosides in the Plants of the Family of the Caprifoliaceæ.** EMILE DANJOU (*Arch. Pharm.*, 1907, 245, 200—210).—*Sambucus nigra* contains invertase in addition to traces of emulsin. The leaves were dried and extracted with boiling 90% alcohol, the extract treated with a few grams of calcium carbonate and freed from alcohol by distillation, the residue filtered, concentrated under diminished pressure, diluted with 95% alcohol, and set aside; potassium nitrate crystallised out. From the mother liquor, crystalline sucrose could be obtained by inoculation with that substance. This mother liquor was diluted with more 95% alcohol, allowed to remain several days, and distilled under diminished pressure until nearly all the alcohol was expelled. The residue was extracted several times with boiling ethyl acetate saturated with water; the extract

evaporated to dryness under diminished pressure; the residue dissolved in cold water, and the solution shaken with a little calcium carbonate, filtered, and evaporated to dryness under diminished pressure; the residue extracted with ethyl acetate saturated with water, and the extract concentrated and left to crystallise; finally the crystals were recrystallised, first from anhydrous ethyl acetate and then from a mixture of this with an equal volume of water. In this way a glucoside, *sambunigrin*,  $C_{14}H_{17}O_6N$ , was obtained; this has m. p.  $150-152^\circ$  and  $\alpha_D -76.3$  in a 2-dcm. tube; it is isomeric with amygdonitrile-glucoside and prulaurasin, and is hydrolysed by emulsin or *Aspergillus niger* to dextrose, benzaldehyde, and hydrocyanic acid in accordance with the equation:



This glucoside only occurs in *Sambucus nigra* and its varieties. Other species of this family do not contain it, but all *Caprifoliaceæ*, whether *Sambucineæ* or *Lonicereæ*, contain enzymes and glucosides that can be hydrolysed with emulsin.

C. F. B.

**Estimation of Sucrose in Osmose-Water and Molasses.** KARL ANDRLÍK and VLADIMÍR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1907, 417—420).—The authors state that owing to the action of hydrochloric acid on the amino-acids the sugar solutions should contain free hydrochloric acid when examined in the polariscope before inversion. As, however, inversion rapidly sets in, it is necessary to add some substance which retards this change for at least ten minutes (carbamide or betaine). As regards the estimation of sucrose in osmose-water, the use of a solution of 5 grams of urea in 7.5 c.c. of strong hydrochloric acid is recommended; the sucrose will then suffer no inversion during the short time required for the polarimetric observation. Another portion is inverted as usual and the amount of sucrose calculated from the formula  $100(P - T)/143.5 - t/2$ .

L. DE K.

**New Colour Reaction for Lignocelluloses.** ALVIN S. WHEELER (*Ber.*, 1907, 40, 1888—1890).—The lignocelluloses give a blood-red coloration with salts of the nitroanilines. The reaction is carried out best with a reagent prepared by dissolving 2 grams of *p*-nitroaniline in 100 c.c. of hydrochloric acid, D 1.06. The full intensity of the coloration is reached instantaneously if the reagent is heated.

G. Y.

**Some Reactions of Formaldehyde in Presence of Sulphuric Acid.** HUGO DIRTZ (*Chem. Zeit.*, 1907, 31, 445—447, 486—487).—Naphthalene, fluorene, and phenanthrene give with sulphuric acid and formaldehyde a blue *product* which is decolorised more or less rapidly by water, alcohol, or methyl alcohol, but the original colour is restored on addition of sulphuric acid. Retene gives a dirty, bluish-green, and chrysene a reddish-violet, coloration. Carbazole also gives a blue, but the colour is not discharged by water. Anthracene gives a dirty green, almost black, coloration. Efforts have been made, but as yet not quite successfully, to apply some of these colour-tests to the direct detection of formaldehyde in milk.

L. DE K.

**The Chemistry of Hehner's Test for Formaldehyde in Milk.** OTTO ROSENHEIM (*Analyst*, 1907, 32, 106—108).—Under the usual conditions of the reaction, the formaldehyde may combine with the protein, the resulting aldehyde-protein being oxidised afterwards; this can be shown by preparing the pure aldehyde-protein compound and submitting it to the action of an oxidising substance and sulphuric acid. There is evidence, however, that the formaldehyde may be oxidised first, as the oxidation compound, obtained by the interaction of hydrogen peroxide and formaldehyde in ammonium sulphate solution, gives the characteristic coloration with proteins and pure sulphuric acid. A coloration is not obtained when the protein is oxidised before adding the formaldehyde. The action depends on the presence of the tryptophan group (*Abstr.*, 1906, i, 696) in the protein molecule, and the intensity of the coloration obtained with different proteins is directly proportional to the amount of tryptophan in the molecule.

W. P. S.

**Detection of Sulphonal in Trional or Tetronal.** ÉMILE GABUTTI (*J. Pharm. Chim.*, 1907, 25, [vi], 483—486).—One part of sulphonal is soluble in 65 of alcohol at 15°, whilst trional and tetronal require 17·5 and 18·5 parts of alcohol respectively for solution under the same conditions. One part of sulphonal is soluble in 133 parts of ether at 15°, whereas trional and tetronal dissolve in 15·57 and 9·83 parts of the same solvent respectively.

A solution of sulphonal in ether when placed on a glass slide deposits fern-like groups of crystals similar to those produced by ammonium magnesium phosphate, whilst trional under the same conditions forms square tablets, and tetronal radiating fibrous groups resembling those obtained with urea oxalate.

The solubilities of sulphonal given above are taken from Scholvein (*Arch. Pharm.*, 1888, 26, 609).

T. A. H.

**Estimation of "Total" and "Volatile" Acids in Coloured Wines.** GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1907, 25, [vi], 491—492).—The wine is boiled for a few minutes under a reflux condenser to remove carbon dioxide. Ten c.c. of the boiled wine are then decolorised by the addition of 5 c.c. of a 10% solution of mercuric acetate, the mixture filtered, and the precipitate washed with distilled water until 300 c.c. have been collected. To this, 10 c.c. of a 20% solution of Rochelle salt are added and the number of c.c. ( $n$ ) of normal potassium hydroxide solution required to neutralise this determined, using phenolphthalein as indicator. The number ( $n'$ ) of c.c. of normal potassium hydroxide solution required to neutralise a mixture made by adding 5 c.c. of 10% mercuric acetate solution and 10 c.c. of 20% Rochelle salt solution to 295 c.c. of distilled water is determined. The relation  $4·9(n-n')/4$  gives the "total" acid calculated as sulphuric acid in a litre of wine. The "volatile" acid is determined by evaporating 10 c.c. of the wine, freed from carbon dioxide, to dryness at 100°, redissolving in a little warm water, and repeating the evaporation. The acid in the dry extract is then determined as before. The result deducted from the "total" acid gives "volatile" acid.

T. A. H.

**Estimation of Non-volatile Organic Acids in Tobacco.** JULIUS TÓTH (*Chem. Zeit.*, 1907, 31, 374).—Two grams of the sample are extracted with ether (*ibid.*, 1906, 30, 57) so as to obtain the total organic acids. One-half of the ethereal solution is evaporated to dryness and the residue taken up with luke-warm water. The oxalic, malic, and citric acids are then separated according to Schläesing's directions.

The results are fairly accurate. The amount of oxalic acid in tobaccos varies from 0.42 to 2.57%, that of citric acid from 0.92 to 2.49%, and that of malic acid from 1.56 to 7.81%.  
L. DE K.

**Estimation of Tartaric Acid.** ALFRED C. CHAPMAN and PERCY WHITTERIDGE (*Analyst*, 1907, 32, 163—166).—A quantity of the sample to be tested (cream of tartar, Seidlitz powders, baking powders, &c.), representing about 0.1 gram of tartaric acid, is dissolved in 40 c.c. of water and neutralised if alkaline with acetic acid, if acid with potassium hydroxide. The liquid is heated to boiling and precipitated by adding 15 c.c. of a bismuth solution (30 grams of crystallised bismuth nitrate dissolved in 20 c.c. of glacial acetic acid and water up to 300 c.c.), and after stirring vigorously for a few minutes, the bismuth tartrate is collected and washed with hot water. It is then dissolved off the filter in 20 c.c. of hot 10 vol. % sulphuric acid, a further 30 c.c. of this being used for washing the paper. A solution containing exactly 1% of potassium permanganate (14 c.c. = 0.1 gram of tartaric acid) is now dropped into the hot solution until there is about 0.5 c.c. in excess, which is then titrated back by oxalic acid solution (19.9 grams per litre).

It is evident that the process can only be employed in the absence of such acids as citric, tannic, malic, or oxalic acids which also yield precipitates oxidisable by permanganate. Succinic acid does not seem to interfere.  
L. DE K.

**Use of Carbon Disulphide in the Estimation of Salicylic Acid in Wine.** WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1907, 29, 293—294).—The wine is shaken with ether and the residue left on evaporation is rubbed with ten successive portions of 5 c.c. of carbon disulphide, which dissolves the salicylic acid and leaves behind several organic impurities which interfere with the ferric chloride test.

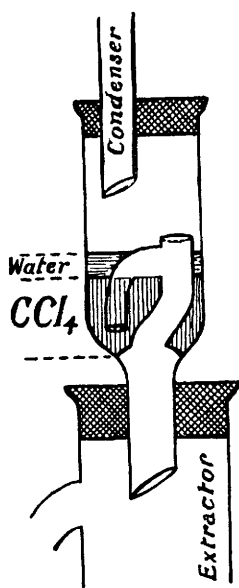
Benzene, carbon tetrachloride, and light petroleum, containing 10% of ether, dissolve the salicylic acid, but very imperfectly. Chloroform redissolves some of the colouring matter and cannot be used (also compare this vol., ii, 58).  
L. DE K.

**Disadvantages of the Use of Potassium Dichromate for the Preservation of Samples of Milk for Analysis.** P. GRÉLOT (*J. Pharm. Chim.*, 1907, [vi], 25, 369—373).—Milk, preserved for analysis by the addition of potassium dichromate, gives abnormal figures for ash, acidity, refractive index, and freezing point. Moreover, the detection of potassium dichromate, previously added, as a preservative is prevented and there is produced, probably by the oxidation of lactose, a volatile product, which simulates formaldehyde and is liable to be mistaken for it.  
T. A. H.



**A Source of Error in the Extraction of Fats by Means of Carbon Tetrachloride and its Elimination.** F. VOLLRATH (*Chem. Zeit.*, 1907, 31, 398).—When extracting substances which contain much moisture with carbon tetrachloride in the usual (Soxhlet) apparatus, drops of water are condensed in the condensing tube and fall back together with the condensed carbon tetrachloride into the mass which causes the fat to be incompletely extracted. In the author's apparatus the water is separated automatically from the condensed carbon tetrachloride which alone finds its way back into the extraction tube.

L. DE K.



**Fat Analysis.** WILHELM FAHRION (*Chem. Zeit.*, 1907, 34, 434—436).—A series of experiments showing the action of heat on fatty acids; also a criticism of the methods for estimating unsaponifiable matters. The matter may be summarised as follows. On heating unsaturated fatty acids, oxidation and polymerisation sets in, and the acid and iodine numbers fall. The autoxidation products contain, besides the carboxyl groups, basic hydrogen, so that on prolonged autoxidation the saponification number is raised. The autoxidation products eliminate secondary water which leads to a loss in weight and to the

formation of small quantities of neutral substances (probably lactones). Fatty acids should therefore be dried at the temperature of the water-bath or else they should be weighed in the form of neutral alkali salts with due regard to the amount of alkali used (*Abstr.*, 1906, ii, 402). The mean molecular weight may be determined from the saponification number. In the estimation of the unsaponifiable matters, light petroleum of low boiling point is preferable to the use of ether.

L. DE K.

**Determination of the Saponification Number [of Fats].** DAVID HOLDE (*Chem. Rev. Fett. Harz. Ind.*, 1907, 14, 105—106).—The use of alcoholic potassium hydroxide involves a source of error as potassium carbonate is not quite insoluble in the alcohol; this may, however, be reduced to a minimum by using almost absolute alcohol. Alcoholic sodium hydroxide dissolves but traces of sodium carbonate, but the soap obtained has the property of solidifying rapidly, so the titration must be carried out while the liquid is still hot. As a rule, the use of alcoholic potassium hydroxide will be found more convenient.

L. DE K.

**Analysis of Camphor.** J. E. CRANE and C. M. JOYCE (*J. Soc. Chem. Ind.*, 1907, 26, 386—388).—The assay of camphor may be carried out by three methods, none of which, however, can lay claim to great accuracy.

**Sublimation Process.**—About 1 gram of the sample is placed in a 2-inch watch-glass, which is then covered with a 3-inch watch-glass. The glass is placed on a metallic plate, and a moderate heat, by means of a tiny flame, is applied from ten to sixty minutes until the camphor has all sublimed on the 3-inch glass. After cooling for five minutes, the 3-inch glass is removed, covered at once with a duplicate glass, and, after being kept in a desiccator for one hour, the whole is weighed and the weight of the watch glasses deducted. The non-volatile matter left in the 2-inch watch-glass may be weighed also. The process, owing to some of the camphor volatilising, gives results which are too low, but this may be remedied by applying a correction of 3%.

**Specific Gravity Process.**—Ten grams of the sample are dissolved in pure benzene, and the liquid is made up to 100 c.c. at 20°. The sp. gr. of the liquid is then taken at 20° and reference made to a table constructed by the authors. For instance, if the sp. gr. be 0.8937, 100 c.c. of the solution contains 9.5 grams of pure camphor, so that the sample would contain 95%. The accuracy of the process is, however, affected by the presence of moisture in the sample, as this dissolves to some extent in the benzene.

**Polarisation Process.**—This process, which cannot be applied to synthetical camphor, consists in observing a solution of the sample in benzene in a Laurent polarimeter and applying the formula  $c = 115.205 (1 = \sqrt{1 + 0.04367 \cdot \alpha / l})$ , in which  $c$  = weight of camphor in 100 c.c. of solution,  $\alpha$  = rotation, and  $l$  = length of tube in decimetres. The accuracy of this process is also affected by the presence of moisture.

L. DE K.

**Evaluation of Rhubarb.** ALEXANDER TSCHIRCH and J. EDNER (*Arch. Pharm.*, 1907, 245, 150—153).—Of the drug, 0.5—1.0 gram is boiled repeatedly with dilute alcoholic potassium hydroxide until no more is dissolved; the alcohol is distilled off from the extract, and the residue is diluted with water and acidified with hydrochloric acid; the precipitate is washed and dried and extracted for several hours with chloroform in a Soxhlet apparatus. The chloroform is distilled off from the extract; the residue is dissolved with the aid of heat in 10 c.c. of 2% aqueous sodium carbonate; 50 c.c. of water are added and 20 c.c. of a diazotised *p*-nitrobenzene solution, and then hydrochloric acid, drop by drop, with vigorous shaking until no more precipitation of azo-dye occurs and the liquid is acid in reaction. After several hours the precipitate is collected on a tared filter, dried, and weighed; its weight, multiplied by 0.58, gives the weight of chrysophanol,  $C_{15}H_8O_2(OH_2)$ , from which it was formed.

The results are rather higher, and probably more correct, than those obtained by the colorimetric method. Drugs of different origin were found to contain on an average the percentages of chrysophanic acid here indicated: Canton round, 3.9; Shanghai, 3.8; Shensi flat and Canton flat, 3.0; Shensi and Shanghai flat, 2.7; Canton II, 2.5; English, 2.0; French, 1.9; Austrian, 1.6.

C. F. B.

**Colour Reaction of the Tannins.** A. BRISSEMORET (*Bull. Soc. chim.*, 1907, [iv], 1, 474—483).—The tannin is dissolved in sufficient

alcohol (60°) or ethyl acetate, and to this is added glacial acetic acid containing a small quantity of ferrous sulphate. On pouring sulphuric acid containing a little ferric sulphate into this mixture so as to form a separate layer, the characteristic colours are produced at the plane of contact of the two layers. Ellagic acid gives a yellowish-green coloration, and as a similar tint is produced by several of the natural tannin glucosides, it is conjectured that these contain an ellagic acid nucleus. Gallotannin gives a yellow coloration, as do also alizarin-yellow A, galloflavin, and the natural tannins of coca leaves and chestnut bark.

The caffetannins, including quinatannin and cinchona red, give scarlet or wine-red colorations, whilst their characteristic decomposition products, catechol and caffeic acid, give violet and scarlet colorations respectively. Protocatechuic acid, formed by the action of fused potassium hydroxide on these tannins, gives no coloration. The phloroglucinol-tannins, such as those contained in male fern, quebracho wood, tormentil, and rhatany roots, give scarlet, wine-red, violet-red, or Bordeaux-red colours, and similar tints are obtained with the tannins of cutch, kola, and guarana.

Directions for the application of this colour reaction in the cases of certain astringent drugs are given. T. A. H.

**Estimation of Ammonia and Urea in Urine.** KARL SPIRO (*Beit. chem. physiol. Path.*, 1907, 9, 481—483).—The estimation of ammonia is most readily effected by Folin's method (*Abstr.*, 1901, ii, 575; 1904, ii, 83), and the hydroxides of sodium, potassium, or barium may be used when the current of air is passed through the solution of a low temperature. Several estimations may be made with the same air current,

The urea may be estimated in the residue by Mörner and Sjöqvist's method, namely, by adding alcohol and ether, filtering, and determining the percentage of nitrogen in the filtrate by Kjeldahl's method after the removal of ether and alcohol. J. J. S.

**Vanillin as a Test for Soluble Ferments.** M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, 12, 141—142).—Vincent (*ibid.*, 1905, 10, 322) has recommended a hydrochloric acid solution of vanillin as a characteristic test for vegetable ferments. The author has applied the test to amylase, pepsin, and zymase which give the characteristic violet-purple coloration, but unfortunately the same reaction is obtained after these substances have been rendered quite inactive by exposure to heat. Milk also gives the reaction whether boiled or not.

The test is given by proteins in general, and even by starch if not prepared with great care. L. DE K.

**Detection of Rice Husk in Bran.** E. KINKELS (*Ann. Chim. anal.*, 1907, 12, 92—93).—When boiled with a solution of *p*-phenylenedimethyldiamine, bran from wheat turns yellow with faint rose-coloured edges, whilst rice husk turns carmine-red. Barley bran gives a faint rose colour. L. DE K.

## General and Physical Chemistry.

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**Spectrochemistry of Nitrogen.** JULIUS W. BRÜHL (*Zeitsch. physikal. Chem.*, 1907, **59**, 507—512).—An unfavourable criticism of Schmidt's recent paper (this vol., ii, 321), more especially in reference to his interpretation of phenomena observed in the case of anthranilic acid derivatives and methyl-*o*-aminobenzaldehyde.

J. C. P.

**Ultimate Rays or Rays of Great Persistence of the Metals in the Dissociation Spectra.** ANTOINE DE GRAMONT (*Compt. rend.*, 1907, **144**, 1101—1104).—In the dissociation spectrum of a mineral, the rays of an element disappear successively in proportion to the diminution of its amount in the various specimens examined, and the order of disappearance is constant. Thus there is a limit of total appearance of the spectrum, above which it is complete, and below which only part of the rays is visible, the latter gradually disappearing. The last rays which persist are the ultimate rays. The author has compared the spectra given by the same element under very different thermal or electrical conditions, and finds that the strongest rays of the dissociation spectrum are not necessarily the ultimate rays, but are rays of relatively low temperature (in the case of metals and some metalloids). The ultimate rays for Li, K, Na, Cu, Ag, Au, Mg, Zn, Ca, Sr, Al, Tl, Ge, Sn, Pb, Bi, Cr, and Fe are given. The ultimate rays are the same in condensed or non-condensed spark spectra, in the arc, and in very hot flame spectra.

E. H.

**Thermo-chemistry of Flame Spectra at High Temperatures.** W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1907, **A**, **79**, 242—261).—The paper is divided into three parts, dealing respectively with the band spectra of the alkali and alkaline earth metals, the chemical reduction of the alkaline earth sulphates, and the thermo-chemistry of the reduction processes in flame reactions.

Spectral observations have been made with a pure dry carbon monoxide flame. On introducing carbonates of lithium, sodium, and potassium, well developed spectra are obtained, but with the oxides, carbonates, and nitrates of calcium, strontium, and barium, no trace of bands or lines can be observed. The chlorides of the alkaline earth metals, on the other hand, show the same spectra as are produced when these salts are heated in a coal-gas flame saturated with hydrogen chloride. In a cyanogen flame, the alkaline earth oxides exhibit spectra if placed at the tip of the inner cone. From these facts, the conclusion is drawn that the bands and lines which are observed when the alkaline earth oxides are heated in the oxyhydrogen flame are not the spectra of the oxides. The spectra are due to the presence of the hydrogen, which reduces the oxides (or sulphides) to the metallic state.

The reduction of the alkaline earth sulphates has been examined by

heating pieces of heavy spar, celestine, and selenite in the oxyhydrogen flame for some minutes, and determining the oxide and sulphide formed.

It was found that heavy spar was completely reduced to sulphide, selenite to oxide, and celestine to a mixture containing about 90% of oxide and 10% of sulphide.

At a red heat in a current of dry hydrogen, barium sulphate is reduced in accordance with the equations:  $\text{BaSO}_4 + 4\text{H}_2 = \text{BaS} + 4\text{H}_2\text{O}$ ,  $\text{BaS} + \text{H}_2\text{O} = \text{BaO} + \text{H}_2\text{S}$ . The second change is a slow one, but the velocity is much greater in the case of calcium.

From a consideration of thermo-chemical data, the author arrives at the conclusion that any reducing process may be effected in the oxyhydrogen flame by a purely chemical change if the energy required to initiate and maintain the action does not exceed 84.8 Cal. per atom of oxygen removed.

H. M. D.

**Absorption Spectra of Salts of the Rare Earths in Various Solvents.** HELEN SCHAEFFER (*Chem. Zentr.*, 1907, i, 1018—1019; from *Physikal. Zeitsch.*, 1906, 7, 822—831).—Experiments on the absorption of salts of the rare earths have shown that the displacement caused by the solvents with the lowest refractive indices are generally the greatest and that Kundt's rule does not hold. The displacements in the yellow and green are usually greater than in the blue or violet. Some of the measurements were made directly, and some by means of photographs. In order to show that the original absorption bands are displaced and that new bands are not formed when other solvents are used, an aqueous solution of didymium nitrate was gradually changed into an acetone solution without altering the concentration of the salt, and by this means the identity of the bands ascertained. Solutions of didymium, cerium, and neodymium nitrates in a series of solvents, of which most were alcohols, and solutions of didymium nitrate in some inorganic and organic acids have been examined. In order to determine the influence of concentration, and therefore of dissociation on the absorption, a very concentrated solution of didymium nitrate containing 30.5 grams in 10 c.c. was diluted to  $\frac{1}{40}$ th the original concentration, the thickness of the layer being increased, however, in the same proportion. It was found that all the absorption bands change their position to some extent on dilution. The violet, blue, and green bands are displaced towards the region of longer wave-length. The fact that the yellow and orange portions of the spectrum of the concentrated solution resemble that of a solution in an organic solvent is in harmony with the dissociation theory, and it might be possible to distinguish the absorption bands of molecules from those of atoms. It would be interesting to examine strong acid solutions and to ascertain the relationship between absorption and dissociation quantitatively. Melde found that coloured solutions, such as carmine and potassium dichromate, did not give the same spectra when mixed and contained in a single trough as when placed separately in two troughs each of half the depth, the one behind the other. No displacement of the bands is caused by mixing solutions of the rare earths or of didymium nitrate with potassium dichromate.

E. W. W.

**Organic Solvent and Ionising Media. VIII. Refractivity and Electrolytic Dissociation.** PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1907, 59, 385—415. Compare Abstr., 1904, ii, 227; 1906, ii, 149, 335, 336, 527; this vol., ii, 231, 437).—The refractive indices of solutions of (1) tetraethylammonium iodide, (2) tetrapropylammonium iodide, and (3) phenyldimethylethylammonium iodide in a number of organic solvents have been determined. From the data obtained, the molecular refraction of the dissolved solid has been calculated and found to vary only slightly with its concentration in a given solvent. The molecular refraction, however, varies considerably from one solvent to another. Thus when the  $(n-1)/d$  formula is taken as the basis of calculation (this formula brings out the differences better than the  $(n^2-1)/(n^2+2).1/d$  formula), the molecular refraction of tetraethylammonium iodide varies from 99.23 (in methyl alcohol) to 107.4 (in methyl thiocyanate). It is shown from the author's previous work that such variation can have nothing to do with the dissociating power of the solvent or with the degree of dissociation of the dissolved salt. On the other hand, there appears to be a connexion between the magnitude of the molecular refraction and the molecular volume of the dissolved salt, as also between this molecular volume and the co-volume of the solvent. The smaller the co-volume of the solvent, the greater is the molecular volume of the dissolved salt, and the greater the molecular volume of the dissolved salt in solution is, the smaller is its molecular refraction. J. C. P.

**Rotatory Power in Solutions.** PAUL WALDEN (*Ber.*, 1907, 40, 2463—2481).—A polemical paper, in which the author replies to the criticisms of Patterson and Thomson (this vol., ii, 322) on his work (Abstr., 1906, ii, 209). T. H. P.

**The Optical Influence of Contiguity of Unsaturated Groups.** RAFFAELE NASINI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 810—817. Compare Brühl, Trans., 1907, 91, 115).—A question of priority. T. H. P.

**Ionic and Chromophore Theory of Indicators.** PAUL ROHLAND (*Ber.*, 1907, 40, 2172—2174).—Polemical. A reply to Hantzsch (this vol., i, 513). A. McK.

**Fluorescence and the Auxochrome Theory.** HUGO KAUFFMANN (*Ber.*, 1907, 40, 2338—2340).—Mainly polemical, in reply to Hantzsch (compare this vol., i, 513). J. J. S.

**Divisibility of Valencies.** HUGO KAUFFMANN (*Ber.*, 1907, 40, 2341—2352).—The strongest luminophores are colourless, and become fluorescent when combined with only feeble fluorogens such as the carboxyl group; conversely, in the case of comparable, fluorescent, coloured compounds, the fluorogen must be the stronger the more intense the colour. As has been shown previously, fluorogens are also chromophores; it follows that strong fluorogenic groups have also strong chromophoric properties. It was argued (Abstr., 1906, i, 283)

that a group functions as a fluorogen the more strongly its partial valencies are rendered inactive by the partial valency of the luminophore; hence strong chromophores, which are also strong fluorogens, must render the partial valencies of the luminophore nucleus inactive to an extent proportional to the strength of their chromophoric effect. Such groups are termed "dependent" (unselbständige) chromophores, in contrast to groups which function as chromophores without interference of partial valencies, and are termed consequently "independent" (selbständige) chromophores. "Independent" chromophores, such as the azo- and nitroso-groups, readily cause colour in the aliphatic series, whereas "dependent" chromophores are the cause of colour in the aliphatic series only when in combination with other unsaturated groups. These views are illustrated and discussed with the aid of Thiele's theory of partial valencies. G. Y.

**Phosphorescence of Manganiferous-Calcium Compounds. Influence of Constitution and Molecular Mass on the Wavelengths of the Radiations Emitted.** L. BRUNINGHAUS (*Compt. rend.*, 1907, 144, 1040—1042. Compare this vol., ii, 419, and De Kowalsky and Garnier, this vol., ii, 418).—Thirteen calcium compounds, each containing manganese in the proportion, manganese : calcium : : 1,254, have been subjected to the action of cathodic rays and the light emitted examined spectrometrically. The spectra never cover the whole of the visible spectrum; they begin at a certain wave-length,  $\lambda_1$ , increase in intensity to a maximum,  $\lambda_m$ , and then decrease to an ill-defined limit,  $\lambda_2$ . The colour of the light emitted and the mean value of  $\lambda_m$  for each of the thirteen calcium compounds examined are quoted in the original, and comparison of these shows that as the molecular weight increases the light emitted becomes more refrangible, but that no simple relation exists among the colours of the light emitted.

The colour appears to depend on (1) the chemical constitution of the diluent molecules, and (2) the mass of the molecule; whence the conclusion is drawn that the movements of the light-emitting centres (electrons?) are directly dependent on the structure and mass of the diluent molecules. T. A. H.

**Chemical Actions of Radium Rays.** WILLEM P. JORISSEN and WILHELM E. RINGER (*Arch. Néerland.*, 1907, ii, 12, 157—174).—A reprint of papers already published (*Abstr.*, 1905, ii, 219; 1906, i, 475; ii, 515). M. A. W.

**Experiments with  $\beta$ -Rays from Radium E.** HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1907, 8, 361—373).—The properties of the  $\beta$ -rays emitted by radium E have been examined. On account of the absence of disturbing factors, this is the most suitable substance for the study of these rays. The coefficient of absorption of the rays by aluminium is for small thicknesses of the metal, 40.0. It increases with increasing thickness of the absorbing layer, but the rate of increase is dependent on the arrangement of the absorbing material with reference to the source of the rays. The velocity of the  $\beta$ -rays,

measured by the deviation in a magnetic field, is 2.49 cm. per second, and this velocity is not measurably altered when the  $\beta$ -rays have traversed a layer of aluminium 0.5 mm. thick. Radium *E* also emits  $\gamma$ -rays, the intensity of these being 0.016% of the intensity of the  $\beta$ -rays. The coefficient of absorption of the  $\gamma$ -rays by aluminium is 0.8.

H. M. D.

**Absorption of the  $\alpha$ -Rays of Radiotellurium (Radium *F*) in Metals.** EDGAR MEYER (*Chem. Zentr.*, 1907, i, 1013; from *Ber. Deut. physikal. Ges.*, 1906, 4, 581—589).—According to Rutherford and Bragg, the ionisation of air caused by an  $\alpha$ -particle,  $r$  cm. from the end of its course, is proportional to  $\sqrt{r+1.3}$ . The absorption must also be proportional to the velocity of the  $\alpha$ -particle. If the absorption of a metallic layer is determined as a function of the distance from the source of radiation, the absorption in a number of layers and at different distances can also be calculated. It can then be predicted how far the absorption will be affected by reversing the order of the screens. Since the calculated values of the absorption for two aluminium leaves at various distances, for tinfoil, and for tin and aluminium agree with the experimental results, it is not necessary to assume that there is secondary radiation or dispersion by diffusion, but merely that ionisation and absorption are proportional.

E. W. W.

**Separation of Radioactive Substances from Ordinary Lead.** JULIUS ELSTER and HANS GEITEL (*Chem. Zentr.*, 1907, i, 937; from *Physikal. Zeitsch.*, 1906, 7, 841—844).—The authors have confirmed the observation that air is more strongly ionised in lead vessels than in vessels of other materials. Lead does not emit any rays which have an appreciable power of penetration, but it has an absorptive action on the strong penetrating rays which are present everywhere. Strongly radioactive lead, prepared from pitchblende, does not show any radium emanation, although it has an enormous power of causing ionisation. An active precipitate is obtained when 1 kilo. of commercial oxide lead is added to concentrated hydrochloric acid, the dissolved lead chloride precipitated by sulphuric acid, and the filtrate treated with hydrogen sulphide, or by treating pure lead nitrate in the same way. Radioactive substances are thus obtained from lead preparations by practically the same method as that by which radium *E* and radium *F* have been obtained, and it is possible, although it has not been proved, that the radioactivity is attributable to the presence of radium.  $\alpha$ -Rays form the major portion of the radiation. The activity decreases slowly.

E. W. W.

**Radioactive Lead and Grignard's Reaction as an Analytical Agent.** KARL A. HOFMANN and V. WÖFL (*Ber.*, 1907, 40, 2425—2430).—The object of this investigation was the isolation of radium *D*, and several methods of separation have been discovered leading to this end. A partial separation of radium *D* may be effected by distillation of the radioactive lead chloride in the presence of ammonium chloride; radium *F*, radium *E*, and radium *D* are more volatile than ordinary lead chloride, and the distillate may be freed from the first two by repeated crystallisation from strong hydro-



chloric acid in which radium *D* is least soluble. The least soluble portions are then further purified by precipitation from aqueous solution with hydrogen sulphide; the precipitate first formed is practically inactive, but gradually develops an  $\alpha$ - and  $\beta$ -activity much greater than that of the original material. Electrolysis of an acetate or nitrate solution, using mercury as a cathode, results in a concentration of radium *D* on the cathode. A sample of this, as sulphate, enclosed in an evacuated capillary tube for several months gave the helium lines  $\lambda = 587.5$ ,  $501.6$ , and  $447.1$ , whilst radium *E* and radium *F* gave only negative results. No radium emanation was obtained from any preparation. The effect of heating the radioactive lead chloride with zinc and silver was also observed, but it seemed that none of these methods would lead to a complete isolation of radium *D*.

The action of magnesium phenyl bromide on lead chloride was then investigated. It is found that lead tetraphenyl is produced, whilst one-half of the lead separates in the metallic state. Now, if lead chloride rich in radium *D* is employed, it is found that most of the radium *D* is present in the metallic lead liberated during the reaction, whilst only a small quantity passes into the lead tetraphenyl.

Mention is made of a compound obtained by the action of a mixture of strong nitric and sulphuric acids on lead tetraphenyl. It forms white prismatic crystals which explode when heated. W. H. G.

**Radiation of Thorium A.** F. VON LERCH (*Chem. Zentr.*, 1907, i, 936; from *Physikal. Zeitsch.*, 1906, 7, 913—915).—The radiations of thorium *A* and thorium *B* and of a mixture of these substances have been absorbed by thin layers of aluminium. If thorium *A* decomposes without radiation, or if the rays emitted are of the same penetrative power as those of thorium *B*, then the results should be the same in each case. Since thin layers of aluminium were found to reduce the radiation of a mixture of thorium *A* and thorium *B* more than that of thorium *B* alone, whilst when thicker layers were used the reverse was found to be the case, it follows that thorium *A* emits a radiation of which one portion has a less, and another portion a greater, penetrative power than that of the  $\alpha$ -rays of thorium *B* or thorium *C*; the latter forms the major part of the radiation. E. W. W.

**Some Properties of Actinium.** MAX LEVIN (*Chem. Zentr.*, 1907, i, 1024; from *Physikal. Zeitsch.*, 1906, 7, 812—815. Compare this vol., ii, 220).—The velocity of volatilisation of the actinium precipitate has been measured in the electric furnace. A platinum wire is made active by charging it negatively and exposing it to the emanation for some hours so that the precipitated products attain the equilibrium state. The activity is determined immediately after heating and is calculated in percentages on the assumption that the activity of the wire decreases during the heating with a period of thirty-six minutes. Actinium *A* is not volatile below  $400^{\circ}$ ; it evaporates above this temperature, but the quantity volatilised is not proportional to the rise of temperature. At  $750^{\circ}$ , all the actinium *A* is evaporated in ten minutes. The temperature of volatilisation of actinium *B* is about  $700^{\circ}$ .

As in the case of thorium, the first component of the active precipitate which decomposes the most slowly is also the most volatile.

When a nitric acid solution of actinium *X* is electrolysed between platinum electrodes, using an *E.M.F.* sufficient to decompose water, a larger quantity of actinium *A* is obtained together with an excess of actinium *B*, whilst only traces of actinium *X* are obtained by secondary reactions. Actinium *X* is separated from ammoniacal solutions, however, together with actinium *A* and actinium *B*. Lucas' theory (*Physikal. Zeitsch.*, 7, 340) that the radioactive decomposition always results in the formation of nobler elements does not take into account the existence of emanations which are electrochemically neutral.

When slightly acid solutions of actinium *X* are used, the solution becomes turbid at the cathode, and a strongly active yellow precipitate of radioactinium is formed on the cathode.

Since the atomic weights and consequently the concentrations of the solutions are unknown, no place in the electrochemical series can be assigned to the actinium products. In this series, however, thorium *A* lies between antimony and mercury, thorium *B* between silver and mercury, radium *C* between antimony and gold, and polonium next to mercury, so that there is a considerable difference of potential between polonium and bismuth.

E. W. W.

#### The $\alpha$ -Particle and the Periodic System of the Elements.

A. VAN DEN BROEK (*Ann. Physik*, 1907, [iv], 23, 199—203).—In connexion with Rutherford's suggestion that the  $\alpha$ -particle might be the half of a helium atom carrying the ionic charge (*Abstr.*, 1906, ii, 719), the author revives Prout's hypothesis with the modification that an element with atomic weight two is taken as the fundamental substance. A table is drawn up consisting of fifteen series, each series containing eight places, in which are put the numbers 2, 4, 6, 8..... up to 240. The known elements are put in the places which best express their mutual relationships as summed up in an ordinary periodic table. There is found to be fair agreement between the atomic weights and the numbers which occupy the same places, and it is noted, when the table as a whole is considered, that the + differences are very nearly balanced by the - differences.

The author concludes that the elements are only secondary modifications of aggregates of  $\alpha$ -particles.

J. C. P.

**Mobility of Ions in Helium.** J. FRANCK and ROBERT POHL (*Ber. Deut. physikal. Ges.*, 1907, 5, 194—199).—The velocity of the ions produced by  $\alpha$ -rays in helium has been measured. The helium was carefully purified by treatment with cocoa-nut charcoal, sodium-potassium alloy, and freshly-ignited platinum black. The mobility of the positive and negative ions is 5.09 and 6.31 cms. per second respectively. These values are smaller than those found for hydrogen, but much larger than for other gases examined.

H. M. D.

**Emanation of Phosphorus.** GERHARD C. SCHMIDT (*Chem. Zentr.*, 1907, i, 1014—1015; from *Ber. Deut. physikal. Ges.*, 1906, 4, 640—679).—Further experiments have confirmed the author's theory that the

cause of the conductivity of air which is induced by the slow oxidation of phosphorus is not to be attributed to ionisation, but is due to the presence of solid oxidation products in the cloud or mist which is produced, and that practically no ions are formed. Air can be made to conduct by suspending solid particles of phosphoric acid in it. The conductivity depends also, however, on the presence of water, since the dry oxides are not conductors. When the phosphorus burns with a flame, the air becomes a very good conductor, but as the air is dried, the conductivity decreases rapidly. Moist air in which the oxides are present conducts as long as it contains mist. When water is dropped on to phosphoric oxide, mist is formed, and the air becomes a conductor; but when the oxide gradually deliquesces in water-vapour, no mist is formed and the air does not conduct. Ions are not formed by the combination of phosphoric oxide and water.

The differences in the curves obtained by various observers are due to the fact that the oxidation of phosphorus does not take place with great regularity and the curves depend on the quantity of moisture contained in the air.

In reference to the fact that air does not become a conductor when laden with ammonium chloride mist, the author points out that ammonium chloride is a much worse conductor than phosphoric acid. He also maintains that the convection theory explains all the facts much more simply than the electron theory. E. W. W.

#### Electrical Conductivity Produced by Heating Salts.

A. E. GARRETT (*Phil. Mag.*, 1907, [vi], 13, 728—747).—Measurements have been made of the conductivity of the air in the neighbourhood of inorganic substances heated at temperatures not higher than 360°. The following substances increase the conducting power: ferric, aluminium, ammonium, magnesium, stannous, manganese, and cadmium chlorides, calcium and aluminium fluorides, cadmium iodide, ammonium, cadmium, and cobalt nitrates. The most active substances are the halogen salts of zinc, and increased conductivity due to these can be detected at the ordinary temperature and pressure. Evidence has been obtained that these phenomena are accompanied by chemical changes in the active substances. The ions formed are similar to those which have been observed in recently prepared gases, gases from flames, and in the neighbourhood of oxidising phosphorus; they are completely stopped by a layer of aluminium 0.0008 cm. in thickness. The velocity of the ions is very small, but increases with the temperature, and although for certain ranges a straight line relationship holds between the velocity and the temperature, yet sudden changes in the direction of the line indicate changes in the nature of the ions as the temperature is increased. The difference in behaviour of ordinary and carefully-dried substances indicates that water-vapour influences the observed conductivity in some cases. H. M. D.

#### Electrical Conductivity of Alloys. II. Relation between Constitution and Temperature-Coefficient of Conductivity.

W. GUERTLER (*Zeitsch. anorg. Chem.*, 1907, 54, 58—88. Compare this vol., ii, 65).—In the former paper, certain rules connecting con-

ductivity and constitution of alloys were established ; it is now shown that measurements of the temperature-coefficient of conductivity may be similarly used to elucidate the constitution of alloys. The data are taken from papers by Matthiessen (1861-64), Dewar and Fleming (1892-93), and others. For convenience, the results are expressed in terms of  $P$ , the percentage decrease of conductivity on raising the temperature from  $0^{\circ}$  to  $100^{\circ}$ .

Matthiessen's rule on the relation between the conductivity and its temperature-coefficient has been extended and is now expressed as follows: with few exceptions the conductivity and the temperature-coefficient of the conductivity of binary alloys are proportional, even when mixed crystals and chemical compounds are present ; in every case the conductivity and temperature-coefficient curves have the same form. From this rule, it follows that the relations already established between constitution and conductivity also hold for constitution and temperature-coefficients.

The value of  $P$  for pure metals varies from 27 to 31, and it is shown that  $P$  has the same value for alloys free from mixed crystals as for pure metals. Conversely, if  $P$  has the value 31 or more, the alloy (magnetic alloys excepted) contains no mixed crystals.

For binary alloys in which mixed crystals are present, the value of  $P$  falls rapidly from the pure metals, and the curves connecting  $P$  and the composition of the alloy show, at least in some cases, breaks corresponding with those in the miscibility of the metals.

The electrical resistance of mixed crystals (as well as of compounds) is not related to the resistance of the constituents, and persists at the absolute temperature, although under these conditions the resistance of the component metals tends to zero.

A bibliography of the subject is appended.

G. S.

**Alloys of Copper with Nickel and with Gold. Electroconductivity of Solid Metal Solutions.** NICOLAI S. KURNAKOFF and S. F. SCHEMCHUSCHNY (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 211-229. Compare Abstr., 1905, ii, 710).—The power possessed by metals of forming solid solutions of considerable concentration is mostly observable in the case of metals of similar atomic weights and situated in the same horizontal row of the periodic system. Especially is this so in the 11th, 5th, and 4th rows. Tables and curves are given for copper and nickel, silver and gold, copper and gold ; showing the relation the relative proportion of the constituents bear to the solidifying points and to the electrical conductivity of the alloys. The study of solid metal solutions by means of their electrical conductivities has been found to be a particularly useful and delicate method. In general, the formation of a solid solution is always accompanied by a fall in electrical conductivity ; thus the addition of 10% of nickel to copper lowers the conductivity to 1/10 of its value for pure copper. On the other hand, although the electrical conductivity of nickel is far less than that of copper, the addition of even considerable quantities of the latter element lowers the conductivity appreciably. From both series of curves it is evident that the metals here investigated, similarly with other pairs of metals

(compare Matthieson, *Ann. Phys. Chem.*, 1861, 100, 190; Heycock and Neville, *Abstr.*, 1897, ii, 245; Roberts-Austen and Rose, *Chem. News*, 1903, 87, 2), form a continuous series of solid solutions. This is further borne out by a study of the microstructure of the alloys, of which diagrams are given. Contrary to Roberts-Austen and Rose (*Abstr.*, 1900, ii, 25), the temperature composition curve for gold and copper contains no eutectic point, but although there is no break in the curve, the minimum temperature on it, which is also the point of least difference between the starting and end point of solidification, corresponds closely with the eutectic point. The three types of composition-electrical conductivity curves are also drawn for the simplest binary systems composed of metals yielding solid solutions.

Z. K.

**Electrical Conductivity of Solutions of the Alcohols in Liquid Hydrogen Bromide.** EBENEZER H. ARCHIBALD (*J. Amer. Chem. Soc.*, 1907, 29, 665—683).—Steele, McIntosh, and Archibald (*Abstr.*, 1905, ii, 222) have shown that many organic substances dissolve in the liquid halogen hydrides with formation of conducting solutions. A study has now been made of liquid hydrogen bromide solutions of the alcohols and phenols, namely, methyl, ethyl, *n*-propyl, amyl, and allyl alcohols, and phenol, *o*-, *m*-, and *p*-cresols, thymol, carvacrol,  $\alpha$ - and  $\beta$ -naphthols, and resorcinol. The methods and apparatus employed are described with the aid of diagrams, the results are tabulated, and the molecular conductivities and temperature coefficients are plotted as curves.

It has been found that most of the alcohols are soluble in hydrogen bromide, and that the solutions show considerable conductivity. Solutions of *m*-phenols have greater conductivity than those of their ortho- and para-isomerides. In the case of the dihydroxybenzenes, resorcinol dissolves readily to form a well-conducting solution, whereas catechol and quinol seem to be insoluble.

In the paraffin series, the lower the alcohol, the greater is the conductivity of its solutions, whilst the reverse is true in the benzene series.

In a few cases of the more dilute solutions, the molecular conductivity increases slightly or remains constant as the dilution increases. In most cases, however, and in all the more concentrated solutions, the molecular conductivity decreases rapidly with increasing dilution.

On calculating the value of the molecular conductivity from the expression  $kv^n$ , where  $n$  is the number of molecules of solute uniting with one molecule of the solvent to form the electrolytic compounds, values are obtained which, in the case of the phenols, vary with the dilution in the same way as the values of the molecular conductivity of aqueous solutions of inorganic salts. In the case of the alcohols of the paraffin series, however, the expression only applies over a narrow range of dilution.

The temperature coefficients of conductivity are in some cases positive and in others negative, and frequently change sign as the solution is diluted.

E. G.

**Relations between the Molecular Conductivity of Electrolytes and the Dilution.** MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1907, [iv], 1, 562—569).—If the ionising action of water is due to the small proportion of free ions it contains, its action is comparable to that of a small amount of acid in effecting the hydrolysis of sucrose, where the relation  $\log.1/1-x=at$  holds, which, on replacing  $t$  by a simple function of the volume,  $V^{1/n}$ , and calling the proportion of the electrolyte ionised  $\lambda$ , becomes  $\log.1/1-\lambda=\alpha V^{1/n}$ , where  $\alpha$  (the "volumetric dissociation constant") and  $1/n$  (the "volumetric index") are constants for a given electrolyte. For limited dilutions where  $\lambda=\Lambda/\Lambda_{10,000}$  ( $\Lambda$  being the molecular conductivity at a given dilution), the value of  $n$  varies from 6 for univalent electrolytes to 2 for semi-electrolytes, such as acetic acid and ammonia. The value of  $\alpha$  for hydrochloric and nitric acids is about 0.780, and is slightly higher than that for salts of these acids with univalent metals; that for sulphuric acid ( $H_2SO_4/2$ ) is intermediate between those of the sulphates of univalent and bivalent metals.

When the molecular conductivity at infinite dilution is taken as unity, the value of  $n$  lies between 8 and 9, and  $\alpha$  is fairly constant for univalent electrolytes, and the following general relations hold between the coefficient of ionisation and the volume of the solvent: (1)  $\gamma V^{-1/n} = \text{constant}$ , and (2)  $V^{1/n}(1-\gamma) = \text{constant}$ , and these relations can be verified experimentally, starting with  $V=100$  or 200. In these cases,  $n=81$  for univalent electrolytes, 54 for those containing a bivalent ion, and 18 for those with two bivalent ions. The values of  $n'$  lie between 2 and 3.

The equations 1 and 2 give the new relations: (3)  $V^{1/p}(1-\gamma)\gamma = \text{constant}$ , and (4)  $V^{-1/p}(\gamma/1-\gamma) = \text{constant}$ . The second of these is analogous to those given by Rupolphi and van't Hoff, which are also deducible from equations 1 and 2. When ionisation is complete, equation 1 becomes  $V^{1/n} = \text{constant}$ , so that the dilution corresponding with the limit of molecular conductivity should have a finite value.

T. A. H.

**Action of Oxygen on Aqueous Solutions: the Processes Involved in the Electrolytic Decomposition of Water and in the Hydrogen-Oxygen Gas Cell.** OTTO MUMM (*Zeitsch. physikal. Chem.*, 1907, 59, 459—491).—Largely theoretical. The author supposes that the action of oxygen on water is somewhat analogous to the action of chlorine on water, and forms hydrogen trioxide which dissociates according to the equation  $HO_3H \rightleftharpoons HO^+ + OOH^+$ . Oxidations which take place in aqueous solutions are supposed to be effected by these two ions; in most cases probably by the positive hydroxyl ion. When a substance is oxidised in aqueous solution by oxygen, the ion not used in the oxidation forms hydrogen dioxide with the oppositely charged ion of water, thus:  $HOO + H^+ = H_2O_2$ , or  $HO^+ + OH^- = H_2O_2$ . A number of facts connected with the electrolytic decomposition of water and with the hydrogen-oxygen gas cell seem to support the author's view as to the existence of hydrogen trioxide and its ions in solution. According to the view here advanced, the production of hydrogen peroxide at a negative electrode, over which oxygen is pass-

ing, is not due to the oxidation of nascent hydrogen; the author holds that the positive hydroxyl ions of the dissolved oxygen, which have a discharge potential far lower than that of the hydrogen ions, are changed at the cathode to negative hydroxyl ions, and that the OOH ions which thereby become available react with hydrogen ions to form hydrogen peroxide.

In the following table the author records a number of decomposition potentials and the reactions with which he believes these potentials to be associated:

0.78 volt	$3\text{H}_2\text{O}_2 = 2\text{H}_2\text{O}_3 + \text{H}_2$
1.08 „	$\text{H}_2\text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_3 + \text{H}_2$
1.232 „	$3\text{H}_2\text{O} = \text{H}_2\text{O}_3 + 2\text{H}_2$
1.38 „	$2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$
1.68 „	$\text{H}_2\text{O}_3 + 3\text{H}_2\text{O} = 3\text{H}_2\text{O}_2 + \text{H}_2$

J. C. P.

**Cathode of a Decomposition Cell as Inductor ("Autoxydator") in Oxidation Process.** Experiments with Sodium Arsenite. OTTO MUMM (*Zeitsch. physikal. Chem.*, 1907, 59, 492—496).

—According to the view advanced in the preceding abstract, oxygen dissolved in water forms hydrogen trioxide, which dissociates thus:  $\text{HOOOH} \rightleftharpoons \text{HO}^\cdot + \text{OOH}^\cdot$ . If this is so, then any agent (a so called "inductor"; see Schiloff, Abstr., 1903, ii, 276; Luther and Schiloff, Abstr., 1904, ii, 244) which removes the  $\text{HO}^\cdot$  ions should lead indirectly to an increase in the concentration of the  $\text{OOH}^\cdot$  ions. Now a substance which is capable of slow oxidation by  $\text{OOH}^\cdot$  ions, might be rapidly oxidised if the concentration of these ions was largely increased, and would therefore play the part of "acceptor" (see Schiloff, *loc. cit.*). The removal of positive hydroxyl ions which would lead to this result might be effected, not only by an inductor, but by the cathode of a decomposition cell. The correctness of this conclusion has been confirmed by experiments in which sodium arsenite solution was oxidised by gaseous oxygen at the cathode of such a cell. Of the oxygen consumed, half was used in the oxidation of the arsenite, the other half went to form water, and this amount was found to be equivalent to the silver deposited in a voltameter put in series with the decomposition cell.

J. C. P.

**Anode of an Electrolytic Decomposition Cell as Acceptor in Oxidation Processes.** Experiments with Oxalic Acid. OTTO MUMM (*Zeitsch. physikal. Chem.*, 1907, 59, 497—506. Compare the preceding abstracts).—The anode consisted of platinised platinum immersed in 0.2*N*-oxalic acid, and oxygen was kept in continuous circulation over the surface of the electrode. Electricity was sent through the cell until the *E.M.F.* at the anode just began to rise above its initial value. The concentration of the oxalic acid was determined before and after each experiment. It was found that when the potential fall at the anode was below a certain value, three equivalents of oxalic acid and two equivalents of oxygen were used up for every one equivalent of silver deposited in the voltameter; when the potential fall at the anode was (within limits) above the value

in question, two equivalents of oxalic acid and one equivalent of oxygen were used up for every one equivalent of silver deposited in the voltameter. The author considers that these facts cannot be explained on the basis of currently accepted views, and suggests an explanation involving the existence and dissociation of hydrogen trioxide in solution (see preceding abstracts). For the details of this explanation, the original must be consulted. J. C. P.

**Electric Synthesis of Colloids.** THE SVEDBERG (*Chem. Zentr.*, 1907, i, 1089—1090; from *Zeitsch. Chem. Ind. Kolloide*, 1, 229—243. Compare Abstr., 1906, ii, 330).—The dependence of the pulverisation of different metals in ethyl ether, isobutyl alcohol, benzene or petroleum, and of the decomposition of the medium on the electric-constant of the discharging circuit, the material of the electrode, &c., has been quantitatively investigated by means of a "spark-immersion micrometer," in which cylindrical rods of the metals, usually of 5.6 mm. diameter, were employed. The square of the effective current strength, measured by means of a hot wire ammeter, was taken as the independent variable. The measurements, which were made in most cases with oscillating discharges, are arranged in tables, and shown graphically in the original paper. When a constant current is used, accurate measurements can be made only under certain conditions, since the colloidal pulverisation is accompanied by the formation of small globules of the metal. The loss of weight of the cathode is greater than that of the anode when either a constant current or an intermittent discharge is used. With the same effective current ( $i_{eff}$ ), the formation of colloid decreases as the capacity or damping increases, but increases as the self-induction becomes greater and the length of the spark less. The form of discharge, nature of the liquid, and surface area of the electrodes, have only a small effect on the amount of pulverisation, which is, however, extraordinarily small in gases (air). The pulverisation of the electrodes and the decomposition of the liquids increases in proportion to  $i_{eff}^{-2}$  when the current strength is small, but the increase is more gradual with a greater current strength, and the values appear to approach the limit asymptotically. The pulverisation is measured by the volume of gas which is formed.

The specific pulverisation becomes less as the capacity, damping, self-induction, and length of spark become greater, and is independent of the surface area of the electrodes; it is very greatly affected, however, by the form of discharge, the effect being least in the case of oscillating discharges. With constant currents, pulverisation increases enormously as the length of the arc becomes greater. The pulverisation capacity or "cathodic hardness" of metals in the vertical series of the periodic system increases with, but much more rapidly than, the atomic weight, and is approximately the same for metals of closely related atomic weights. The decomposition of the medium is distinctly greater in the case of extremely positive metals (calcium, magnesium) than in that of the negative metals, and this relationship also holds for nickel and cobalt, which act as strong catalytic agents; platinum, antimony, bismuth, and tin have the least effect. E. W. W.



**Magnetic Compounds from Non-magnetic Elements** EDGAR WEDEKIND (*Chem. Zentr.*, 1907, i, 936—937; from *Ber. Deut. physikal. Ges.*, 1906, 4, 412—416. Compare Abstr., 1906, ii, 70; 1907, ii, 353).—Magnetic magnesium nitride ( $Mg_3N_2$ ?) can only be obtained by heating at the temperature of the oxyhydrogen blow-pipe, and must be prepared with ammonia and not with nitrogen. The nitrides,  $Mn_3N_2$  and  $Mn_5N_2$ , do not show ferromagnetism. The temperature is of great importance in these cases. The sulphide becomes somewhat more magnetic on heating. The completely anhydrous iodide is ferromagnetic. Aqueous solutions of manganese salts show a greater susceptibility than solutions of ferric salts. The quantitative examination of manganese compounds is difficult because the products usually consist of imperfectly melted pieces, and only the boride and antimonide yield homogeneous lumps. The magnetism of these compounds is of the same order as that of iron, but a condition of saturation could not be attained.

The effect of the high temperature does not appear to be due to increase of energy, but to the formation of the compounds richest in manganese, which are magnetically stable. Ferromagnetism is not only an atomic, but also a molecular, property. Chromium, manganese, iron, cobalt, and nickel are magnetic in certain compounds.

E. W. W.

**Specific Heats of the Solid Elements.** RUDOLF LÄMMEL (*Ann. Physik*, 1907, [iv], 23, 61—72. Compare Abstr., 1905, ii, 300).—The author argues further in favour of his view that the atomic heats of the elements are equal only when the melting points are taken as the comparable temperatures. Small atomic weight and small atomic volume are considered to have nothing to do with the deviations from Dulong and Petit's law as is usually stated. The atomic heats of carbon, boron, and silicon at the ordinary temperature are very low, because the melting points of these elements are very high.

The specific heat of lithium has been determined over a wide range of temperature, and the curve expressing the change of specific heat with temperature has a point of inflexion; it is suggested that this will be found typical of all similar curves.

J. C. P.

**The Direction of the Freezing-point Curve of a Binary System at a Point Corresponding with the Formation of a Compound.** R. NACKEN (*Centr. Min.*, 1907, 11, 329—336).—The author discusses the direction of the two curves which meet at the melting point of calcium chloride hexahydrate in the temperature-pressure and the temperature-concentration diagram. It is shown that the two branches do not form a continuous curve, but that a break occurs at the melting point of the hydrate, the sharpness of the break being determined by the volume change which accompanies the melting of the hydrate. The two branches are only continuous when this volume change is *nil*; in this case, the tangent to the continuous curve is perpendicular to the temperature axis.

In general, the formation of a compound will, however, be accom-

panied by such breaks in the vapour pressure and freezing-point curves, the two branches being independent of each other.

H. M. D.

**Application of Trouton's Law to the Determination of the Molecular Elevations of the Boiling Points of Solutions.** D. E. TSAKALOTOS (*Compt. rend.*, 1907, 144, 1104—1106).—By combining Nernst's expression  $ML/T = 9.5 \log T - 0.007T$  of Trouton's Law with the van't Hoff-Le Chatelier equation  $E = 0.02T^2/L$  applied by Arrhenius and by Beckmann (Abstr., 1890, 323) to the calculation of ebullioscopic constants, the expression  $E = M/(475 \log T/T - 0.35)$  is obtained, in which  $E$  represents the molecular elevation of the absolute boiling point  $T$  of a solvent of molecular weight  $M$ . By means of this equation, ebullioscopic constants can be calculated, given only the molecular weight and boiling point of the solvent, and by its use the author has obtained values of  $E$  for oxygen, chlorine, bromine, sulphur dioxide, ethyl ether, acetone, carbon disulphide, chloroform, carbon tetrachloride, ethylene dibromide, benzene, nitrobenzene, and aniline which agree remarkably well both with Beckmann's experimental values and with those obtained with van't Hoff's equation.

In the case of liquids polymerised in the liquid condition, the large variation of  $L$  with  $T$  renders the equation inapplicable, but here it becomes a criterion of the molecular association of the substance. Since, however, the expression  $ML/T$  is approximately constant (Luginin, Abstr., 1895, ii, 101; R. Schiff, Abstr., 1887, 9) for the same homologous organic series even when its members are associated compounds, the equation  $E/E_x = MT/M'T'$  permits of the calculation of the ebullioscopic constants of an homologous series if that of one of the members is known. In this way the constants found for methyl, propyl, isobutyl, and isoamyl alcohols from that of ethyl alcohol agree well with Beckmann's experimental values and those calculated by van't Hoff's formula. In the case of substances polymerised in the gaseous state, the same equation is applicable when the values for  $M$  calculated from the densities at the boiling points are substituted, and has been successfully used for formic and acetic acids. E. H.

**Fractional Distillation by Means of Steam.** HERBERT HARDY and BERNARD E. RICHENS (*Analyst*, 1907, 32, 197—200).—From experiments with mixtures consisting of limonene and citral, limonene and eugenol, cineol and citral, chloroform and carbon tetrachloride, and benzene and acetic acid, it was found that the passage of water-vapour through a mixture of volatile liquids will, in many cases, produce a more complete separation than ordinary distillation by dry heat. It is not, however, an efficient method if the substances to be separated boil much below 100°. The influence of a fractionating head is less than when dry heat is used, and the rate of distillation makes but little difference in the results obtained, but a rapid current of steam tends to give better results. A specially good fractionation can often, if not generally, be obtained by steam distillation under reduced pressure. W. P. S.

**Application of Thermal Analysis to Ternary Systems.**

R. SAHMEN and A. VON VEGESACK (*Zeitsch. physikal. Chem.*, 1907, **59**, 257—283. Compare Tammann, Abstr., 1904, ii, 113; 1905, ii, 444; 1906, ii, 10).—A theoretical paper, in which Tammann's argument is extended to systems of three components, *A*, *B*, and *C*. It is supposed that the fused components are miscible in all proportions, and the authors deal (1) with the case in which *A*, *B*, and *C* form neither compounds nor mixed crystals with each other, and (2) with the case in which *A* and *B* form mixed crystals, whilst *C* forms neither compounds nor mixed crystals with *A* or *B*.  
J. C. P.

**Heat of Combustion of Vegetable Proteins.** FRANCIS G.

BENEDICT and THOMAS B. OSBORNE (*J. Biol. Chem.*, 1907, **3**, 119—133).—The substances were burnt in the Berthelot-Atwater bomb; the heat of combustion per gram varied from 5358 cal. for conglutin  $\beta$  and wheat-globulin to 5916 cal. for hordein. In general, the higher heats correspond with the proteins of high carbon percentage, and the irregularities noted to this rule are doubtless due to the varying proportions of the amino-acids in the different proteins.  
W. D. H.

**Specific Gravities in Isomorphous Series.** B. GOSSNER (*Ber.*,

1907, **40**, 2373—2376).—The members of an isomorphous series have similar, but not identical, molecular volumes, mol.wt./*D*, hence, as has been shown by Tutton (*Trans.*, 1896, **69**, 344) and by the present author (*Zeitsch. Kryst. Min.*, 1907, **43**, 130); the specific gravities of isomorphous salts are not proportional to their molecular weights, in some cases the salt with the smaller molecular weight having the greater specific gravity. The following new cases are given:

$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$  (*D* 2.000) and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (*D* 2.036).

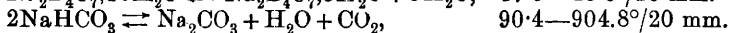
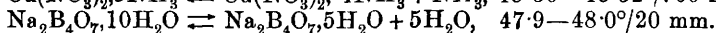
$\text{SiF}_6\text{Ni} \cdot 6\text{H}_2\text{O}$  (*D* 2.134),  $\text{SiF}_6\text{Co} \cdot 6\text{H}_2\text{O}$  (*D* 2.087),  $\text{SiF}_6\text{Cu} \cdot 6\text{H}_2\text{O}$  (*D* 2.222), and  $\text{SiF}_6\text{Zn} \cdot 6\text{H}_2\text{O}$  (*D* 2.139). It is found that, whilst intermixture of the nickel and zinc salts takes place in all proportions, a gap occurs in the series of mixed crystals of the cobalt and copper salts, the red mixed crystals having the form of the cobalt salt containing a maximum of 70% of the copper salt and those in the form of the bluish-violet copper salt containing a maximum of 10% of the cobalt salt.

$\text{SiF}_6\text{Zn} \cdot 6\text{H}_2\text{O}$  (*D* 2.139),  $\text{TiF}_6\text{Zn} \cdot 6\text{H}_2\text{O}$  (*D* 2.106),  $\text{ZrF}_6\text{Zn} \cdot 6\text{H}_2\text{O}$  (*D* 2.258), and  $\text{SnF}_6\text{Zn} \cdot 6\text{H}_2\text{O}$  (*D* 2.445).  
G. Y.

**Determination of Transition Temperatures.** DAVID W. HORN

(*Amer. Chem. J.*, 1907, **37**, 619—628).—A simple method is described for determining transition temperatures in systems of the second order, consisting of two solid phases and a vapour phase. It is applicable to dissociation in systems in which one of the two components has a negligible vapour pressure, whilst the other component, under the same conditions, constitutes the vapour phase. The method has been applied to the determination of the transition temperatures of the dissociation of cuprammonium nitrate, borax, sodium hydrogen carbonate, and

ammonio-silver chloride. The results of the experiments are tabulated and plotted as curves. The following constants have been obtained :



The transition temperature was determined in the case of ammonio-silver chloride in order to test the method; the result,  $19.4^\circ/760 \text{ mm.}$ , agrees well with the values obtained by previous observers. E. G.

**Viscosity of Lehmann's Liquid Crystals.** LUIGI PUCCIANI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 754-757).—Using the method of flow through narrow tubes, the author has determined the viscosities, compared with water at  $0^\circ$  as 100, of cholesteryl benzoate, *p*-azoxyanisole, and *p*-azoxyphenetole at temperatures just below and just above that at which they are transformed from crystalline liquids into the isotropic state (compare Schenck, Abstr., 1898, ii, 563).

In the case of cholesteryl benzoate, which readily undergoes change, the various measurements made vary considerably among themselves, but all indicate an appreciable increase in the viscosity when the liquid is heated above about  $177^\circ$  and its crystalline nature thus destroyed.

With *p*-azoxyanisole, the results obtained are in accord with those of Schenck (*loc. cit.*), the viscosity rising from about 137 at  $134^\circ$  to about 173 at  $135^\circ$ .

In the case of *p*-azoxyphenetole, the viscosity begins to rise gradually at a temperature somewhat below the transition point, and at the latter a considerable increase is observed. T. H. P.

**Stratifications Observed in Cases of Diffusion.** RAPHAEL E. LIESEGANG (*Zeitsch. physikal. Chem.*, 1907, 59, 444-447. Compare Abstr., 1906, ii, 273; also Morse and Pierce, Abstr., 1904, ii, 14; Bechhold, Abstr., 1905, ii, 513).—The intermittent concentric precipitation of silver dichromate, observed when silver nitrate is allowed to diffuse into a gelatin film containing potassium dichromate, has been attributed to supersaturation, but some experiments made by the author are opposed to this view. If a drop of potassium dichromate solution is placed on the diffusion zone of concentric rings obtained as described in the previous sentence, the dichromate diffuses into the jelly, reacts there with the excess of silver nitrate from the previous stage, and causes a fresh concentric precipitation of silver dichromate, quite independent of, and frequently crossing, the earlier lines of precipitation. This could not happen if supersaturation were the explanation of the phenomenon. J. C. P.

**Osmotic Pressure of Dextrose Solutions in the Vicinity of the Freezing Point of Water.** HARMON N. MORSE, JOSEPH C. W. FRAZER, and F. M. ROGERS (*Amer. Chem. J.*, 1907, 37, 558-595).

The methods employed for the direct determination of osmotic pressure have been described in previous papers (Abstr., 1901, ii, 543; 1902, ii, 553; 1903, ii, 272; 1904, ii, 651; 1905, ii, 575; 1906, ii, 600; this vol., ii, 439, 440).

A series of determinations have been made of the osmotic pressure

of dextrose at concentrations from  $N/10$  to  $N$  at temperatures in the neighbourhood of  $0^\circ$ . The various measurements and results are tabulated. In connexion with each determination are recorded (1) the molecular osmotic pressure, that is, the pressure divided by the weight-normal concentration of the solution; (2) the ratio of the osmotic to the calculated gas pressure for the same temperature, the volume of gas being that of the solvent in the pure state; and (3) the ratio of the observed molecular depression of the freezing point of each solution to 1.85, the calculated molecular depression of the freezing point of water.

The ratio of osmotic pressure to gas pressure seems to be greatest in the case of the  $N/10$  solution, then to decrease somewhat, and afterwards to increase slightly as the concentration increases, but the relation is not at present regarded as well established.

It is found that in the neighbourhood of  $0^\circ$  both dextrose and sucrose solutions exert osmotic pressures, which differ from the calculated gas pressure to about the same degree as the observed depressions of the freezing points of such solutions differ from those calculated by means of the value 1.85.

It has been observed that the resistance of the membrane in an osmotic cell is greater at low temperatures. E. G.

**Adsorption of Dyes by Charcoal and Textile Fabrics.** HERBERT FREUNDLICH and G. LOSEV (*Zeitsch. physikal. Chem.*, 1907, 59, 284—312. Compare Freundlich, this vol., ii, 155).—The distribution of crystal-violet, crystal-ponceau, new magenta, and patent blue between charcoal, wool, silk, or cotton, on the one hand, and an aqueous solution of the dye on the other, is governed in all cases by the same laws. The experimental figures are in good agreement with the equation for the adsorption isotherm previously given (*loc. cit.*). When the dyes are arranged according to the values of  $k$ , the order is practically the same whatever is the adsorbing material. The value of  $1/n$  is independent of the nature of the adsorbing material, but is somewhat higher for the dyes than for the organic acids previously studied (*loc. cit.*), and is actually greater than 1 for crystal-violet.

It is noteworthy that charcoal, as well as wool, silk, and cotton, causes in the case of dyes of a basic character a separation of the latter into base and acid; the acid remains in the solution and the base is adsorbed. The colouring matter thus adsorbed by charcoal from crystal-violet solutions has a brownish-violet, shiny appearance, is insoluble in water, but soluble in acids, alcohols, pyridine, and other organic solvents to bluish-violet solutions. The colouring matter adsorbed by charcoal from new magenta solutions has a green appearance, and is soluble in the aforementioned solvents to red solutions. Similar observations are made when wool, silk, and cotton are used as adsorbent material.

The colouring matter adsorbed by charcoal from crystal-violet solutions is in many respects similar to the polymerisation products obtained by Baeyer and Villiger (*Abstr.*, 1904, i, 454, 786) by treating paramagenta with concentrated sodium hydroxide. When crystal-

violet is treated in the same fashion, a brownish-violet, amorphous powder is obtained, very sparingly soluble in water, but readily soluble in alcohols and pyridine to bluish-violet solutions. The view is accordingly adopted that the dye base forms amorphous polymerisation products, and that these are adsorbed, forming colloid complexes with the charcoal, wool, silk, or cotton.

When the acid colouring matters, patent blue and orange IV, are adsorbed by charcoal, no decomposition of the dye salt into base and acid takes place.

J. C. P.

**Stability of Colloidal Solutions. I. THE SVEDBERG** (*Chem. Zentr.*, 1907, i, 1088; from *Zeitsch. Chem. Ind. Kolloide*, 1, 161—164. Compare Abstr., 1905, ii, 138).—Perrin's rule that the stability depends on the dielectric constant does not obtain in the case of colloidal solutions. Stable colloidal solutions of platinum are formed by electric pulverisation in the following liquids, the dielectric constants of which are indicated by the figures: amyl acetate, 4.81; ethyl acetate, 6.11; amyl alcohol, 15.9; isobutyl alcohol, 18.9; acetone, 21.8; propyl alcohol, 22.5, and water, 81.7. Unstable solutions are formed in ethyl ether, 4.37; chloroform, 5.20; ethyl alcohol, 28.8, and methyl alcohol, 35.4. Various examples have also shown that Burton's theory (Abstr., 1906, ii, 275) does not hold.

The viscosity of the solvent has a great effect on the stability of colloidal solutions. The hydrosols of platinum ethyl acetate and platinum propyl alcohol when heated at 125° in a sealed tube of Jena glass do not coagulate, whilst platinum ethyl ether and platinum ethyl alcohol hydrosols are unstable even at the ordinary temperature.

E. W. W.

**Stability of Colloidal Solutions. JEAN BILLITZER** (*Chem. Zentr.*, 1907, i, 1088—1089; from *Zeitsch. Chem. Ind. Kolloide*, 1, 225—227. Compare Abstr., 1905, ii, 305, and preceding abstract).—The stability of colloidal solutions depends on the density of the suspended particles, and that of the medium, on the relationship between the frictional forces which must be overcome in the process of precipitation and the forces of gravitation and on the quantity and constancy of the electric charges. The quantity of the charge depends on the dielectric constant of the medium, since ions are formed the more readily the greater the value of this constant. Constancy is determined by a fixed *E.M.F.* or a constant concentration of definite kinds of ions at a constant temperature. In the case of organic liquids, oxidation by the air frequently destroys the constancy, and the stability then appears to be a matter of chance. Although the platinum ethyl alcohol hydrosols are usually rather unstable, they are sometimes found to be stable, and stable hydrosols are obtained in chloroform; the migration of the platinum to the cathode in the stable hydrosols is attributed to the influence of oxidation products. The author confirms Svedberg's observation that neither the Perrin nor the Burton rule holds in these cases.

E. W. W.

**Significance of the Movement of Particles in Colloidal Solutions in Relation to the Limits of Validity of the Second Law of Thermodynamics.** THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1907, 59, 451—458. Compare this vol., ii, 17, 160).—It is asserted that, on the basis of our present knowledge of the movement of particles in colloidal solutions, it is possible to construct a system which permits the realisation of a perpetuum mobile. J. C. P.

**Solubility.** I. EUGENE C. BINGHAM (*Amer. Chem. J.*, 1907, 37, 549—557).—The solubility of liquids in liquids has been studied by Alexéeff (Abstr., 1886, 847). He found that, in general, with a pair of immiscible liquids the solubility increased with the temperature, until, in a few cases, at a certain point termed by Masson (Abstr., 1891, 791) the "critical solution temperature," the liquids became miscible in all proportions. Guthrie (Abstr., 1885, 337, 339), however, found that in certain cases the solubility increased as the temperature diminished, until the liquids became completely miscible at the "lower critical solution temperature." The present investigation has been carried out with the object of studying the conditions in which liquids are immiscible, and of ascertaining the change of temperature which will render such liquids miscible.

A large number of liquids have been tested, and the results are summarised in a table. It is shown that substances of very small molecular volume are often immiscible with substances of large molecular volume. For example, water is miscible in all proportions with methyl, ethyl and propyl alcohols, has a critical solution temperature with *sec.*-butyl, *isobutyl* and *isoamyl* alcohols, and is immiscible with the higher alcohols. The presence of small quantities of water often appears to render certain substances immiscible, and it is therefore suggested that some substances in which water is very slightly soluble, such as light petroleum, melted paraffin, or carbon disulphide, may be of use for testing the dehydration of organic liquids and easily fusible solids. E. G.

**Water of Crystallisation.** NICOLAI MOROZOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, ii, 480—496. Compare Abegg, Abstr., 1903, ii, 536; 1904, ii, 475).—The theory is propounded that every element has in all eight valencies, of which some are positive and some negative. Starting from left to right of the horizontal lines of Mendeléeff's periodic system, the positive valencies increase from lithium 1 to argon 8, but as the number of valencies increase, so the strength of each one decreases, and this explains the completely inert character of argon. Similarly, the negative valencies increase in the opposite direction from 0 for argon, 1 for fluorine, to 7 for lithium. The element hydrogen, however, forms an exception, and together with helium seems to be outside the periodic classification altogether. On the basis of this theory, and regarding the molecules of water of crystallisation as being attached to the substances by means of the unused valencies, the number of possible molecules of water of crystallisation of about 2000 substances have been studied, all of which, with the exception of about eight, conform to the theory, and the exceptions

themselves are shown, really, only to prove the rule. All the substances are divided into nine fundamental types.

The peculiar crystalline forms of water are also explained on the same principles, and, in general, the formation of crystals in any solution depend on the greater strength of the attractive forces of these valencies as compared with the disrupting force of the solution, the regularity of form, &c., also depending on the relation between these two opposing forces. Thus the same forces which are the cause of the chemical properties of the elements also give rise to the peculiar crystalline form.

Z. K.

**Calculation of Some Chemical Equilibria.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1907, 29, 683—688).—Equilibrium constants of sulphur trioxide with sulphur dioxide and oxygen and of the halogen hydrides with hydrogen and the halogens at high temperatures have been calculated by Nernst's method (Abstr., 1906, ii, 727) from the heat of reaction, the molecular heats of the reacting substances, and the chemical constants of these substances.

E. G.

**Chemical Statics and Kinetics of the Mercury-Ethylene Compounds.** JULIUS SAND and F. BREEST (*Zeitsch. physikal. Chem.*, 1907, 59, 424—443).—If ethylene is passed at the ordinary temperature into a solution of mercuric chloride, the solution becomes strongly acid, and mercuryethanol chloride is formed. On the other hand, if crystals of mercuryethanol chloride are treated with strong hydrochloric acid, effervescence takes place and ethylene is evolved. For the equilibrium which is thus indicated and which may be expressed by the equation :  $\text{HgCl}_2 + \text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{O} \cdot \text{HgCl} + \text{H}^+ + \text{Cl}^-$ , there should be an equilibrium constant,  $K = [\text{H}^+][\text{Cl}^-][\text{C}_2\text{H}_5\text{OHgCl}]/[\text{HgCl}_2][\text{C}_2\text{H}_4]$ . The value of  $K$  has been determined, firstly, by passing ethylene into mercuric chloride solutions and following the increase of conductivity until it reaches a steady value, and, secondly, by measuring the pressure developed when hydrochloric acid is allowed to act on mercuryethanol chloride in a closed vessel. By the first method,  $K$  was found on the average  $= 2.81 \times 10^{-7} \cdot 1/a$  at  $25^\circ$ ,  $a$  being the solubility of ethylene at this temperature under a pressure of 1 mm. mercury. The values found for  $K$  by the second method were  $1.21 \times 10^{-7} \cdot 1/a$  and  $1.34 \times 10^{-7} \cdot 1/a$ .

Incidentally it has been shown that the formation of a complex between chlorine ion and mercuric chloride is to be represented, not by the equation  $\text{HgCl}_2 + 2\text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$  (Sherrill, Abstr., 1903, ii, 534, 649), but by the equation  $\text{HgCl}_2 + \text{Cl}^- \rightleftharpoons \text{HgCl}_3^-$ . This conclusion is based on Sherrill's own figures and a control experiment by the authors, who show that  $[\text{HgCl}_3^-]/[\text{HgCl}_2][\text{Cl}^-] = 11.5$  at  $25^\circ$ .

The order of the reaction in which mercuryethanol chloride is formed from ethylene, mercuric chloride, and water is discussed in the light of the rate of change of conductivity. The order of reaction is apparently determined according to the equation already quoted, or it may be supposed that the compound  $\text{HgCl} \cdot \text{OH}$ , which is always present in aqueous solutions of mercuric chloride, joins directly, although slowly, with ethylene, that this union is catalytically



accelerated by the hydrogen ions which are produced, these hydrogen ions accelerating also the decomposition of the ethanol salt.

J. C. P.

**Chemical Reaction between Salts in the Solid State.** EDGAR P. PERMAN (*Proc. Roy. Soc.*, 1907, *A*, 79, 310—319).—Experiments have been made to determine the conditions under which solid substances react together. Potassium iodide and lead chloride, dried over sulphuric acid, react very slowly. The rate of the change is unaltered by light, but is increased by a rise of temperature.

Potassium iodide and mercuric chloride, after being dried carefully over freshly prepared phosphoric oxide, were found not to have reacted after a period of three years. Under ordinary conditions, immediate reaction can be observed when these substances are mixed. The greater velocity of the reaction between potassium iodide and mercuric chloride as compared with that of the action of the former on lead chloride is probably due to the greater solubility and volatility of the mercuric chloride.

Potassium iodide and lead chloride, both dried over phosphoric oxide, were found to react in presence of methyl alcohol, but not in presence of benzene, chloroform, or ammonia.

The author supposes that, in general, the observed changes take place in a thin film formed by water or other ionising solvent on the surface of the solid substances, the reaction proper being preceded by the solution of the solid substances in the superficial film.

H. M. D.

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## Inorganic Chemistry.

**The Equilibrium of the Deacon Process.** KURT VOGEL VON FALCKENSTEIN (*Zeitsch. physikal. Chem.*, 1907, **59**, 313—335).—Details are given of the method and results already recorded (this vol., ii, 19).  
J. C. P.

**New Experimental Arrangement for the Synthesis of Hydrogen Chloride and Water.** FRIEDRICH C. G. MÜLLER (*Chem. Zentr.*, 1907, i, 1086; from *Zeitsch. physikal.-chem. Unterr.*, **20**, 11—14).—A conical flask is closed by a cork through which pass two glass tubes, the one which is bent at right angles outside the flask and does not project far into the flask serves to fill the vessel with hydrogen. To the second, which passes further into the flask, a side tube is sealed on to the portion above the cork. Two wires which are insulated at the top by a plug, which serves also to close the tube, pass down the vertical portion of the T-tube and terminate at the lower end. The wires are connected with a battery so that small sparks pass between the points. As the chlorine is passed through the side

tube into the hydrogen contained in the flask, it burns continuously at the bottom of the delivery tube with a faintly luminous flame; the hydrogen chloride which is formed may be absorbed by a layer of water. In a similar manner, oxygen may be burnt in hydrogen.

E. W. W.

**Two Polymorphous Modifications of Iodine.** EUGRAPH S. VON FEDOROFF (*Chem. Zentr.*, 1907, i, 1171; from *Bull. Acad. St. Petersbourg*, [v], 22, 287—293).—Two kinds of crystals have been found in a sample of iodine, namely, small rhombic plates and aggregates of monoclinic prisms. The latter form has also been observed by A. Kupffer on the bottom of a flask in which aqueous hydriodic acid had been kept for a long time.

E. W. W.

**Apparatus for the Continuous Preparation of Oxygen at Constant Pressure.** GUSTAVE D. HINRICHS (*Compt. rend.*, 1907, 144, 1213—1214. Compare Seyewetz and Poizat, this vol., ii, 162).—The middle reservoir of a Kipp's apparatus is almost completely filled with large pieces (washed free from powder) of pyrolusite. The latter, when acted on by a reagent obtained by adding to commercial hydrogen peroxide (10 vols. or, better, 23 vols. strength) one-twelfth of its volume of concentrated sulphuric acid (keeping the mixture cold), gives oxygen as readily as zinc and hydrochloric acid give hydrogen. A simple device for relieving the pressure inside the apparatus when not in use is described.

E. H.

[**Change of State of Liquid Sulphur.**] FRIEDRICH HOFFMANN and R. ROTHE (*Zeitsch. physikal. Chem.*, 1907, 59, 448—450).—The authors maintain that their experiments (Abstr., 1906, ii, 279) disproved the view held by Smith and his pupils (Abstr., 1905, ii, 382, 580) with regard to the behaviour of liquid sulphur at 160°, and they hold that in his latest papers (see this vol., ii, 20) Smith has adopted their position without due acknowledgment.

J. C. P.

**The Rôle of Caro's Acid in the Electrolytic Formation of Persulphuric Acid and its Salts.** ERICH MÜLLER and HUGO SCHELLHAAS (*Zeitsch. Elektrochem.*, 1907, 13, 257—280).—When sulphuric acid is electrolysed, the yield of active oxygen compounds (persulphuric and Caro's acids and hydrogen peroxide) first increases and then falls off again. The initial increase is due to a rise in the anodic potential. The subsequent fall in yield is accompanied by a steady increase in the quantity of Caro's acid present in the solution. Hydrogen peroxide is always found in very small quantities. Caro's acid appears to be formed, by a secondary reaction, from persulphuric acid and water, and it is destroyed again at the anode, thus:  $\text{H}_2\text{SO}_5 + 2\text{OH}^- + 2F = \text{H}_2\text{SO}_4 + \text{O}_2 + \text{H}_2\text{O}$ . The quantities of Caro's acid formed and destroyed in unit time therefore increase as the concentration of the persulphuric acid increases. The current efficiency may be improved in two ways: (a) by adding a substance which raises the anode potential, (b) by destroying Caro's acid chemically without acting on persulphuric acid. Hydrofluoric acid acts in the first way, sulphurous

acid or hydrogen sulphide in the second, and hydrochloric acid in both ways simultaneously. In all these cases, considerable improvement in the current efficiency is observed; for example, a saturated solution of sulphur dioxide in sulphuric acid of D 1.39, electrolysed with a current density of 0.5 ampere per sq. cm. at the anode, gave a current efficiency of 91% to 92%.

A number of experiments were made with sulphuric acid containing the sulphates of ammonium, sodium, potassium, aluminium, and magnesium. The anode potential is sometimes raised, sometimes depressed, and the current efficiency varies in a corresponding way; the cause of this effect is unexplained.

The preparation of persulphates by the electrolysis of strongly acid solutions is then investigated. The solubility of ammonium persulphate in sulphuric acid of D 1.4 to 1.5 is so small that the Caro's acid is formed very slowly and the current efficiency is not seriously affected; the solubility of sodium persulphate is, however, great enough to lead to the formation of considerable quantities of Caro's acid, and in order to maintain a good current efficiency this substance must be removed by means of sulphurous acid.

The paper concludes with an attempt to give a theory of the observed phenomena, but the authors do not regard their results as final.

T. E.

**Action of Fluorine on Selenium. Selenium Tetrafluoride.** PAUL LEBEAU (*Compt. rend.*, 1907, 144, 1042—1044. Compare Moissan, *Ann. Chim. Phys.*, 1891, [vi], 24, 214).—The selenium hexafluoride described by Prideaux (*Trans.*, 1906, 89, 316), obtained by the action of fluorine on selenium contained in glass vessels, is probably an oxyfluoride, since, in repeating the experiment in copper vessels, the author has only been able to obtain *selenium tetrafluoride*. This is a colourless, intensely irritating liquid, b. p. a little above 100°, which solidifies to a white, crystalline solid at  $-80^{\circ}$ ; its vapour colours a Bunsen flame intensely blue. It attacks glass energetically, is decomposed by water, forming selenious and hydrofluoric acids, does not absorb fluorine, dissolves iodine, giving a reddish solution, and does not attack boron, silicon, or carbon on boiling. With phosphorus there is a vivid reaction, selenium and phosphorus fluoride being formed. The fluoride is decomposed by alkali metals, and it attacks mercury in the cold, but is without action on platinum. T. A. H.

**Selenium Hexafluoride.** Sir WILLIAM RAMSAY (*Compt. rend.*, 1907, 144, 1196).—The author has found that the density of the gas prepared by Prideaux in his laboratory is 97.23. Consequently the gas cannot be selenium oxyfluoride,  $\text{SeOF}_4$  (density 85.5), as suggested by Lebeau (preceding abstract), nor an oxyfluoride of the formula  $\text{SeO}_2\text{F}_2$ , which would have a density 74.5. E. H.

**Hydroxylamine.** G. M. JOHNSTONE MACKAY (*Trans. Nova Scotia Inst. Sci.*, 1906, 11, 324—337).—A study of solutions of hydroxylamine of greater constitution than those previously examined by Ross (*Abstr.*, 1906, ii, 19). Since, as was shown by this author, solutions

of hydroxylamine and its salts are decomposed by platinum, electrodes of other metals were tried, with the result that they were found to decompose the solutions in the following order: tin, platinum, silver, nickel plate, mercury, copper; the latter metal decomposes hydroxylamine solutions completely, whilst tin does not decompose them at all, so that, in this investigation, tin electrodes were employed. The following values, which express the equivalent conductivity ( $\mu \times 10^7$ ) at  $18^\circ$  in terms of mercury,  $v$  being the volume per gram-molecule of substance, are consequently more accurate than those of Ross, who used platinum electrodes:

$v = 0.0994.$	0.2.	0.5.	1.0.	2.0.	5.0.	10.	20.	50.
$\mu_v = 0.031.$	0.018.	0.027.	0.051.	0.093.	0.098.	0.28.	0.40.	0.52.
			100.	200.	500.			
			0.76.	1.3.	1.4.			

It will be seen that there is a minimum molecular conductivity between the concentrations  $2N$  and  $10N$ , which may indicate that at high concentrations hydrates are formed which are dissociated on further dilution, but this point was not further investigated. The specific conductivity in reciprocal ohms of pure hydroxylamine at a temperature slightly above  $33^\circ$  was found to be approx.  $83 \times 10^{-6}$ , a value which lies between that of liquid ammonia at  $30^\circ$ ,  $150 \times 10^{-6}$ , and that of hydrazine hydrate,  $34 \times 10^{-6}$ .

The freezing points of solutions of hydroxylamine were also determined, the molecular depression obtained being:

$v =$	1.	2.	5.	10.	20.	50.	100.	500.
	1.77.	1.78.	1.80.	1.81.	1.90.	1.96.	2.04.	2.25.

These results are in general agreement with the conductivity measurements in showing the slight dissociation of hydroxylamine in solution.

W. H. G.

**Phosphorus Nitride.** ALFRED STOCK and HANS GRÜNEBERG (*Ber.*, 1907, 40, 2573—2578).—After repeating and discarding the methods of previous investigators, the authors returned to that of Stock and Hoffmann (*Abstr.*, 1903, ii, 207); they studied systematically the errors which result in the bad yield of phosphorus nitride, and succeeded finally in obtaining the nitride quantitatively by the following process. Pure phosphorus pentasulphide is saturated with pure dry ammonia at the ordinary temperature and the product heated in an atmosphere of ammonia until the containing Jena glass-tube begins to soften; the complicated mixture of ammonium thiophosphates so obtained is heated for twelve hours at  $850^\circ$  in a current of ammonia (or of the products of its decomposition). The resulting phosphorus nitride is absolutely pure, has  $D^{18}$  2.51, varies in colour from pure white to dark red according to the time it has been heated above  $850^\circ$ , is chemically inactive at the ordinary temperature, but at high temperatures acts as a powerful reducing agent in consequence of its decomposition into phosphorus and nitrogen, which begins at  $760^\circ$  in a vacuum.

Attempts to prepare other phosphorus nitrides have been unsuccessful. C. S.

**Phase Relations of the System: Sodium Carbonate and Water.** ROGER C. WELLS and D. J. McADAM, jun. (*J. Amer. Chem. Soc.*, 1907, 29, 721—727).—Epple (*Inaug. Diss.*, 1899) has described the lower hydrates of sodium carbonate as octa- and di-hydrates, whilst Ketner (*Abstr.*, 1902, ii, 308) has regarded them as hepta- and mono-hydrates. A study has now been made of the phase relations between 25° and 45°, and has shown that three hydrates exist, namely, deca-, hepta-, and mono-hydrates. The solubilities of these hydrates have been determined, and the results are tabulated and plotted in a diagram. Of the two heptahydrates described by Loewel (*Ann. Chim. Phys.*, 1851, [iii], 33, 382), only the less soluble form could be obtained. The transition temperatures of sodium carbonate are found to be:  $10\text{H}_2\text{O}-7\text{H}_2\text{O}$ , 32.00°;  $10\text{H}_2\text{O}-1\text{H}_2\text{O}$ , 32.96°;  $7\text{H}_2\text{O}-1\text{H}_2\text{O}$ , 35.37°; these results are compared with those of previous observers. The transition points and solubility data are in good accord. E. G.

**Use of Potassium Permanganate to Eliminate Sodium Thiosulphate in Photography.** ALBERT GRANGER (*Compt. rend.*, 1907, 144, 1017—1018).—The developed print or negative (13 × 18 cms.) is washed two or three times in water and placed in a glass or porcelain vessel with 250 c.c. of a solution of permanganate containing 0.04 gram per litre, and this treatment is repeated until the colour of the permanganate solution added remains unchanged. The negative is then placed in a 1% solution of oxalic acid for a few minutes, and finally washed in water to remove the excess of oxalic acid. This proceeding may be simplified by using a solution containing both potassium permanganate and an alkali hydrogen sulphate, but the elimination of the latter by washing with water is more difficult than the removal of oxalic acid. No ill effect is produced by allowing prints or negatives to remain in the permanganate solution during one hour, but it is advisable to complete the operation as rapidly as possible. T. A. H.

**Borates. II.** M. DUKELSKI (*Zeitsch. anorg. Chem.*, 1907, 54, 45—49).—In continuation of his work on the alkali borates (*Abstr.* 1906, ii, 610), the author has now investigated the equilibrium in the system lithium hydroxide-boric acid-water at 30°, and the results are represented on the usual triangular diagram. Under the given conditions, only mono-, di-, and penta-borates exist. The monoborate has the formula  $\text{Li}_2\text{O}, \text{B}_2\text{O}_3, 16\text{H}_2\text{O}$  (Le Chatelier, *Abstr.*, 1897, ii, 448); the pentaborate,  $\text{Li}_2\text{O}, 5\text{B}_2\text{O}_3, 10\text{H}_2\text{O}$ ; the latter decomposes on recrystallisation from water. The diborate appears to be amorphous, and forms colloidal solutions; the amount of water of crystallisation could not be determined. G. S.

**Dissociation of the Lithium Silicates.** EDGARD DEROME (*Compt. rend.*, 1907, 144, 1116—1118. Compare Lebeau, *Abstr.*, 1903, ii, 477).—When the glass, obtained by heating at 900° a mixture

of silica and lithium carbonate in a current of hydrogen for several hours, is heated in a vacuum in the electric furnace, it gradually loses lithia. The rapidity of the dissociation slowly decreases from the beginning of the experiment, and diminishes suddenly when the composition of the residue is approximately represented by  $2\text{Li}_2\text{O}, \text{SiO}_2$ . On similarly heating the silicate,  $\text{SiO}_2, \text{Li}_2\text{O}$ , obtained in the crystalline form by heating a mixture of  $5\text{SiO}_2$  with  $2\text{Li}_2\text{O}$  suspended in fused  $\text{LiCl}$  at a red heat for six hours (compare Hautefeuille and Margottet, *Abstr.*, 1882, 278), dissociation of diminishing rapidity is again observed, but in this case the greatest slackening occurs when the residue has the composition  $\text{Li}_2\text{O}, 5\text{SiO}_2$ , from which the author draws the conclusion that the latter silicate is very slightly dissociated at  $1300^\circ$ . Micro-chemical examination of the residue reveals the presence of lamellæ, probably consisting of  $\text{Li}_2\text{O}, 5\text{SiO}_2$ . E. H.

### Action of Silicon Tetrachloride on Silver and Copper.

EMILE VIGOUROUX (*Compt. rend.*, 1907, 144, 1214—1216. Compare *Abstr.*, 1906, ii, 287, 451; this vol., ii, 176).—When finely powdered silver is heated for about three hours (in a Mermet furnace) in a current of gaseous silicon tetrachloride, fusion being prevented until near the end of the heating, an ingot of silver covered with silver chloride is obtained. 8.33% of the silver is converted into chloride, but the unchanged silver contains neither free nor combined silicon (compare Moissan and Siemens, *Abstr.*, 1904, ii, 332, 560). A second heating of the unchanged silver in the same manner effects a further, but smaller, conversion into chloride. On similarly heating copper at  $1200^\circ$  in a current of silicon tetrachloride, the weight is reduced 20% on the first occasion, but on repeated treatment (after re-powdering) gradually becomes constant. The copper ingot obtained retains its red colour and its malleability, is easily attacked by nitric acid, but is acted on with difficulty or not at all by other acids and alkalis. It contains 2.33—2.37% of silicon in the combined condition. When a Mermet furnace is used, the resulting copper contains 2.34—2.39% of silicon, whilst chemically pure copper gives a product containing 2.4—2.48% of silicon. The author considers that the inferior limit of the silicuration of copper by excess of silicon chloride is 2.7%, corresponding with the formula  $\text{Cu}_{16}\text{Si}$ . E. H.

**Hydrolite [Calcium Hydride].** JOSÉ PRATS AYMERICH (*Anal. Fis. Quim.*, 1907, 5, 173—174).—Jaubert's "hydrolite" (compare *Abstr.*, 1906, ii, 352), 90% of which consists of calcium hydride, liberates about 100 c.c. of hydrogen per gram when acted on by water; the hydrogen is free from ammonia and acetylene. The residual lime formed in this way, when dissolved in hydrochloric acid, gives bubbles of a spontaneously inflammable gas, similar in its behaviour to hydrogen phosphide, but the presence of a phosphide in the lime cannot be detected by subjecting the latter to the action of an oxidising agent (for example, potassium permanganate or fused nitre) and then testing for phosphoric acid. The source and nature of the spontaneously inflammable gas remain still to be determined. W. A. D.

**Action of Concentrated Solutions of Potassium Hydroxide and Potassium Carbonate on Calcium Carbonate, and the Two Double Salts of Calcium Carbonate and Potassium Carbonate Formed.** O. BÜTSCHLI (*Chem. Zentr.*, 1907, i, 1138—1139; from *Verh. naturhist.-med. Vereins Heidelberg*, [ii], 8, 277—330. Compare *Zeitsch. wiss. Zool.*, 69, 235—286).—The siliceous needles of *Spongix* contain only a small quantity of organic matter, and consist mainly of amorphous silicic acid which resembles opal or artificial siliceous jellies; after ignition, only a fine honeycombed structure is left. The brittle, axial threads after treatment with hydrofluoric acid gave reactions which indicated a protein nature. When treated with a 35% solution of potassium hydroxide, a portion of the lime spicula dissolved and only a thin, fine combed, structural skeleton of the same form remained, which probably consisted of organic material. A double compound of calcium and potassium carbonates separated from the solution in six-sided plates. The latter is instantly decomposed by water and leaves a residue of globules and rhombohedra of calcspar. Maas (*Verh. Deutsch. Zool. Ges.*, 1904, 190—198) and Weinschenk (*Zentr. Min. Geol.*, 1905, 581—588) regarded the six-sided plates as potassium carbonate and the needles as rhombohedra of calcium carbonate held together by organic matter.

When lime water is gradually added to a concentrated solution of potassium carbonate, preferably containing some solid carbonate, a double compound *A* separates. When gelatinous calcium carbonate is spread out in a dish with a cold concentrated solution of potassium carbonate, the compound *A* is formed after a few hours. A compound, *B*, prepared by mixing a small quantity of calcium hydroxide with potassium carbonate, or by treating calcium carbonate with a saturated solution of potassium carbonate at 40—60°, forms hexagonal prisms. By treating the crystalline carbonates, obtained from gelatinous calcium carbonate and concentrated potassium carbonate solution, with equal parts of a concentrated solution of potassium carbonate and a 35% solution of potassium hydroxide, hexagonal plates of the compound *A* and acute rhombohedra of *B* are formed; both are decomposed by water and leave globules of calcium carbonate. The compound *A*,  $2\text{CaCO}_3 \cdot 3\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$ , is highly doubly refractive, optically negative, and separates in hexagonal plates, short prisms, twinned crystals, and circular plates. The additive compound *B*,  $\text{CaCO}_3 \cdot \text{K}_2\text{CO}_3$ , is also highly doubly refractive and is optically negative. There is no crystalline hydrate of potassium carbonate which resembles *A*.

The author confirms Hofmann's observation that the hexagonal plates formed by treating calcium carbonate with a 35% solution of potassium hydroxide are really calcium hydroxide. E. W. W.

**Calcium Magnesium Orthosilicate Series.** HERMANN (*Chem. Zentr.*, 1907, i, 912; from *Mitt. K. Materialprüf.-Amt. Gross-Lichterfelde West*, 24, 246—252).—Experiments have been made to determine the relationship between the composition of the mixture and the silicates obtained by fusion, and the influence of the latter on the decomposition limit of cements. Several mixtures of calcium carbonate, silica, and magnesia in various proportions were heated under the same



conditions in a coke blast furnace. The melting points of the mixtures were determined by Seger cones. The decomposition of the cement which occurred when less than 18·75% of magnesium silicate,  $Mg_2SiO_4$ , was present, was found to depend on the formation of a felspar-like mineral. When more than 25% of magnesium silicate is present, monticellite begins to separate and with 50%, this mineral alone is formed. Mixed crystals of monticellite and forsterite separate when the quantity of magnesium silicate is greater than 56·25%, and at 75% the two silicates form separate crystals. When the mass contains more than 81·25% of magnesium silicate, forsterite is formed. E. W. W.

**Behaviour of Heavy Spar at High Temperatures.** F. O. DOELTZ and WL. MOSTOWITSCH (*Zeitsch. anorg. Chem.*, 1907, **54**, 146—148).—When heated on platinum at 1400—1500°, Kahlbaum's barium sulphate and a specimen prepared from barium chloride and sulphuric acid changed to a white enamel. A specially pure specimen, prepared by interaction of ammonium sulphate and barium hydroxide, fused after heating in the air for ten to twenty minutes on platinum at 1580° and lost about 9% by weight. G. S.

**Glucinum Chromate.** BORIS GLASSMANN (*Ber.*, 1907, **40**, 2602—2604).—*Glucinum chromate*,  $GlCrO_4 \cdot H_2O$ , obtained by the evaporation of the solution of the carbonate in concentrated chromic acid, forms reddish-yellow, monoclinic crystals, and is decomposed by water with the formation of a yellow basic *chromate*,  $GlCrO_4 \cdot 6Gl(OH)_2$ , which is also obtained by precipitating a solution of glucinum sulphate by ammonium chromate. C. S.

**Action of Iron Oxides on Zinc Sulphide.** CARL A. GRAUMANN (*Metallurgie*, 1907, **4**, 69—77).—Mixtures of ferric oxide and zinc sulphide contained in magnesia-lined crucibles were heated in an electrical furnace in an atmosphere of nitrogen. Under these conditions, only a very slight reaction takes place at 1280°. In a slow current of air at 1280°, sulphur dioxide and zinc vapour are evolved, but the reaction soon comes to a standstill. On igniting mixtures of zinc sulphide and ferrous oxide or of zinc oxide and ferrous sulphide, zinc is not set free. In an atmosphere of carbon monoxide, ferric oxide is reduced to iron, which then sets free zinc, forming iron sulphide. When carbon is used as the reducing agent, a part of the sulphur is lost as sulphur dioxide. Complete reduction of zinc sulphide may be effected by heating with spongy metallic iron at 1300°. C. H. D.

**Reactions in Liquid Ammonia.** Potassium Ammonio-zincate, Cuprous Nitride, and an Ammonio-basic Mercuric Bromide. F. F. FITZGERALD (*J. Amer. Chem. Soc.*, 1907, **29**, 656—665).—It has been shown by Franklin and Stafford (*Abstr.*, 1902, **i**, 748) that acid amides and metallic amides dissolved in liquid ammonia react with one another to form compounds which bear the same relation to ammonia that the ordinary oxygen salts bear to water. Further, Franklin has found (*Abstr.*, 1905, **ii**, 581) that certain metallic amides dissolve in excess of an amide of a more basic element, probably with formation

of ammonio-salts analogous to such compounds as potassium zincate. The present investigation was undertaken with the object of preparing such ammonio-salts.

When potassamide is added to a solution of copper nitrate in liquid ammonia, an olive green precipitate is produced. If this precipitate is heated at  $160^{\circ}$  in a vacuum, nitrogen is evolved and cuprous nitride (Schötter, *Annalen*, 1841, 37, 144) remains as a black, amorphous mass. The reaction is represented thus:  $3\text{Cu}(\text{NO}_3)_2 + 6\text{KNH}_2 = \text{Cu}_3\text{N} + 6\text{KNO}_3 + 4\text{NH}_3 + \text{N}$ .

The formation of ammonio-basic mercuric bromide,  $\text{Hg}\cdot\text{N}\cdot\text{HgBr}$  (Franklin, *loc. cit.*), by the action of potassamide on excess of mercuric bromide is confirmed.

A solution of potassamide in liquid ammonia reacts with zinc with formation of a well crystallised *potassium ammonio-zincate*, but the results of analysis of this compound do not lead to any simple definite formula. The compound can also be prepared by the action of a solution of potassamide on zincamide. The apparatus used in these experiments is illustrated by means of diagrams. E. G.

**Miscibility of the Cadmium Halides.** R. NACKEN (*Centr. Min.*, 1907, 301—305).—The freezing point curves of the three pairs yielded by cadmium chloride, bromide, and iodide have been determined. The freezing points of the pure substances found from the cooling curve are  $563^{\circ}$ ,  $567^{\circ}$ , and  $385^{\circ}$  respectively. The chloride and bromide form a complete series of mixed crystals, the mixture containing 40 mols. % cadmium chloride having a minimum freezing point ( $550^{\circ}$ ). The bromide and iodide are also completely miscible in the crystalline condition and the freezing points of all mixtures lie between those of the components. The chloride and iodide form two limiting series of mixed crystals. The freezing point curves meet at  $359^{\circ}$ , this temperature corresponding with a fused mixture containing 69 mols. % of the iodide. The eutectic consists of a mixture of the two kinds of mixed crystals, which contain respectively 92 mols. % and 4 mols. % of the iodide. H. M. D.

**Equilibrium in the Reaction between Lead Sulphide and its Oxidation Products.** RUDOLF SCHENCK and W. RASSBACH (*Ber.*, 1907, 40, 2185—2210).—The reactions between lead sulphide and its oxidation products are not adequately expressed by equations, such as  $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$ ;  $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2$ ;  $\text{PbS} + 3\text{PbSO}_4 = 4\text{PbO} + 4\text{SO}_2$ , since reversible actions also take place.

Four conditions of equilibrium are possible, namely, (1)  $\text{PbS} + \text{PbSO}_4 \rightleftharpoons 2\text{Pb} + 2\text{SO}_2$ ; (2)  $\text{PbS} + 2\text{PbO} \rightleftharpoons 3\text{Pb} + \text{SO}_2$ ; (3)  $\text{PbS} + 3\text{PbSO}_4 \rightleftharpoons 4\text{PbO} + 4\text{SO}_2$ , and (4)  $\text{Pb} + \text{PbSO}_4 \rightleftharpoons 2\text{PbO} + \text{SO}_2$ . The authors have investigated the problem as to which of these equilibrium conditions are capable of being observed. The problem was complicated owing to the solubility of lead sulphate in lead oxide and by the solubility of the sulphide in the metal.

If a mixture of lead sulphide and lead sulphate together with a little lead is heated in an evacuated apparatus, gas begins to be evolved at  $550^{\circ}$ . At comparatively low temperatures the rate of the reaction

was quite appreciable and increased quickly on rise of temperature. The reaction pressures were measured at varying temperatures where the gas was either evolved or absorbed. The equilibrium,  $\text{PbS} + \text{PbSO}_4 \rightleftharpoons 2\text{Pb} + 2\text{SO}_2$ , accordingly exists.

The equilibrium attained on heating the following mixtures was also studied: (1) lead sulphide, lead oxide, lead; (2) lead sulphide, lead sulphate, lead oxide; (3) lead, lead oxide, and lead sulphate.

The equilibrium,  $\text{PbS} + \text{PbSO}_4 \rightleftharpoons 2\text{Pb} + 2\text{SO}_2$ , may be attained from both sides.

The action of sulphur dioxide on lead oxide at  $750^\circ$  takes place according to the equation:  $4\text{PbO} + 4\text{SO}_2 = 3\text{PbSO}_4 + \text{PbS}$ .

A. McK.

**Lead Selenide.** HENRI PELABON (*Compt. rend.*, 1907, **144**, 1159—1161).—Lead combines directly with selenium, giving a compound which forms homogeneous mixtures with excess of either of its components. The author has studied the variation of the temperature of "commencing solidification" of these mixtures with the total percentage of selenium they contain. Pure lead commences to solidify at  $325^\circ$ , lead containing 2% of selenium at  $745^\circ$ , and lead containing 4.5% of selenium at  $830^\circ$ . The temperature of completion of solidification in these cases is  $325^\circ$ . With an increasing amount of selenium, the initial solidification temperature rises to a maximum of  $1065^\circ$ , which corresponds with 27% of selenium. This temperature must be the melting point of lead selenide,  $\text{PbSe}$ , since the latter contains 27.62% of selenium, and the liquids obtained by melting together lead and a smaller proportion of selenium are solutions of  $\text{PbSe}$  in metallic lead. As the amount of selenium is increased above 27%, the temperature of initial solidification falls rapidly to the value  $673^\circ$ , which is constant for mixtures containing 45—100% of selenium. Mixtures containing more than 45% of selenium separate into two layers, an upper one of pure selenium and a lower one solidifying at  $673^\circ$  to a greyish-black solid with a lamellaceous fracture. The latter seems to be a saturated solution of selenium in lead selenide, and is not lead diselenide,  $\text{PbSe}_2$  (which would contain 43.35% Se), since (1) when allowed to solidify in a vacuum it rapidly loses selenium; (2) on heating it loses selenium, without melting, until  $\text{PbSe}$  remains; (3) selenium can be removed by washing with hot concentrated potassium cyanide solution.

Thus the liquids containing 27—45% of selenium are mixtures of lead selenide and selenium.

E. H.

**Thallium.** VICTOR THOMAS (*Ann. Chim. Phys.*, 1907, [viii], **11**, 204—262).—A detailed description of the preparation and properties of the halogen derivatives of thallium of which an account has already been published (compare *Abstr.*, 1900, ii, 442; 1901, ii, 60, 100, 159, 507; 1902, ii, 79, 322, 357, 472, 531; 1903, ii, 147; 1906, ii, 356, 662; this vol., i, 117). The following corrections and additions are recorded. Perfectly dry liquid chlorine has no action on thallous chloride. Chlorine and thallous chloride in sealed tubes under 6—7 atmospheres pressure unite to form thallic chloride, m. p.  $60-70^\circ$ ,

having a heat of solution 8.43 Cal. Thallic chloride absorbs hydrogen chloride yielding the compound  $\text{TiCl}_3 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ , which forms long, hygroscopic needles. M. A. W.

**The So-called Allotropic Copper.** CARL BENEDICKS (*Metallurgie*, 1907, 4, 5—17, 33—43).—It was shown by Schützenberger (Abstr., 1878, 706) that the copper deposited on electrolysis of neutral copper acetate solutions differs from ordinary copper in its great brittleness, light colour, and low specific gravity, and in the readiness with which it oxidises in the air. It also dissolves in dilute nitric acid with evolution of nitrous oxide. Schützenberger's product contained cuprous oxide, but by regulation of the current density it is possible to obtain a product free from oxide. With higher current densities, tree-shaped, hollow growths are obtained on the cathode.

Analysis shows these copper deposits to contain acetic acid, which is given off when heated to  $140^\circ$ , and is even occasionally exuded at the ordinary temperature. No copper mirror or coloured vapour is formed on heating in a current of hydrogen, indicating that the metal does not contain copper acetate. The electrical conductivity is much lower than that of pure copper. Microscopic examination does not reveal the presence of any distinct constituent. The specific gravity is greater than that calculated for copper holding the observed proportion of acetic acid mechanically. The conclusion is drawn that the "allotropic" copper is really a solid solution of acetic acid in copper. The paper is illustrated with photo-micrographs. C. H. D.

**Copper-Tellurium Alloys.** MASUMI CHIKASHIGÉ (*Zeitsch. anorg. Chem.*, 1907, 54, 50—57).—From an investigation of this system by thermal analysis, supplemented by microscopic observations, the conclusion is drawn that two well-defined compounds of copper and tellurium exist, the respective formulæ of which are  $\text{Cu}_4\text{Te}_3$  and  $\text{Cu}_2\text{Te}$ . The freezing point curve of the system shows a eutectic point at  $340^\circ$  and 17.3% by weight of copper, and breaks at  $623^\circ$  and about 34%, and  $855^\circ$  and 50% by weight of copper respectively; beyond the latter point two layers are present. The break at 50% copper corresponds with the compound  $\text{Cu}_2\text{Te}$ , which is only miscible with copper to a very limited extent; at about  $1030^\circ$ ,  $\text{Cu}_2\text{Te}$  dissolves 1—2% of copper, and the latter about 4% of tellurium. From 32.7—50% of copper, the above-mentioned compound crystallises primarily in a series of mixed crystals containing tellurium. At  $623^\circ$ , the mixed crystals containing 45% of copper react with the fused mass to form the compound  $\text{Cu}_4\text{Te}_3$ . The latter has a transition point at  $365^\circ$ , marked by a considerable development of heat. The compound  $\text{Cu}_2\text{Te}$  has two transition points at  $387^\circ$  and  $351^\circ$  respectively; the latter is lowered to  $334^\circ$  by the addition of 5% of tellurium.

The compound  $\text{Cu}_4\text{Te}_3$  is violet in colour, whilst  $\text{Cu}_2\text{Te}$  occurs in grey crystals.

As little as 0.01% of tellurium can be recognised microscopically in copper. G. S.

**Copper Peroxide.** L. MOSER (*Zeitsch. anorg. Chem.*, 1907, 54, 121—140).—The action of various oxidising agents on copper salts has been investigated and it was found that a stable peroxide could be obtained only by the action of hydrogen peroxide in neutral solution.

Neither chlorine nor bromine in alkaline solution gives rise to a peroxide which could be isolated, although the intermediate formation of an unstable peroxide is probable. Ozone has no oxidising action on cupric salts. Persulphates in alkaline solution do not oxidise cupric hydroxide, nor, contrary to the opinion of Schmidt (1886), do the peroxides of manganese or lead.

Copper peroxide,  $\text{CuO}_2$  (Thenard, 1818), was readily obtained as a brown, crystalline powder by the action of a slight excess of 10—30% hydrogen peroxide in neutral solution at  $0^\circ$  on freshly precipitated cupric hydroxide. The formula was established by estimation of the ratio of cupric oxide to active oxygen in the moist salt. After washing with alcohol and ether and rapidly drying, it loses a considerable proportion of active oxygen. It sets free a considerable amount of chlorine from concentrated hydrochloric acid and gives hydrogen peroxide with the dilute acid. It appears to have  $1\text{H}_2\text{O}$  in chemical combination.

The same peroxide is formed by the action of sodium peroxide on cupric salts, but could not be satisfactorily isolated owing to rapid catalytic decomposition in the alkaline solution. G. S.

**Preparation of Green Neodymium Chromate and Pure Cerium Salts from Monazite Residues.** N. A. ORLOFF (*Chem. Zeit.*, 1907, 31, 562—563).—Since the method of preparation of pure cerium compounds previously described (*Abstr.*, 1906, ii, 675) necessitates the use of large quantities of ammonium oxalate and yields but a small proportion of pure cerium oxalate, it has been slightly modified, whereby it is now possible to separate practically the whole of the cerium in a pure state. The oxides of the elements of the cerium group are dissolved in warm, strong, sulphuric acid, the solution diluted with water and acetic acid, ammonia added until the precipitate formed redissolves, and the solution then poured into an ammonium oxalate solution, quickly filtered, and either ammonium sulphite or sulphurous acid added to the filtrate, whereby a white precipitate of practically pure cerium oxalate is obtained.

In order to obtain a good moss-green neodymium chromate, the oxalates of neodymium and lanthanum, which remained undissolved in the ammonium oxalate solution, are recrystallised from hot nitric acid and the last neodymium fraction converted into chromate.

W. H. G.

**Hydrates of Aluminium Fluoride.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 775—784. Compare Berzelius, *Ann. Phys. Chem.*, 1824, [ii], 1, 23; Deville, *Ann. Chim. Phys.*, 1861, [iii], 61, 321—331; Baud, *Abstr.*, 1903, ii, 150).—The author finds that the contradictory observations made by different investigators concerning aluminium fluoride and its hydrates are due to complications traceable to phenomena of metastability and supersaturation, to the slowness with which solutions and solid phases attain a state of equilibrium,

and to the existence of hydrates having the same composition, but differing in solubility and in degree of resistance to the action of heat.

The most convenient method of preparing a solution of aluminium fluoride is to suspend 42 grams of basic aluminium acetate and 54 grams of alumina in about 100 c.c. of water and add 66 grams of hydrofluoric acid solution (40% by weight). Under these conditions, complete solution occurs either at once or after boiling for a short time. This solution gradually deposits a gelatinous hydrate of aluminium fluoride; contact with filter paper accelerating the change. More dilute solutions gradually deposit a crystalline crust, apparently of the same composition as the gelatinous hydrate, which has the formula  $\text{Al}_2\text{F}_6 \cdot 6\text{H}_2\text{O}$ .

If, in the above method of preparing aluminium fluoride solution, 75 instead of 100 c.c. of water are used, the liquid becomes violently heated and, on cooling, deposits large, transparent crystals of the hydrate,  $\text{Al}_2\text{F}_6 \cdot 17\text{H}_2\text{O}$ . This hydrate may be obtained as a felted mass of short needles by cooling below  $0^\circ$  a more dilute aluminium fluoride solution. A saturated aqueous solution of the hydrate,  $\text{Al}_2\text{F}_6 \cdot 17\text{H}_2\text{O}$ , contains 3.85 grams of  $\text{Al}_2\text{F}_6$  per 100 grams at  $11^\circ$  and 1.20 grams at  $-0.2^\circ$ . This hydrate rapidly effloresces and all the crystals become opaque, even when kept in a sealed tube. This change is non-reversible and results in the transformation of the soluble, metastable hydrate into the hydrate  $\text{Al}_2\text{F}_6 \cdot 6\text{H}_2\text{O}$ , which is the most stable under ordinary conditions.

The author has confirmed qualitatively Baud's results (*loc. cit.*), and finds that the latter's hydrate,  $\text{Al}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$ , as well as the hydrate  $\text{Al}_2\text{F}_6 \cdot 17\text{H}_2\text{O}$ , become gradually transformed into the less soluble hydrate  $\text{Al}_2\text{F}_6 \cdot 6\text{H}_2\text{O}$  if left in contact with water.

If a dilute solution or a small quantity of a concentrated solution of neutral aluminium fluoride is evaporated to dryness on a water-bath, it deposits silky filaments of the hydrate  $\text{Al}_2\text{F}_6 \cdot 2\text{H}_2\text{O}$  (compare Baud, *loc. cit.*), which is completely, but only sparingly, soluble in water, by which it is transformed into the hydrate  $\text{Al}_2\text{F}_6 \cdot 6\text{H}_2\text{O}$ . T. H. P.

**Double Compounds of Aluminium Sulphide with Chromium, Nickel, Cobalt, and Magnesium Protosulphides.** MARCEL HOUDARD (*Compt. rend.*, 1907, 144, 1114—1116. Compare this vol., ii, 468; Schneider, *Abstr.*, 1898, ii, 229; Christensen, *Abstr.*, 1892, 1000).—By heating a mixture of aluminium (7 grams) and chromium (5.6 grams) in a current of hydrogen sulphide, a black, crystalline mass is obtained, which evolves hydrogen sulphide with water giving a deposit of alumina and leaving a reddish-black, crystalline residue. The latter after washing with dilute hydrochloric acid gives analytical results corresponding approximately with the composition,  $\text{Al}_2\text{S}_3 \cdot \text{CrS}$ . If excess of chromium is used, the sesquisulphide seems to be formed and the crystalline mass obtained is only with difficulty attacked by dilute hydrochloric acid, whilst nitric acid slowly destroys the double compound, leaving a black, crystalline residue of  $\text{CrS}$ . The product from nickel and aluminium gives, after treatment with water, red, crystalline spangles which gradually become black. No definite com-

pound can be isolated. Similarly, the product from cobalt, when treated with water, yields golden-yellow spangles which rapidly become black. With aluminium and magnesium, the product is crystalline with a rose-red fracture; on treatment with water, 90% alcohol, glacial acetic acid diluted with absolute alcohol, or water deprived of oxygen and saturated with hydrogen, it is decomposed with evolution of hydrogen sulphide and production of rose-red spangles which quickly become deep green. On drying in air or in a vacuum, they are oxidised and become colourless.

Optical and crystallographic examination of these crude products shows a cubical structure. The compounds  $\text{Al}_2\text{S}_3\text{MnS}$ ,  $\text{Al}_2\text{S}_3\text{FeS}$ , and  $\text{Al}_2\text{S}_3\text{CrS}$  isolated, are analogous to spinel. E. H.

**Constitution and Properties of the Hydrate of Aluminium Bromate.** DIMITRI DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 133—139. Compare Abstr., 1904, ii, 564).—The few data given by Rammelsberg regarding aluminium bromate (*Ann. Phys. Chem.*, 1842, [ii], 55, 63) have been found to be incorrect. The salt, the formula of which is probably  $\text{Al}_2(\text{Br}_3\text{O}_3)_6 \cdot 18\text{H}_2\text{O}$  or  $\text{Al}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ , is prepared by the action of barium bromate on aluminium sulphate. It is crystalline, m. p.  $62.3^\circ$ , is strongly oxidising, and cannot be dehydrated without decomposition. When heated above its melting point, vapours are evolved, and at  $100^\circ$  a red, hygroscopic mass is obtained, probably of the formula  $\text{Al}(\text{BrO}_3)_3, \text{Al}_2\text{O}_3, \text{Al}(\text{BrO}_4)_3, \text{Al}_2\text{O}_3$ . Z. K.

**Aluminium Calcium Silicates.** OCTAVE BOUDOUARD (*Compt. rend.*, 1907, 144, 1047—1049).—A systematic investigation of the fusibility of aluminium calcium silicates has been made and the results plotted as a triangular diagram (*Rev. Metallurgie*, 1905, 462). The surface of fusibility presents two maxima at the temperatures  $1510^\circ$  and  $1500^\circ$  corresponding with silicates of the following formulæ,  $2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$  and  $8\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ . The first of these is regarded as a definite chemical compound, since its polished surface, washed with 10% hydrochloric acid and examined under the microscope, exhibits almost complete homogeneity. Further, analyses of three different specimens of crystals isolated by hand or by washing with methylene iodide gave results closely approximating to those required by the formula quoted above. T. A. H.

**Solubility of Potassium Permanganate.** EDWARD C. WORDEN (*J. Soc. Chem. Ind.*, 1907, 26, 452—453).—Tables showing the solubility of potassium permanganate in water at temperatures from  $4-75^\circ$ . L. DE K.

**Constitution and Properties of Boron Steels.** LÉON GUILLET (*Compt. rend.*, 1907, 144, 1049—1050).—Microscopic examination of boron steels containing 0.215—0.844% of boron shows that they are constituted by (1) a solid ferroboron solution, containing a minute quantity of boron, (2) perlite, and (3) a substance which appears to be an iron borocarbide. To the last is due the brittleness of the normal

boron steels, which disappears on tempering, this substance passing into solution during this operation. The general effect of the addition of boron is to increase the breaking stress of steel, especially after tempering (compare Moissan and Charpy, *Abstr.*, 1895, ii, 269), but the maximum effect is obtained by the addition of 0.8% of boron to steels of low carbon content. T. A. H.

**Iron-Arsenic Alloys.** K. FRIEDRICH (*Metallurgie*, 1907, 4, 129—137).—Iron alloys containing up to 56% of arsenic have been examined. The freezing point curve falls from the freezing point of iron to a eutectic point at 30% of arsenic and 835°, then rises to a maximum at 40.1% and 919°. Less distinct maxima are indicated at 51.7% of arsenic and 984° and at 57.3% and 1031°, the latter point being obtained by extrapolation of the curve of solidification times. A reaction between the solid products takes place at 800° in all alloys containing from 40% to 56% of arsenic, the maximum development of heat occurring at 47.2%, indicating the formation of  $\text{Fe}_3\text{As}_2$ . The other compounds indicated are  $\text{Fe}_3\text{As}$ ,  $\text{FeAs}$ , and  $\text{Fe}_5\text{As}_4$ , the existence of the last being uncertain. The paper contains eighteen photomicrographs of the alloys, etched by means of a hot solution of iodine in potassium iodide, the results confirming the conclusions drawn from the freezing point curve. The alloys are brittle, especially in the neighbourhood of a maximum. Alloys containing more than 40% of arsenic are not attracted by a magnet. C. H. D.

**Absorption of Nitric Oxide by Solutions of Ferrous, Nickelous, Cobaltous, and Manganous Salts.** GUSTAV VON HÜFNER (*Zeitsch. physikal. Chem.*, 1907, 59, 416—423).—So far as the experiments with ferrous salts go, the author arrives at the same result as that recently recorded by Manchot and Zechentmayer (this vol., ii, 93).

Nickel, cobalt, and manganese salts, provided the metal is in the bivalent condition, also absorb notable quantities of nitric oxide, although this absorption is not accompanied by any change of colour. In these three cases, as in the case of the ferrous salt, the amount of gas absorbed increases with the concentration of the salt solution. The gas must therefore be in some way attached to the metal, and yet the connexion is so loose that, within certain limits of pressure, the absorption is in accordance with Henry's law. J. C. P.

**Ferric Sulphate.** ALBERT RECOURA (*Ann. Chim. Phys.*, 1907, [viii], 9, 263—288).—A résumé of work already published (*Abstr* 1902, ii, 563; 1903, ii, 599, 600; 1905, ii, 527, 590).

M. A. W.

**Some New Double Phosphates of Iron (Ferric) and Aluminium.** LOUIS J. COHEN (*J. Amer. Chem. Soc.*, 1907, 29, 714—721).—In an unpublished paper, Danziger has stated that when a large excess of diammonium hydrogen phosphate is added to a strongly acid solution of ferric chloride, a white precipitate is formed which is probably the double salt,  $(\text{NH}_4)_2\text{H}_2\text{PO}_4 \cdot \text{FePO}_4$ . The existence



of this salt has now been confirmed and its properties are described. When the salt is repeatedly washed with water, it undergoes partial hydrolysis and a brownish-yellow residue is obtained, which contains smaller proportions of phosphorus and ammonia than the original substance. If alcohol is added to an ammoniacal solution of the double salt, a brown, gelatinous *precipitate* is produced of the composition  $2(\text{NH}_4)_2\text{HPO}_4, 3\text{FePO}_4, 3\text{Fe}(\text{OH})_3$ .

A similar *ammonium aluminium phosphate*,  $(\text{NH}_4)_2\text{H}_2\text{PO}_4, \text{AlPO}_4$ , has been prepared which undergoes hydrolysis in the same way as the iron salt. E. G.

**Spontaneous Oxidation of Cobalt Hydroxide Dissolved in an Alkaline Medium.** ANDRE JOB (*Compt. rend.*, 1907, 144, 1044—1047).—When equal volumes of a solution of sodium tartrate (50%), cobalt sulphate (30%), and sodium hydroxide (30%) are mixed, a violet-red solution is obtained, which on exposure to air or oxygen develops a green tint which slowly becomes more intense (compare Durrant, *Trans.*, 1905, 87, 1781). The amount of oxygen absorbed increases indefinitely under these conditions, but if a quantity of glycerol is added, it reaches a maximum, equivalent to one atom of oxygen for each atom of cobalt present. The cobaltic compound formed requires merely the absorption of an atom of oxygen for every two atoms of cobalt present, and it is suggested that the reaction which takes place may be represented by one of the two following sets of equations: (1)  $2\text{CoO} + \text{O}_2 = 2\text{CoO}_2$ ;  $2\text{CoO}_2 + A = \text{Co}_2\text{O}_3 + \text{AO}$ . (2)  $2\text{CoO} + \text{H}_2\text{O} = \text{Co}_2\text{O}_3 + \text{H}_2$ ;  $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$ ;  $\text{H}_2\text{O}_2 + A = \text{AO} + \text{H}_2\text{O}$ , the former being that suggested by Job (*Abstr.*, 1899, ii, 61), Engler (*Abstr.*, 1904, ii, 165), and Baur (*Abstr.*, 1903, ii, 729) in the case of cerium compounds, and the second that proposed by Manchot (*Abstr.*, 1900, i, 300; 1901, ii, 658). In each case, *A* (the acceptor) is an oxidisable compound—tartaric acid in this case. The author prefers the first of these explanations, and in confirmation finds that manganous hydroxide, dissolved in an alkaline solution of a tartrate, passes first into manganese dioxide and finally into the sesquioxide. Both cobaltous and manganous hydroxides under these conditions also absorb nitrosyl, but whereas the manganese solution absorbs oxygen fifty times as quickly as the cobalt solution, the latter absorbs nitrosyl at least ten times as rapidly as the manganese solution. T. A. H.

**Nickel-Arsenic Alloys.** K. FRIEDRICH and F. BENNIGSON (*Metal-lurgie*, 1907, 4, 200—216).—Nickel alloys containing up to 57.4% of arsenic have been studied. The freezing point of iron is lowered by the addition of arsenic until a eutectic point is reached at 900° and 27.8%. The curve then rises to a maximum at 998° and 34.3% of arsenic, corresponding with the compound  $\text{Ni}_5\text{As}_2$ . Another eutectic point is reached at 804° and 43.3%, and the curve then rises to a second maximum at 968° and 56.0%, corresponding with the compound  $\text{NiAs}$ . Solid solutions are formed between the limits 0—5.5% and 33.5—35.7% of arsenic. The compound  $\text{Ni}_5\text{As}_2$ , holding iron in solution, occurs in two modifications. Alloys containing from 35.7% to 56% of arsenic undergo a change at a temperature which could not be

determined accurately owing to supercooling; the maximum development of heat occurs at 45.5% of arsenic, thus indicating the formation of a compound  $\text{Ni}_3\text{As}_2$ . The microscopic structure of the alloys is in accordance with these conclusions.

The alloys are hard, the maximum hardness corresponding with the compound  $\text{Ni}_5\text{As}_2$ . The brittleness is greatest at the points indicated by maxima on the freezing point curve. Alloys containing more than 29% of arsenic are no longer attracted by a magnet.

The paper is illustrated by thirty photo-micrographs. C. H. D.

**Chromic Chloride.** I. NIELS BJERRUM (*Zeitsch. physikal. Chem.*, 1907, 59, 336—383).—Modified methods are described for the preparation of the blue and green chromic chlorides.

The extent of hydrolysis of the blue salt has been determined by two methods, depending respectively on the measurement of the *P.D.* at a hydrogen electrode immersed in the salt solution, and on the measurement of the conductivity at different dilutions. The values of the hydrolysis constant deduced in these two ways agree fairly well and are approximately  $0.9 \times 10^{-4}$  at  $25^\circ$ . The hydrolytic dissociation involved appears to be that expressed by the equation  $\text{CrCl}_3 + \text{H}_2\text{O} = \text{CrCl}_2 \cdot \text{OH} + \text{HCl}$ . The product of hydrolysis  $\text{CrCl}_2 \cdot \text{OH}$  is formed also when one equivalent of sodium hydroxide is added to a solution of the blue chromic chloride; it is soluble in water, green in colour, and undergoes slow transformation. The further addition of sodium hydroxide leads to the precipitation of normal chromium hydroxide, thus:  $\text{CrCl}_2 \cdot \text{OH} + 2\text{NaOH} = \text{Cr}(\text{OH})_3 + 2\text{NaCl}$ . Dilute solutions of the blue chromic chloride become green on warming or on addition of sodium acetate, owing to the formation in considerable quantity of the product of hydrolysis  $\text{CrCl}_2 \cdot \text{OH}$ . If the green solution is immediately cooled again or is acidified with hydrochloric acid before the substance  $\text{CrCl}_2 \cdot \text{OH}$  has had time to undergo change, the blue chromic chloride is reformed.

The hydrolysis constant of the green chromic chloride is found by different methods to have approximately the value  $4 \times 10^{-6}$  at  $25^\circ$ . This green chloride may also be termed dichlorochromium chloride, because only one out of the three chlorine atoms is ionised (compare Werner and Gubser, *Abstr.*, 1901, ii, 453).

In dilute solutions the green chloride is gradually changed into the blue chloride, and the course of the change may be deduced from the conductivity. The observed rate of change can be interpreted only by supposing that there is intermediate formation of a monochlorochromium chloride, and that the change is retarded by acids. The relation between the velocity constants of the reaction and the amount of free acid in the solution has been found by determining the rate of change in hydrochloric acid solutions of different concentrations. It may then be shown that the rate of change of the green chloride in pure water is such as would be expected in view of the hydrochloric acid produced by the hydrolytic dissociation. The negative catalytic effect of acids may be explained by supposing that the products of hydrolysis undergo change more rapidly than the chlorides themselves. It is in harmony with this explanation that the velocity of transforma-

tion has an exceptionally large temperature coefficient; for rise of temperature increases not only the rate of transformation, but also the quantity of the products of hydrolysis. J. C. P.

**Oxidation Reduction Processes. I. Reduction of Chromic Acid.** ROBERT LUTHER and THOMAS F. RUTTER (*Zeitsch. anorg. Chem.* 1907, 54, 1—30. Compare Schiloff, Abstr., 1903, ii, 276; Luther and Schiloff, Abstr., 1904, ii, 244; Manchot, Abstr., 1906, ii, 364, 859).—In continuation of the work on induced reactions (*loc. cit.*), the action of chromic acid on mixtures of hydriodic acid (the "acceptor") and vanadium salts (as "inductors") has now been investigated. The experiments were mainly carried out at 25°, the iodine set free being titrated with thiosulphate.

The rate of reaction between chromic acid and hydriodic acid in dilute solution is considerably accelerated by the presence of bi-, ter-, and quadrivalent vanadium salts, the latter being ultimately oxidised to quinquivalent vanadium. From the results of quantitative measurements of these reactions, it is shown that the "induction factor" for all the vanadium salts is 2; in other words, for one equivalent of vanadium oxidised, two equivalents of iodine are set free. Vanadic acid does not effect the rate of oxidation of hydriodic acid by chromic acid, and only acts comparatively slowly on hydriodic acid, so that the process is not greatly complicated by side reactions.

Some experiments have also been made with uranous sulphate as inductor; the induction factor with a large excess of potassium iodide was 0.74, whilst Manchot (*loc. cit.*) with less of the iodide obtained the values 0.5—0.6. A large number of qualitative experiments have also been made with hydrobromic acid as acceptor. Further, the rate of formation of the double salt of pyridine and chlorochromic acid derived from quinquivalent chromium (Weinland and Friedrich, Abstr., 1906, i, 37) has been qualitatively investigated.

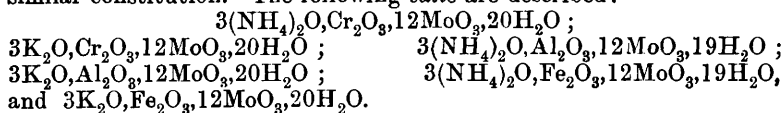
As regards the mechanisms of these reactions, Manchot has suggested that the inductor is oxidised by chromic acid to a peroxide which is then reduced by the acceptor, whilst in the present paper it is contended that the inductor reduces chromic acid to quinquivalent chromium, which is a more rapid oxidising agent than the acid itself. In favour of the latter view, it is shown from the quantitative results that whereas Manchot's theory requires the formation of intermediate peroxides of very diverse formulæ, the assumption of the intermediate formation of quinquivalent chromium alone accounts for nearly all the reactions so far investigated.

On the basis of the above and other evidence, it is suggested that the reduction of chromic acid proceeds in the following stages  $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$ , and that chromic acid contains sexavalent and not quadrivalent chromium as Manchot has recently suggested.

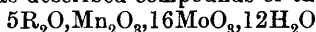
G. S.

**Compounds of the Sesquioxides with the Acid Molybdates.** ROY D. HALL (*J. Amer. Chem. Soc.*, 1907, 29, 692—714).—Ammonium and potassium chromico-molybdates and aluminico-molybdates (Struve, *J. pr. Chem.*, 1854, 61, 449) have been prepared together with a series of salts derived from them by double decomposition. The chromico-

molybdates have been studied with the object of ascertaining whether the alkali salts are double salts or derivatives of a complex acid containing  $\text{Cr}_2\text{O}_3$  and  $\text{MoO}_3$ , and the results indicate that the latter assumption is correct. The alkali ferrico-molybdates doubtless have a similar constitution. The following *salts* are described:



Struve (*loc. cit.*) has described compounds of the type



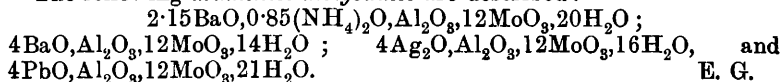
(compare Péchard, *Abstr.*, 1897, ii, 498; Rosenheim and Itzig, *Abstr.*, 1898, ii, 164, and Friedheim and Samelson, *Abstr.*, 1900, ii, 547). Some of this work has been repeated, and the conclusions have been reached that the salts obtained from potassium molybdate and manganese sulphate in presence of bromine or potassium permanganate are of only one type, namely,  $3\text{K}_2\text{O}, \text{Mn}_2\text{O}_3, 9\text{MoO}_3$ , and that in those salts which contain more manganese than  $1\text{MnO}$  for one atom of active oxygen, the excess of manganese replaces potassium, and is itself replaceable by barium. The following *salts* have been prepared:  $3\text{K}_2\text{O}, \text{Mn}_2\text{O}_3, 9\text{MoO}_3, 6\text{H}_2\text{O}$ ;  $2\cdot6\text{K}_2\text{O}, 0\cdot4\text{MnO}, \text{Mn}_2\text{O}_3, 9\text{MoO}_3, 7\text{H}_2\text{O}$ ;  $3\text{BaO}, \text{Mn}_2\text{O}_3, 9\text{MoO}_3, 12\text{H}_2\text{O}$ ;  $3\text{Ag}_2\text{O}, \text{Mn}_2\text{O}_3, 9\text{MoO}_3, 6\text{H}_2\text{O}$ .

The following *salts* containing nickel or cobalt have been prepared and analysed:  $5\text{K}_2\text{O}, 3\text{NiO}, 16\text{MoO}_3, 21\text{H}_2\text{O}$ ;  $3\text{K}_2\text{O}, \text{NiO}, 9\text{MoO}_3, 6\frac{1}{2}\text{H}_2\text{O}$ ;  $5(\text{NH}_4)_2\text{O}, 3\text{NiO}, 16\text{MoO}_3, 16\text{H}_2\text{O}$ ;  $3\text{BaO}, \text{NiO}, 9\text{MoO}_3, 12\text{H}_2\text{O}$ , and  $3\text{K}_2\text{O}, \text{CoO}, 9\text{MoO}_3, 6\frac{1}{2}\text{H}_2\text{O}$ .

The following *compounds* were obtained by adding solutions of salts to a solution of potassium chromico-molybdate:  $2\text{Fe}_2\text{O}_3, 7\text{MoO}_3, 34\text{H}_2\text{O}$ ;  $2\cdot15\text{BaO}, 0\cdot85\text{K}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 20\text{H}_2\text{O}$ ;  $4\text{BaO}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 15\text{H}_2\text{O}$ ;  $4\text{BaO}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 18\text{H}_2\text{O}$ ;  $5\text{BaO}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 16\text{H}_2\text{O}$ ;  $4\text{PbO}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 24\text{H}_2\text{O}$ ;  $4\text{PbO}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 22\text{H}_2\text{O}$ ;  $2\cdot25\text{Ag}_2\text{O}, 0\cdot75\text{K}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 18\text{H}_2\text{O}$ ;  $5\text{Ag}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 17\text{H}_2\text{O}$ ;  $8\text{Hg}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 16\text{H}_2\text{O}$ ;  $22\text{BaO}, (\text{NH}_4)_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 20\text{H}_2\text{O}$ .

*Chromico-molybdic acid*,  $\text{Cr}_2\text{O}_3, 12\text{MoO}_3, 28\text{H}_2\text{O}$ , was obtained as a green powder. On crystallising the salt,  $3\text{K}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3$ , from solutions containing varying quantities of potassium hydroxide, the following *compounds* were produced:  $7\text{K}_2\text{O}, 2\text{Cr}_2\text{O}_3, 24\text{MoO}_3, 32\text{H}_2\text{O}$ ;  $4\text{K}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 15\text{H}_2\text{O}$ ;  $4\text{K}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 20\text{H}_2\text{O}$ . Potassium chromico-molybdate,  $3\text{K}_2\text{O}, \text{Cr}_2\text{O}_3, 12\text{MoO}_3, 15\text{H}_2\text{O}$ , does not undergo any change on dialysis.

The following *aluminico-molybdates* are described:



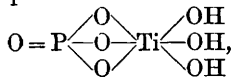
**Complex Formation in Molybdic Acid Solutions.** HERMANN GROSSMANN (*Zeitsch. anorg. Chem.*, 1907, 40—44).—Rimbach and Neizert (this vol., ii, 269) assume that since the conductivity of mixtures of molybdic acid and certain organic acids is smaller than the calculated value, no complex compounds are formed, but the author shows, from the results of previous investigations by himself

(compare Grossmann and Krämer, Abstr., 1903, i, 549) and others, that this does not always hold. Mixtures of oxalic and molybdic acids have a conductivity lower than the calculated value, but both solubility and ionic velocity measurements indicate that the acids are partially combined in solution. Further, since molybdic acid has a very high molecular weight in solution, the results of conductivity measurements are somewhat difficult to interpret. When practicable, the results of conductivity measurements should be controlled by solubility and other determinations. G. S.

**Preparation of Uranous Salts.** JULES ALOY and AUBER (*Bull. Soc. chim.*, 1907, [iv], 1, 569—571).—Crystallised uranous sulphate,  $U(SO_4)_2 \cdot 4H_2O$ , may be obtained by adding sodium hyposulphite to a solution of uranic sulphate until a precipitate begins to form. On addition of alcohol, a mixture of the two sulphates is precipitated from which the uranic salt may be eliminated by washing with a mixture of alcohol and water. The residue is then dissolved in dilute sulphuric acid and evaporated at a low temperature until crystals begin to separate. The oxalate, arsenate, or phosphate may be prepared by analogous methods, or by double decomposition from uranous sulphate. The presence of uranic in uranous salts may be revealed by the fluorescence they exhibit when their solutions are illuminated by an arc light. T. A. H.

**Nature of Sexavalent Titanium.** PAUL FABER (*Zeitsch. anal. Chem.*, 1907, 46, 277—291).—Pertitanic acid behaves like hydrogen peroxide, but is not quite so energetic. In presence of organic reducing agents, such as formic or oxalic acid, hydrogen peroxide cannot be detected by the chromic acid—ether reaction, but is shown readily by the titanic acid test. The conversion of the quadrivalent titanium into the sexavalent state is due to a combination with the hydroxyl groups of the hydrogen peroxide. There exists an acetate of the sexavalent titanium which is stable at low temperatures. It has a yellow colour and is insoluble in acetic acid, but soluble in mineral acids and also in alkalis and ammonia. On heating, it shows decidedly explosive properties.

There also exists a phosphate of sexavalent titanium,



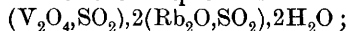
which is stable at low temperatures. It is insoluble in acetic acid, but soluble in mineral acids, alkalis, and ammonia. L. DE K.

**Observations on Mixtures of Thorium and Cerium.** RICHARD J. MEYER and ARNOLD ANSCHÜTZ (*Ber.*, 1907, 40, 2639—2647).—Although the theory of the light emission of the Auer mantle from the physical standpoint has been carefully worked out by Le Chatelier and Boudouard, Nernst and Bose, and by Rubens, the chemistry has been overlooked. The authors show that there is no loss in weight when thorium dioxide and cerium dioxide are heated together, such as would have occurred if basic cerium sesquioxide were formed. If, however, the “active” oxygen in the

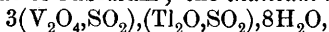
mixture be determined by distillation with potassium iodide and hydrochloric acid, it is found that under all conditions only a certain portion of the cerium dioxide reacts with the potassium iodide; the conclusion is drawn from a series of thirteen experiments that 100 parts of thorium dioxide dissolve 6—7 parts of cerium dioxide and that in such a solid solution the cerium dioxide has lost its power of oxidation. As the Welsbach mixture contains 1% of  $\text{CeO}_2$ , it is all dissolved by the  $\text{ThO}_2$ . The saturation point depends on the temperature employed; at  $500^\circ$ , 3.3, at  $650^\circ$ , 7.6, and at  $1000^\circ$ , 7.2 parts of  $\text{CeO}_2$  are dissolved by the  $\text{ThO}_2$ . When cerium nitrate is heated at  $500^\circ$ , the product obtained is not pure cerium dioxide, but always contains more oxygen than is required by the formula  $\text{CeO}_2$ ; in one case it approximated to  $\text{CeO}_3$ . These results explain the non-additive physical characteristics of the Welsbach mixture.

W. R.

**Some Double Sulphites of Hypovanadic Acid.** GUSTAVE GAIN (*Compt. rend.*, 1907, 144, 1157—1159).—The alkali bases, in the presence of sulphurous acid, combine easily with hypovanadic acid, giving well-defined double sulphites. The latter are prepared by mixing the blue solution (this vol., ii, 32), obtained by treating ammonium metavanadate with a saturated solution of sulphurous acid, with a solution of the alkali hydrogen sulphite and slowly evaporating the product at a low temperature or in a vacuum. The *potassium* double sulphite forms blue crystals having a composition corresponding with the formula  $3(\text{V}_2\text{O}_4, \text{SO}_2), (\text{K}_2\text{O}, \text{SO}_2), 5\text{H}_2\text{O}$ . The *ammonium* salt,  $3(\text{V}_2\text{O}_4, \text{SO}_2), (\text{NH}_4)_2\text{O}, \text{SO}_2, 4\text{H}_2\text{O}$ , forms brilliant, black, elongated crystals; the *rubidium* salt, slender needles drying to a grey, crystalline powder of the composition



the *caesium* salt,  $(\text{V}_2\text{O}_4, \text{SO}_2), 3(\text{Cs}_2\text{O}, \text{SO}_2), 8\text{H}_2\text{O}$ , a crystalline powder exactly similar to that of rubidium; the *thallium* salt,



very brilliant, bluish-green crystals with a reddish-brown reflex; the *sodium* salt,  $(5\text{V}_2\text{O}_4, \text{SO}_2), (\text{Na}_2\text{O}, \text{SO}_2), 2\text{H}_2\text{O}$ , black crystals, and the *lithium* salt,  $(\text{V}_2\text{O}_4, \text{SO}_2), 5(\text{Li}_2\text{O}, \text{SO}_2), 8\text{H}_2\text{O}$ , a clear blue, microcrystalline crust.

E. H.

**Double Decomposition between Gold Chloride and Formaldehyde in Presence of Sodium Hydroxide.** LUDWIG VANINO and F. HARTL (*Chem. Zentr.*, 1907, i, 1099; from *Zeitsch. Chem. Ind. Kolloide*, 1, 272—274. Compare Vanino, *Abstr.*, 1898, ii, 545; 1904, i, 13).—Gold is precipitated quantitatively from a solution containing aurichloric acid (2 mols.), sodium hydroxide (5 mols.), and formaldehyde (3 mols.), or after neutralising with sodium hydroxide; the precipitation is even better when the solution contains sodium aurichloride (2 mols.), sodium hydroxide (9 mols.), and formaldehyde (3 mols.). If the liquid is not vigorously stirred, some colloidal gold remains in solution, and, in order to prevent the formation of a gold mirror, care should be taken that the sides of the vessel are not rubbed. The precipitate is dried at  $105^\circ$ . The results agree with those obtained

by the hydrogen peroxide and sodium hydroxide method (Abstr., 1899, ii, 578).

When the molecular proportions of sodium aurichloride, sodium hydroxide, and formaldehyde are 2 : 6 : 3, the precipitation is incomplete even when the mixture is heated ; a large excess of formaldehyde and sodium hydroxide entirely prevent precipitation. Hydrogen is not evolved. By the action of potassium hydroxide or sodium hydroxide purified by alcohol, colloidal solutions of gold, which are dark green, deep violet, indigo blue, or of the colour of potassium permanganate, are formed.

E. W. W.

**Catalytic Actions of Colloidal Metals of the Platinum Group. I.** CARL PAAL and CONRAD AMBERGER (*Ber.*, 1907, 40, 2201—2208).—The authors have studied the catalytic action on the decomposition of hydrogen peroxide of the colloidal platinum, palladium, iridium, and osmium prepared by methods already described (Abstr., 1904, ii, 180 ; 1905, ii, 397 ; this vol., ii, 360). The acceleration of the decomposition of the peroxide is most marked with osmium ; then come palladium, platinum, and, finally, iridium. The results are contrasted with those obtained by Bredig, whose colloidal metals were prepared by other methods than those of the authors.

The colloidal solutions used were treated with hydrogen, and then had a much greater catalytic effect than when that treatment was not adopted.

A. McK.

**Catalytic Actions of Colloidal Metals of the Platinum Group. II.** CARL PAAL and JOSEF GERUM (*Ber.*, 1907, 40, 2209—2220. Compare preceding abstract).—The stability of colloidal palladium, both in the liquid and in the solid form, and the possibility of heating its concentrated solution at temperatures up to 100° for a considerable time without the formation of the hydroxyl form render this colloid particularly suitable for reduction experiments.

Paal and Amberger had previously shown (Abstr., 1905, ii, 397, 533) that aniline is formed when a current of hydrogen is passed through an aqueous-alcoholic solution of nitrobenzene to which a small amount of palladium hydrosol had been added. These experiments have now been extended and the influence of temperature on the reduction examined. The influence of the amount of the catalyst and the time, during which the reduction was effected, were also studied. A curious result was obtained with a specimen of colloidal palladium which had been kept for more than three years and had not been treated with hydrogen previously to use for reduction. Although this specimen had undergone partial oxidation in the course of these years, it exerted the strongest catalytic action of any of the specimens examined. The effect of treating the colloidal platinum with specially purified hydrogen before using it in the reduction experiments was marked in several cases.

The catalytic action of platinum hydrosol is not so marked as that of palladium hydrosol ; the experiments were conducted both at the ordinary temperature and at 65—80°.

Colloidal iridium gave varying results according to its method of

preparation, as did also the varying specimens of colloidal palladium and platinum examined.

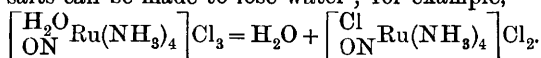
Nitrobenzene apparently was not reduced by the aid of colloidal copper and colloidal gold under similar conditions to those obtaining in the preceding experiments. Colloidal silver and colloidal osmium were found, however, to have a very slight influence on the reduction.

A. McK.

**Theory of Hydrolysis. III. Ammonioruthenium Compounds.** ALFRED WERNER (*Ber.*, 1907, 40, 2614—2628).—The potassium analogue of Joly's ammonium nitrosopentachlororuthenate,

$\left[ \text{Ru}^{\text{NO}}_{\text{Cl}_5} \right] (\text{NH}_4)_2$  (compare Abstr., 1889, 948), is obtained most conveniently by evaporating ruthenium chloride twice with concentrated nitric acid, dissolving the residue in hydrochloric acid, and precipitating the solution with potassium chloride, whereby reddish-blue crystals of potassium nitrosopentachlororuthenate are obtained. By treating the solution of this potassium compound with ammonium hydroxide, and, after heating on the water-bath, with potassium bromide or hydrobromic acid, a yellow precipitate of a *bromide* is obtained. This salt and others of the same series are classified by the author as hydroxo-nitrosotetra-ammineruthenium salts,  $\left[ \text{HO} \text{Ru}(\text{NH}_3)_4 \right]_{\text{ON}} \text{X}_2$ ; in addition to the bromide, the *chloride*, *iodide*, and *nitrate* have been prepared. These salts are light yellow, crystalline substances, which have a neutral reaction in aqueous solution; in the haloid salts all the halogen is in an ionisable state. The neutral character of these salts indicates that the hydroxyl group attached to the ruthenium atom has a much smaller tendency to combine with hydrogen ions than is the case with the hydroxyl group in other hydroxometalammonia compounds, but that this tendency still exists is proved by the increased solubility of hydroxonitrosotetra-ammineruthenium salts in acidified water; from such solutions, nitrosoaquotetra-ammineruthenium salts are obtained in accordance with the equation:  $\left[ \text{HO} \text{Ru}(\text{NH}_3)_4 \right]_{\text{ON}} \text{X}_2 + \text{HX} = \left[ \text{H}_2\text{O} \text{Ru}(\text{NH}_3)_4 \right]_{\text{ON}} \text{X}_3$  (compare also Joly, Abstr., 1891, 401). These salts, of which the *chloride*, *bromide*, *nitrate*, and *sulphate* are described, form intensely coloured reddish-yellow crystals, and are hydrolysed by water or alcohol with extraordinary ease, the hydroxonitroso-salts being regenerated. Aqueous solutions of these aquo-salts consequently exhibit a strongly acid reaction, and by the addition of potassium bromide or iodide, or of hydrogen platinoso-chloride, yield precipitates of the neutral hydroxo-salts.

Like all aquometalammonia salts, the nitrosoaquotetra-ammineruthenium salts can be made to lose water; for example,



This *chloronitrosotetra-ammineruthenium chloride*, in which one-third of the halogen is not in an ionisable state, is obtained by heating hydroxo-nitrosotetra-ammineruthenium bromide with hydrochloric acid; it forms



slender, orange-red crystals, and from it the corresponding *iodide* and *nitrate* have been prepared. The similarly constituted *bromonitroso-tetra-ammineruthenium bromide*,  $\left[ \begin{smallmatrix} \text{Br} \\ \text{ON} \end{smallmatrix} \text{Ru}(\text{NH}_3)_4 \right] \text{Br}_2$ , is prepared by heating nitrosoaquotetra-ammineruthenium bromide with an excess of hydrobromic acid; it forms very sparingly soluble, orange-red crystals, and from it the corresponding *iodide*, *nitrate*, and *sulphate* have been obtained.

C. S.

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## Mineralogical Chemistry.

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**Inclusions of Liquid Carbon Dioxide in Calcite from Traversella.** GIORGIO SPEZIA (*Atti R. Accad. Sci. Torino*, 1907, 42, 409—417).—Certain samples of calcite, found in Traversella, contain liquid inclusions, and become ruptured when warmed by the hand. That these inclusions consist of liquid carbon dioxide is shown by an approximate microscopic measurement of their contraction on cooling, and by the action on lime-water of the gas evolved on heating the crystals. Liquid carbon dioxide appears to occur only in calcite crystals enclosed in gangue or massive rocks, and not in crystals found in non-enclosed, drusy masses. T. H. P.

**Pyrargyrite from the Pervoblagodatsk Mine in the Urals.** G. CASPEROWICZ (*Bull. Acad. Imp. Sci. St. Petersburg*, 1907, 171—173). The author describes a sample of pyrargyrite, either mechanically mixed with a small quantity of proustite or containing the latter in isomorphous mixture. T. H. P.

**Stolpenite from the Rhone.** A FERSMANN (*Bull. Acad. Imp. Sci. St. Petersburg*, 1907, 168—169).—The author describes a pale, rose-coloured, moderately-soft mineral found between the basalt columns of Roth near Nordheim or, with a concentric scaly structure, within the bubble-spaces of tufa. It decrepitates vigorously in water, melts to a white enamel in the blowpipe flame, and is readily decomposed, with separation of silica, by sulphuric acid. In dry air, it gradually loses a portion of its water. Analysis gave :

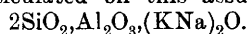
H <sub>2</sub> O (below 110°).	H <sub>2</sub> O (above 110°).	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Total.
16·81	8·94	48·54	19·38	0·20	1·07	5·29	Traces	100·23

These results indicate that the mineral belongs to the Montmorillonite group, and that it is mixed with an unknown magnesium silicate. It approximates most nearly to stolpenite, which it resembles both in physico-chemical characters and in genetic relations ; stolpenite, however, contains lime instead of magnesia. T. H. P.

**Nepheline Bed on the White Sea.** EUGRAPH S. VON FEDOROFF (*Chem. Zentr.*, 1907, i, 1217; from *Bull. Acad. St. Petersburg*, 1906, [v], 23, 149—152).—The nepheline beds of the Turjin peninsula, which lies in the middle portion of the S. coast of the Kola peninsula, have already been described (*Gorny J.*, 1904). The purified material has D 2·914. The following analyses were made by A. Kupffer:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	CaO.	MgO.	Cl.	Pleonast.	Fe <sub>2</sub> O <sub>3</sub> .	Ignit. Loss.
I.	39·72	33·77	15·62	6·89	1·27	1·73	0·12	0·17	0·55	0·80	—
II.	39·53	33·26	15·76	6·82	1·48	1·32	0·22	—	0·34	1·12	0·34

The presence of phosphoric acid shows that apatite is present; the formula of nepheline calculated on this assumption is



E. W. W.

## Physiological Chemistry.

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**Modifications of Blood-pressure in Birds by Drugs.** OSCAR RIDDLE and SAMUEL A. MATTHEWS (*Amer. J. Physiol.*, 1907, 19, 108—116).—The blood-pressure of birds is practically the same as in mammals, and is affected by drugs in the same way. The presence in the blood of digitalis or barium chloride aids the nutrition of the superficial structures and their use is recommended to ostrich farmers. The presence of amyl nitrite, magnesium sulphate, or ergot interferes with the nutrition of the skin and its appendages. W. D. H.

**Conductivity of Blood in Coagulation.** THOMAS M. WILSON (*Bio-Chem. J.*, 1907, 2, 377—382).—Doubt is cast on Bayliss' observation (*Abstr.*, 1906, ii, 346) that the conductivity of blood falls during clotting. It is suggested that this diminution is due to sedimentation of the corpuscles. W. D. H.

**A Clinical Method for Determining the Alkalinity of the Blood.** HERMANN M. ADLER (*Amer. J. Physiol.*, 1907, 19, 1—4).—Slight variations in hydrogen and hydroxyl ionisation, heretofore detected only by the aid of the concentration cell, can be determined by the aid of properly chosen indicators. The indicator mainly used in the present experiments is rosolic acid paper. This is orange-yellow in acid, pink in neutral and red in alkaline media. It is yellow at  $1 \cdot 10^{-6}n.H$ , pink at  $1 \cdot 10^{-7}n.H$ , and red at  $1 \cdot 10^{-8}n.H$ . The blood is removed in small quantity (1 c.c. is enough), diluted with salt solution, and a little sodium fluoride to prevent clotting added. It is then centrifugalised and the colour of the paper dipped into the supernatant fluid noted. W. D. H.

**Sugar of the Blood.** RAPHAEL LEFINE and BOULUD (*Compt. rend.*, 1907, 144, 1014—1016).—The addition of water, emulsin, and especially invertin to defibrinated blood increases the amount of dextrose

it contains, provided glycolysis has been stopped by raising the temperature previously to 58°. The quantity of sugar thus liberated from glucosides may amount to 0.04%. Usually the liberation of sugar is completed in fifteen minutes. Addition of fibrin to normal arterial defibrinated blood has a similar, but less marked, effect; but if venous blood or the blood in certain pathological conditions is used, the effect of fibrin is the opposite. These facts indicate the many difficulties attending the estimation of sugar in the blood. The glycolytic action may be inhibited by receiving the blood into a solution of sodium acetate; at the same time, this salt assists the liberation of sugar.

W. D. H.

**The Source of Uric Acid in the Blood in Gout.** BRUNO BLOCH (*Zeitsch. physiol. Chem.*, 1907, 51, 472—477).—In gout, there are alterations in both endogenous and exogenous uric acid metabolism. The exogenous uric acid is in part retained in the body, and in part more slowly and irregularly excreted than in health; retention may lead to a typical attack of gout. The endogenous uric acid excretion is usually smaller and more irregular than in health, especially during an attack. The excess of the acid in the blood is of endogenous origin. In gout there is evidently a lessening of these ferment processes, which naturally lead to destruction of uric acid.

W. D. H.

**Inhibitory Action of Potassium Salts on the Heart.** H. BUSQUET and V. PACHON (*Compt. rend.*, 1907, 144, 1065—1067). Potassium salts exercise an inhibitory action on cardiac activity, but the effect varies with different salts even when employed in the same molecular concentration. The salts may be arranged in a scale of toxicity, which is in direct relation to that of their electrolytic dissociation.

W. D. H.

**Is the Saliva of the Dog Amylolytically Active?** LAFAYETTE B. MENDEL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1907, 3, 135—143).—As a rule, the answer to the question is in the negative. No evidence of the adaptation of the salivary glands to diet was discoverable.

W. D. H.

**Digestion in the Animal Body. IX.** E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 51, 468—471. Compare Abstr., 1905, ii, 730, 838; 1906, ii, 464; 1907, ii, 107, 108, 367).—Technical details for the performance of Eck's operation.

W. D. H.

**The Digestion of Egg-white by Papain.** FRITZ SACHS (*Zeitsch. physiol. Chem.*, 1907, 51, 488—505).—The main point investigated is the influence of reaction at different temperatures on papain-digestion. The chief result is the inhibiting influence of alkali at incubator temperature; but in the cold, digestion is brisker if the reaction is neutral or alkaline than if it is acid.

W. D. H.

**Assimilation of Elastoses.** L. BORCHARDT (*Zeitsch. physiol. Chem.*, 1907, 51, 506—518).—The method of enteral and parenteral

administration of protein material is valuable in investigations on protein metabolism. If hemi-elastin is injected intravenously, it can be detected in the organs three hours later, and is especially abundant in the wall of the small intestine. If given with the food, it can be detected in the blood and certain organs at the height of digestion in traces in an unchanged condition. This is considered to prove that albumoses contained in food pass as such into the blood. W. D. H.

**Nuclein Metabolism.** ALFRED SCHITTENHELM (*Chem. Zentr.*, 1907, i, 979—980; from *Arch. Klin. Med.*, 89, 267—276).—Xanthine and hypoxanthine are regarded as links between the aminopurines and uric acids. But whether they are only products of intermediary metabolism or are integral portions (Bausteine) of the animal organism is not yet certain. From the examination of a large number of organs, it was found that adenine and guanine are present in much greater amount than the two oxypurines; the aminopurines are therefore regarded as "Bausteine," the oxypurines as products of further metabolism. The same holds good for vegetable structures. The part played by these substances in building up the nucleus of cells, the amount of cleavage of nuclein material during digestion, and the destruction by certain organs of uric acid after it is formed, are the questions which are discussed. Uric acid was not found in the fæces even in leucæmia, where the amount of purine bases is increased. Uric acid is, however, found in meconium and the amniotic fluid. The chief origin of purine substances in the fæces is probably epithelial and other debris, bacteria, &c. W. D. H.

**Human Pancreatic Juice.** IV. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1907, 4, 271—280).—Delezenne (*Compt. rend. Sci. Biol.*, 1904, 55, 171) stated that dog's pancreatic juice has no hæmolytic power until it is activated by intestinal juice. It is now found, however, that human pancreatic juice has hæmolytic properties; this is the first time the occurrence of an auto-hæmolysin has been proved to exist in man. The part it plays in health and disease is still unknown. The hæmolytic action is probably related to the lipolytic action of the juice, and both are increased by the addition of lecithin. The presence of lecithin increases the hæmolysis twenty-fold, and it is suggested that the agent is a pro-lecithid similar to that found in cobra poison (Kyes, Ehrlich) and in bee poison (Morgenroth and Carpi, this vol., ii, 286). As in these cases, manganese sulphate acts also as an activator. The toxo-lecithid is insoluble in ether, easily soluble in water and in alcohol, is resistant to heat, and produces complete hæmolysis almost instantaneously. Proteolysis, as well as lipolysis, comes into play. W. D. H.

**The Cæcum of Herbivora.** W. USTJANZEFF (*Biochem. Zeitsch.*, 1907, 4, 154—171).—The conclusion drawn from the experiments on feeding, &c., recorded is that in rabbits, the cæcum is a specific organ for the digestion and absorption of cellulose and pentosans.

W. D. H.

**Osmotic Stimulation of Unfertilised Sea Urchin Eggs.** JACQUES LOEB (*Pflüger's Archiv*, 1907, 118, 181—204).—Alkalinity (concentration of hydroxyl ions) is a factor to be considered in addition to changes in osmotic pressure in promoting changes in unfertilised eggs. In low concentration,  $C_{HO} < 10^{-6}$ , no amount of elevation of the osmotic pressure will cause unfertilised eggs to develop. In higher concentrations ( $4 \cdot 10^{-3}$ ), a relatively small elevation of the pressure will produce formation of larvæ. Purely osmotic treatment of the developing eggs usually produces the formation of a membrane thicker than usual. The necessity for free oxygen and the importance of oxidation changes in the eggs are again insisted upon. W. D. H.

**Glucothionic Acid in Leucocytes.** JOHN H. MANDEL and PHÆBUS A. LEVENE (*Biochem. Zeitsch.*, 1907, 4, 78—79).—Whether the glucothionic acid obtained from various tissues and organs is derived wholly from the connective tissue is uncertain. Pus, which was obtained in large amount from pyothorax artificially produced in horses, was therefore examined as material completely free from connective tissue elements. The question was also of interest because pus formation, as is well known, leads to amyloid degeneration, and amyloid is a derivative of glucothionic acid. Further, according to some, the granules in leucocytes which give the glycogen reaction with iodine are regarded as being of mucoid nature. The outcome of the investigation was that glucothionic acid was proved to be present. W. D. H.

**Formation of Glycogen in the Liver.** KARL GRUBE (*Pflüger's Archiv*, 1907, 118, 1—29).—The experiments were performed on tortoises; the general course of metabolism is slower in these animals than in warm-blooded animals, but is not on main points qualitatively different. Perfusion with Ringer's solution produces either no change in the amount of glycogen, or a slight fall. Various substances were then added to the perfusing liquid, and estimations of glycogen made in one lobe of the liver before, and in another after, the perfusion. The following substances caused an increase in the glycogen: dextrose (an increase of 53 to 1,000% in different experiments); lævulose (50 to 85%); galactose (5 to 52%); glycerol (38 to 118%). The following substances caused no increase in the hepatic glycogen: lactose, sucrose, arabinose, the carbohydrate free protein caseinogen, and optically active and inactive amino-acids (glycine, alanine, leucine). W. D. H.

**Behaviour of Uric Acid towards Animal Extracts and Alkalis.** PHILIP H. MITCHELL (*J. Biol. Chem.*, 1907, 3, 145—149). Uric acid is not destroyed by extracts of embryo pigs' livers, but it is destroyed if extracts of liver from the adult pig are used; this action is removed by boiling the extract. The destruction is thus probably due to ferment action, as most previous writers have considered to be the case, and the present experiments dispose of Austin's criticism

(*J. Med. Research*, 1906, 15, 309) that the destruction may be wholly or in part produced by the alkali used for obtaining a solution of uric acid.

W. D. H.

**Choline, the Substance in the Suprarenal Bodies which Lowers Blood-pressure.** ALFRED LOHMANN (*Pflüger's Archiv*, 1907, 118, 215—227).—Many previous observers have noted that in addition to adrenaline, suprarenal extracts contain an antagonistic substance which lowers blood-pressure. In the present research, this was separated out as the gold salt, and it was proved that its composition and physiological action are identical with those of choline.

W. D. H.

**Heat Rigor in Vertebrate Muscle.** C. H. VROOMAN (*Bio-Chem. J.*, 1907, 2, 363—367).—Both striped and unstriped muscle show, on being subjected to rising temperature, two shortenings only; the first in mammals is at 47°, and in frogs at 40°; the second occurs at 62° and 50° respectively. If the muscle has already passed into rigor mortis, the first is absent. The protein present in the living muscle is considered to be a single one, and the first shortening is due to its coagulation by heat. The second shortening is regarded as being due to the action of a more elevated temperature on the connective tissue elements.

W. D. H.

**Lecithin in Bone-Marrow.** W. GLIKEN (*Biochem. Zeitsch.*, 1907, 4, 235—243).—Estimations of the fat and lecithin in the bone-marrow of different animals, including man, are given. The amount of lecithin is deduced from the phosphorus content of the ethereal extract. The amount of lecithin in the fat averages 2—4%. In horses, it is lower (1.45%); in general, its amount diminishes with age. The highest numbers were obtained in very young pigs (28—47%).

W. D. H.

**Properties of the Pigments from Batrachians.** A. MAGNAN (*Compt. rend.*, 1907, 144, 1130—1132).—Green, yellow, brownish-yellow, red, and black pigments have been obtained from the skins of Batrachians. Their solubilities and reactions with various reagents are described.

E. H.

**Spiders' Silk.** EMIL FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 440—450).—An investigation of the silk-like web of *Nephila madagascariensis*, a large spider found in the woods of Madagascar. The silk of this spider is found to differ chiefly from ordinary silk in that it contains only about 3% of substances soluble in water. It is, like silk fibroin, soluble in strong hydrochloric acid, and gives on the addition of alcohol a product similar in properties to sericoin (Weyl, *Abstr.*, 1888, 857). The dried spiders' silk when hydrolysed with acids yields: glycine, 35.13%, *D*-alanine, 23.4%, *L*-leucine, 1.76%, *L*-tyrosine, 8.2%, proline, 3.68%, *D*-glutamic acid, 6.1%, diamino-acids, 5.24% (calculated as arginine), ammonia, 1.16%, and fatty acids, 0.66%; that is, it contains the first four compounds to about the same extent as



ordinary silk, slightly more proline and diamino-acids, whilst, what is most remarkable, it contains large quantities of glutamic acid, the presence of which in ordinary silk has not yet been observed. Spiders' silk differs also from ordinary silk in that it appears to contain neither serine nor  $\alpha$ -anilinopropionic acid. The fact that the secretions of organs of such great morphological difference, as the spinning-pap of a spider and the glands of a silkworm, are so similar chemically, is one of great biological importance.

W. H. G.

### Relations between Fishes and their Surrounding Medium.

FRANCIS B. SUMNER (*Amer. J. Physiol.*, 1907, 19, 61—96).—There are seasonal differences in the osmotic phenomena displayed by certain fishes, but whether these depend on temperature or variations in the physiological conditions of the fishes is uncertain. In winter, dilution of the sea-water without injury can be carried to an extreme degree; 1% of sea water in ordinary fresh water will keep them normal; pure fresh water is always fatal within a few days. Sucrose added to the same extent did not prevent the fatal issue, although sugar itself, if sea water is present, does no harm. Pure sodium chloride in distilled water keeps the fishes alive for a long time. It is therefore this salt which the fish chiefly miss. The relative toxicity of various poisons was studied; these usually are more fatal in fresh than in sea water. The amount of salt in the fishes' bodies undergoes considerable changes in response to changes in the water. So far as osmosis and diffusion play any part, it is the gills which are chiefly affected.

W. D. H.

### Fluorine in the Shells of Non-marine Molluscs.

P. CARLES (*Compt. rend.*, 1907, 144, 1240. Compare this vol., ii, 282).—The author finds that the shells of mussels from Tarn (from fresh running water) contain 3—4 mg. of fluorine per 100 grams, lymnées and planorbes (fresh, stagnant water), 2—3 mg. per 100 grams, and snails (living in air), 2—3 mg. per 100 grams. The conclusions drawn are: (1) that non-marine mollusc shells contain alkaline earth fluorides, although in much smaller amount than do the marine shells; (2) that fluorine is more widely distributed in river and marsh waters than was previously supposed; (3) that fluorine exists in the leaves on which snails live, and (4) that alkaline earth fluorides appear to be a general agent of the formation and consolidation of the skeleton of all animals.

E. H.

**Manganese, a Normal Element in the Tissues of the Fresh Water Clams, Unio, and Anodonta.** HAROLD C. BRADLEY (*J. Biol. Chem.*, 1907, 3, 151—157).—The amount of manganese present varies from 0.6—1.2%. It is also present in the eggs. Further investigation is promised regarding the source of the metal and its physiological function.

W. D. H.

### Milk-Serum.

E. LANDOLF (*Biochem. Zeitsch.*, 1907, 4, 172—195).

In addition to its well known constituents, the fluid part of milk contains a carbohydrate, *lactosin*, which is optically inactive, does not

ferment with yeast, and is active in reducing Fehling's solution. During the menstrual period in women, another reducing substance is found which is nitrogenous and termed *azolactin*; on acid hydrolysis it yields *azolactosin*; this is dextrorotatory, but not fermentable; *lactoglucose* is a third carbohydrate which is fermentable. The methods employed and typical analyses are given in full.

W. D. H.

**Ammonia in Milk.** HENRY C. SHERMAN, W. N. BERG, L. J. COHEN, and W. G. WHITMAN (*J. Biol. Chem.*, 1907, 3, 171—175).—Analysis of samples of New York milk gave an average of 0.0004% of preformed ammonia, and an additional 0.0003% of "cleavage" ammonia. When milk becomes stale, both usually increase. Addition of 3% of chloroform or 0.1% of formaldehyde retards, but does not stop, the proteolysis which results in the formation of cleavage ammonia. The greater the freedom from contamination, the less apparent is the influence of the antiseptic on the development of ammonia, and "spontaneous" souring inhibits its production to a greater extent than the addition of antiseptics.

W. D. H.

**The Urine of Calves during the First Few Days of Life.** LEO LANGSTEIN and CARL NEUBERG (*Biochem. Zeitsch.*, 1907, 4, 292—298).—The points mainly noteworthy are the occurrence of lactose and of abundance of allantoin in the urine. In some cases, *lævulose* was present also.

W. D. H.

**Influence of Certain Drugs on the Excretion of Uric Acid and Creatinine.** ELBERT W. ROCKWOOD and CLARENCE VAN EPPS (*Amer. J. Physiol.*, 1907, 19, 97—107).—When the purine in the diet is small in amount or absent, colchicum, lithium carbonate, sodium citrate, sodium hydrogen carbonate, and potassium acetate do not increase uric acid secretion, or may decrease it. Sodium salicylate and aspirin markedly increase the urinary uric acid, except in one case where albuminuria was present. If chocolate is added to the food, the uric acid is not increased. Creatinine excretion was constant in quantity, and was unaffected by the drugs given.

W. D. H.

**Recognition of Toxic Bases in Urine. IV.** FRIEDRICH KÜTSCHER (*Zeitsch. physiol. Chem.*, 1907, 51, 457—463. Compare Abstr., 1906, ii, 471, 786, 875).—The following bases have been isolated from the oily aurichlorides obtained from human urine. (a) *Mingine*,  $C_{13}H_{18}O_2N_2$ , a diacid base, the *hydrochloride* of which forms long, colourless needles insoluble in cold absolute alcohol. The *aurichloride*,  $C_{13}H_{18}O_2N_2 \cdot 2HAuCl_4$ , crystallises from water containing hydrochloric acid in small, transparent, yellowish-red, quadratic prisms, m. p. 194°.

(b) *Reductonovaine*,  $C_7H_{15}ON$ , which yields a mercurichloride insoluble in alcohol. It appears to stand in the same relationship to novaine that neurine does to choline. The *aurichloride*,  $C_7H_{15}ON \cdot HAuCl_4$ ,

separates from water in oily drops, which gradually solidify to plates and needles. It is acted on by light, begins to sinter at  $80^{\circ}$ , and melts between  $155^{\circ}$  and  $160^{\circ}$ . When heated with barium hydroxide, the base yields trimethylamine. The occurrence of novaine and reductonovaine in urines accounts for the fact that trimethylamine is formed when human urine is heated with fixed alkalis (Dessaignes, *Annalen*, 1856, 100, 218).

(c) Vitiatin, a base which has been obtained previously from Liebig's extract of meat. J. J. S.

**The Fate of Ammonia in the Dog when Ammonium Carbonate is Injected into the Blood.** KATHARINA KOWALEVSKY and M. MARKEWICZ (*Biochem. Zeitsch.*, 1907, 4, 196—209).—After the injection, the ammonia of the blood soon sinks to the normal; it first forms loose compounds in various tissues. The organism then frees itself from ammonia, which either as urea or as ammonium salts passes into the urine. The liver is concerned in urea formation.

W. D. H.

**Action of Magnesium Sulphate on the Heart.** SAMUEL A. MATTHEWS and D. E. JACKSON (*Amer. J. Physiol.*, 1907, 19, 5—13).—In the complete anaesthesia which magnesium sulphate produces in frogs, impulses pass readily through the spinal cord and produce normal effects on motor nerve-endings. The action on the heart of all classes of vertebrates is a marked depression. This may culminate in stoppage; the heart recovers under artificial stimulation, but not by the administration of adrenaline or squill; barium chloride and calcium chloride are more effective in promoting recovery. Magnesium sulphate does not affect the nerve-endings of vagus, sympathetic, motor, or secretory nerves, nor the muscles, nerves, or movements of the intestine.

W. D. H.

**Physiological Action of Allyl Sulphide.** E. WACE CARLIER and C. LOVATT EVANS (*Bio-Chem. J.*, 1907, 2, 325—339).—See this vol., ii, 572.

**Toxicity of Arsenic Trihydride.** ALEXANDRE HEBERT and F. HEIM (*Bull. Soc. chim.*, 1907, [iv], 1, 571—573).—By experiments on guinea-pigs, it was found that the presence of 0.35% of arsenic trihydride in the surrounding atmosphere was the minimum dose producing a rapid fatal effect, whilst continued exposure to an atmosphere containing 0.005% was fatal eventually. For birds, the corresponding quantities were 0.009% and 0.002%.

T. A. H.

**The Lecithids of Snake-Poison.** PRESTON KYES (*Biochem. Zeitsch.*, 1907, 4, 99—123).—This research continues previous work in which the importance of lecithin as an amboceptor in snake-poisoning was shown. The formation of the lecithids is a synthetic process of the nature of adsorption, and the lecithin found in the compound is of the mono-fatty-acid variety. The lecithids are grouped as follows.

1. Complete lecithids, soluble in alcohol, not increased in activity by more lecithin, and not reacting with antivenin; among them is a hæmolytic material.

2. Incomplete lecithids, insoluble in alcohol, not neutralisable by antivenin, but increased in strength by lecithin.

3. Incomplete lecithids, which have no hæmolytic action on the addition of lecithin.

4. A hæmolysin, which is possibly the natural cobra amboceptor, and perhaps an extremely incomplete lecithid. This is insoluble in alcohol, increased in strength by lecithin, and neutralisable by antivenin.

W. D. H.

**Toxolecithids.** I. J. MORGENROTH and U. CARPI (*Biochem. Zeitsch.*, 1907, 4, 248—267. Compare this vol., ii, 286).—In reference to the important part Kyes believes lecithin to play in the action of snake venom, the term *prolecithid* is adopted for the naturally occurring lecithin compound, which on further union with lecithin is converted into *toxolecithids*. The hæmolytic prolecithid of cobra venom rapidly loses its activity when treated with pepsin-hydrochloric acid; this is inhibited by horse-serum. Pepsin without hydrochloric acid has no such effect. The toxolecithid is much more resistant. It is doubtful whether prolecithid is of proteose nature. In alkaline solutions, trypsin rapidly destroys prolecithid, but the alkali alone is equally efficacious in this direction. In neutral solutions, trypsin acts like pepsin, but the difference between prolecithid and toxolecithid are not so marked. Papain destroys neither. Toxolecithids prepared by either of Kyes' two methods are toxic to mice and rabbits. Contrary to Kyes' statement, the symptoms are different from those of ordinary cobra poisoning. The toxic action is thermolabile and also suffers diminution by keeping the preparation in the ice-chest. In this there is a difference from what happens to the hæmolytic action. Contrary to what occurs to the hæmolytic action, the neurotoxic action is increased by specific serum. The toxo-lecithid appears to be formed from the original neurotoxin of the cobra venom.

W. D. H.

**Lipolysis, Agglutination, and Hæmolysis.** II. CARL NEUBERG and C. REICHER (*Biochem. Zeitsch.*, 1907, 4, 281—291).—Hæmolysis and agglutination are not the principal actions of toxins and similar agents, but are to be regarded as intermediate stages in lipolysis. This view, originally advanced by Neuberg and Rosenberg (*Berlin. klin. Woch.*, Jan., 1907), is here confirmed. Experiments are given to show the parallelism between fat-splitting and hæmolysis. This is true also for the gastric and pancreatic juices, and for bactericidal and antitoxic serum.

Whether saponification also occurs is uncertain. Fermentative hæmolysis must, of course, be distinguished from that brought about by such agents as water, acids, alkalis, saponin, &c., where the processes are, in part, purely chemical saponification, or due to alterations in physical conditions (solution, diffusion, changes in surface tension, &c.).

W. D. H.

**The Action of Pancreatic Juice on the Hæmolysin of Cobra Venom, and its Compounds with Antitoxin and Lecithin.** YUTAKA TERUUCHI (*Zeitsch. physiol. Chem.*, 1907, 51, 478—487).—The pure pancreatic juice of the dog activated by intestinal juice acts destructively on cobra hæmolysin, antivenin, but not on the compound with lecithin. Pure intestinal juice has no such action. Pancreatic action leads to a restitution in part of the toxin in a neutral mixture of the cobra poison and its antitoxin; but if this mixture is combined with lecithins, the appearance of the free toxin under the influence of pancreatic action does not occur.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Researches on Expressed Yeast Juice.** EDUARD BUCHNER and ROBERT HOFFMANN (*Biochem. Zeitsch.*, 1907, 4, 215—234).—Unsuccessful attempts to separate zymase from the other enzymes (invertase, maltase, endotryptase) of the juice are described. Passing ozone through the juice causes it to become cloudy, and destroys or lessens the activity of zymase. Experiments on the inhibiting influence of phenol are also described. The last section is polemical against T. Bokorny and Hugo Fischer. W. D. H.

**Effect of Acids, Alkalis, and Neutral Salts on the Activity and Multiplication of Yeast Cells.** ERIC DRABBLE and DAISY G. SCOTT (*Bio-Chem. J.*, 1907, 2, 340—349).—Sodium and potassium chlorides and nitrates of 0·1 gram-molecular strength or less do not affect the fermentative action of yeast. Reproduction occurred most rapidly when the strength of sodium nitrate was raised to 0·2, beyond which it became less active and ceased when the strength was 0·7. Hydrochloric and nitric acids and sodium and potassium hydroxides of 0·1 strength prevent fermentation and reproduction; lesser strengths have a depressing action; 0·1 hydrochloric acid causes marked shrinkage of the cells. W. D. H.

**Production of Hydrogen during the Respiration of Fungi.** S. KOSTYTSCHIEFF (*Ber. deut. bot. Ges.*, 1907, 25, 178—188. Compare this vol., ii, 381 and 385).—Hydrogen is not produced during the normal and anærobic respiration of fungi supplied with mannitol. The production of hydrogen observed by Müntz in the anærobic respiration of *Agaricus campestris* is attributed to the activity of bacteria.

N. H. J. M.

**Anærobic Respiration without Production of Alcohol.** S. KOSTYTSCHIEFF (*Ber. deut. bot. Ges.*, 1907, 25, 188—191).—The results of experiments with *Agaricus campestris* showed that not a trace of alcohol is produced during anærobic respiration.

N. H. J. M.

**Cyanogenesis in Plants. Part VI. Phaseolunatin and the Associated Enzymes in Flax, Cassava, and the "Lima Bean."** WYNDHAM R. DUNSTAN, THOMAS A. HENRY, and SAMUEL J. M. AULD (*Proc. Roy. Soc.*, 1907, B, 79, 315—322. Compare Abstr., 1902, ii, 578; 1904, ii, 71, and 1906, ii, 794 and 795).—The evolution of hydrogen cyanide from a solution of phaseolunatin to which a commercial emulsin preparation was added (Abstr., 1904, ii, 71) is now shown to have been due to some secondary cause and not to the emulsin. The enzymes of *Phaseolus lunatus* beans, flax, and cassava differ from the emulsin of almonds as they decompose phaseolunatin in addition to amygdalin and salicin; two enzymes are no doubt present in the three plants, one of the emulsin and one of the maltase type, and it is to the latter that the decomposition of phaseolunatin is due.

Phaseolunatin is decomposed by yeast-maltase and is therefore an  $\alpha$ -glucoside, probably the  $\alpha$ -dextrose ether of acetonecyanohydrin, as the sugar initially produced by its decomposition was found to be  $\alpha$ -dextrose. All other glucosides hitherto examined yielded the  $\beta$ -forms of the sugars when completely hydrolysed by enzymes.

N. H. J. M.

**Mode of Production of Asparagine and Glutamine in Seedlings.** ERNST SCHULZE (*Ber. deut. bot. Ges.*, 1907, 25, 213—216).—Dried, finely-powdered lupin seedlings, when subjected to autolysis in presence of water and an antiseptic at 35—40°, were found to contain increased amounts of ammonia. The fact that ammonia does not accumulate in living seedlings is due probably to its being utilised for the production of asparagine. The favourable effect of oxygen in the production of asparagine, observed by Suzuki and by Godlewski, may be due to ammonia formed by the oxidation of mono- and diamino-acids, or it may be due to the production of succinic acid by the oxidation of arginine.

N. H. J. M.

**Physiological Action of Allyl Sulphide, with an Analysis of the Leek (*Allium porrum*).** E. WACE CARLIER and C. LOVATT EVANS (*Bio-Chem J.*, 1907, 2, 325—339).—Analyses of the common leek gave the following percentage results: water and volatile oil, 88; fixed oil and glucoside (?), 0.65; resinous substance, 0.48; organic acids, colours, &c., precipitable by lead acetate, 1.1; sugars (and extractives not precipitable by lead acetate), 2.24; gums and pectous substances soluble in water, 2.2; proteins, 1.55; pectous substances soluble in dilute alkali, 1.69; cellulose, 0.77; ash, 0.86. This plant and others of the onion class owe their garlic-like odour to allyl sulphide. In large doses, this substance paralyses the respiratory centre, and to a less degree the vaso-motor centre. In small doses the latter centre is affected most. It diminishes vagus action on the heart, but has no direct action on cardiac or skeletal muscle. Half a minim per kilo. of body-weight is fatal.

W. D. H.

**Treatment of Soils with Carbon Disulphide.** BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1907, ii, 18, 624—634 and 790—798. Compare this vol., ii, 502).—The fact that increased yields have been

obtained two and three years after the application of carbon disulphide, is opposed to the supposition that the beneficial effect of carbon bisulphide is due to its acting as a stimulant.

The increased yields, which are sometimes very considerable, are due in part to the favourable action of the carbon bisulphide on nitrogen-fixing and nitrifying organisms of the soil, and partly to its action on mineral constituents of the soil.

N. H. J. M.

**Soil Acidity in its Relation to Lack of Available Phosphates.** A. R. WHITSON and CHARLES W. STODDART (*J. Amer. Chem. Soc.*, 1907, **29**, 757—759).—From their own observations and those of others, the authors consider that the acidity of a soil indicates the need of phosphatic manure.

E. G.

**Employment of Calcium Cyanamide as Manure.** PAUL WAGNER, ROBERT DORSCH, SIEGMUND HALS, and M. POPP (*Landw. Versuchs-Stat.*, 1907, **66**, 285—372).—The manurial value of calcium cyanamide was found to be 90 as compared with sodium nitrate=100. Its value is diminished when dicyanodiamide is produced in the soil by the action of carbon dioxide or humic acid, or by a high temperature. The manure should therefore not be applied to acid soils or during the summer. It is important to distribute the manure evenly, and to mix it as completely as possible with the soil; and the best results will be obtained with moist loamy soils containing plenty of bacteria.

N. H. J. M.

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## Analytical Chemistry.

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**Azo-dyes as Indicators.** JOSE PRATS AYMERICH (*Anal. Fis. Quim.*, 1907, 5, 119—124).—The majority of azo-dyes are not sufficiently sensitive to the action of acids and alkalis to be of any use as indicators; of a large number tried, only Congo-red, methyl-orange, and chrysoidine lent themselves to this purpose. The following values show the comparative sensitiveness of these three indicators; they give the number of c.c. of a solution of sulphuric acid, 1 in 5000, required to produce a distinct colour change with eight drops of a 1:1000 solution of the indicator added to 100 c.c. of water: Congo-red, 2·8, methyl-orange, 4·6, chrysoidine, 0·8. Chrysoidine, although very sensitive, cannot generally be employed with advantage as the change of colour is from yellow to orange; it is not affected by organic acids such as oxalic acid. Congo-red is preferable in most cases to methyl-orange, and even to litmus in the case of bases such as ammonia and lime-water, to the action of which it is very sensitive. It is hardly so responsive to acids as litmus, but as the change of colour is very distinct (red with alkalis, blue with acids), its use is in many cases to be recommended. W. A. D.

**Volumetric Estimation of Hydrogen.** ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 195—208, 208—211).—Hydrogen can be determined both qualitatively and quantitatively by igniting the substance to be tested with powdered magnesium. A hard glass-tube 12—13 cms. long is partly filled with powdered magnesium, after which the substance, mixed intimately with a further quantity of magnesium, is introduced. The apparatus is then connected with a pump to remove the air, which is then replaced by a stream of dry hydrogen; after connecting with a measuring burette, the tube is heated carefully and the hydrogen collected. This method is claimed to yield very good results and is applicable to most organic and inorganic substances in the solid, liquid, or gaseous states, but not to the fatty-acids of high molecular weight or to some of the organic nitrogenous derivatives. Sulphur, the halogens, and, with more difficulty, nitrogen can be estimated in the residue. In some cases it is best to mix the substance with aluminium, and also to use a mixture of aluminium and magnesium instead of pure magnesium in the rest of the tube.

Z. K.

**A New Reaction for Detecting Traces of Moisture.** WILHELM BILTZ (*Ber.*, 1907, **40**, 2182—2184).—Potassium lead iodide, which is almost colourless, is decomposed by water with the formation of lead iodide. When potassium lead iodide is dissolved in acetone and precipitated from the acetone solution by ether or, better, when the solution is evaporated on filter paper or on silk so as to present a finely-divided product, a reagent is obtained, which is very sensitive towards traces of moisture. The presence of water is indicated by the colour, due to the formation of lead iodide. As an indication of the efficiency of the reagent for detecting traces of moisture, various examples are quoted, for example, absolute alcohol, which, in presence of anhydrous copper sulphate for one hour, did not appear to contain moisture, at once caused the new reagent to assume a strong yellow tint.

A. McK.

**Volumetric Estimation of Free Acid in Presence of Copper or Other Metallic Salts.** W. EDGAR SIMS (*Chem. News*, 1907, **95**, 253).—The solution containing about 3 grams of copper sulphate is diluted with water to 100 c.c. and 4 drops of methyl-orange solution are added. If the liquid turns pink, the solution is titrated with  $N/2$  sodium hydrogen carbonate until colourless. After adding 0.1 c.c. for correction, the amount of  $N/2$  carbonate used represents the acidity. If, however, the solution turns green, the acidity cannot be greater than 0.1 c.c.  $N/2$  carbonate, and in this case the liquid is titrated with  $N/2$  sulphuric acid until colourless, and the amount of free acid is equivalent to 0.1 c.c. minus the number of c.c. of  $N/2$  acid used.

The method is also applicable to nickel, &amp;c.

L. DE K.

**Detection of Anions in the Electrolytic Way.** JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1907, **29**, 447—455).—The solution is submitted to electrolysis in a special apparatus and the metals are obtained as amalgams, and in case of alkali metals may be dissolved in water and titrated. The chlorine, bromine, iodine, the thiocyanate,

ferro- and ferri-cyanide, phosphoric and carbonic anions are deposited on metallic silver and weighed as silver salts. For particulars the original paper and illustrations should be consulted. L. DE K.

### Density Curve of Mixtures of Bromine and Chlorine.

LAUNCELOT W. ANDREWS and HENRY A. CARLTON (*J. Amer. Chem. Soc.*, 1907, 29, 688—692).—When small quantities of chlorine are mixed with bromine, the density of the bromine is reduced so considerably that the amount of chlorine present can be estimated from a density determination. The investigation was undertaken with the object of obtaining the data required for this purpose.

Carefully purified bromine has been found to have  $D^{20}$  3.11932,  $D^{25}$  3.10227, and  $D^{30}$  3.08479. These results are compared with those obtained by Pierre (*Ann. Chim. Phys.*, 1847, [iii], 20, 45) and by Thorpe (*Trans.*, 1880, 37, 172).

With the aid of the constants  $D^{25/4}$  3.10227 for bromine and  $D^{25}$  1.39778 for liquid chlorine (Knietzsch, *Abstr.*, 1891, 14), the percentage,  $p$ , of chlorine is given by the formula:  $p = 88.593\{(3.10227/d) - 1\} = (274.840/d) - 88.593$ , where  $d$  is the density of the mixture. When the mixture is saturated with water the following expression is approximately correct:  $p = 88.59\{(3.1004/d) - 1\} = (274.665/d) - 88.59$ . The quantities of chlorine in mixtures of bromine and chlorine as determined by this method agree closely with those found by analysis. The organic and other impurities usually present in crude bromine do not seriously influence the results of the density determinations.

The contraction which occurs when liquid chlorine is mixed with bromine can be calculated from the first equation and indicates that chemical combination probably occurs between the elements to a limited extent (compare Bornemann, *Abstr.*, 1878, 11).

The coefficient of expansion of bromine in glass between  $25^\circ$  and  $30^\circ$  was found to be 0.00110, which is in good agreement with Thorpe's results (*loc. cit.*). E. G.

**Estimation of Iodides in Presence of Bromides and Chlorides.** EMANUEL RIEGLER (*Zeitsch. anal. Chem.*, 1907, 46, 315—318).—Forty c.c. of the solution, which should not contain more than 0.2 gram of potassium iodide, are put into a 200 c.c. beaker and heated to boiling, and a few crystals of potassium permanganate are added from time to time until the liquid becomes permanently red. The excess of permanganate is then decomposed by cautious addition of dextrose. The solution is filtered into a 150 c.c. flask and the manganese dioxide well washed (the total filtrate should be about 60 c.c.). The liquid is acidified with sulphuric acid, well shaken to expel any carbon dioxide, and decomposed in a suitable apparatus (the Knop-Wagner azotometer, for instance) by means of 0.5 gram of hydrazine sulphate. The nitrogen evolved is a measure for the amount of iodine. The weight  $\times 3.01 =$  mg. of iodine.

Bromides and chlorides do not interfere with the reaction as they are not oxidised by permanganate. Nitrites may be rendered harmless by boiling the liquid with a little carbamide previously to introducing it into the azotometer. L. DE K.

**Quantitative Estimation of Fluorine in Fluorides.** EGON BÖHM (*Chem. Zentr.*, 1907, i, 1149; from *Oesterr. Chem. Zeit.*, [ii], 10, 61).—In order to render Hempel's *Fluorometer* suitable for fluorides which are decomposed by cold sulphuric acid, the author replaces the glass stopper of the generating flask by a ground dropping funnel of exactly 50 c.c. capacity, and introduces a 50 c.c. enlargement into the upper portion of the calibrated tube. The sulphuric acid contained in the dropping funnel is introduced into the apparatus by lowering the mercury level. L. DE K.

**Estimation of Oxygen in Water.** S. W. KORSCHUN (*Arch. Hygiene*, 1907, 61, 324—335).—From a comparison of the results yielded by different methods for the estimation of dissolved oxygen in water, the author concludes that Winkler's method (*Abstr.*, 1906, ii, 48) is more trustworthy than the one recommended by Müller, in which the water is treated with permanganate, rendered alkaline, and the dissolved air expelled by heating the water under a layer of paraffin, the air or gases being analysed subsequently. The method described by Ramsay and Homfray (*Abstr.*, 1902, ii, 171) is considered to be complicated owing to the necessity of standardising the reagents repeatedly, a further objection being that the scale of the apparatus only reads up to 6 c.c. of oxygen per litre. W. P. S.

**Estimation of Sulphur in Iron and Steel.** AIMÉ BARRAUD (*Chem. Zentr.*, 1907, i, 988; from *Rev. gén. Chim. pure appl.*, 1906, 9, 429—431).—The substance is placed in a 500 c.c. Erlenmeyer flask fitted with a Allihn condenser which is connected with a three-way stopcock, in turn connected with a 40 cm. long, enamelled, porcelain tube placed in an electric furnace in connexion with a rheostat. The tube leads to a 500 c.c. Erlenmeyer flask and a gas cylinder to create counter pressure and prevent escape of gas. The generating flask is also connected with three wash-bottles through which pure hydrogen and carbon dioxide can be passed. The porcelain tube is heated to redness, a slow current of carbon dioxide is passed, the generating flask is connected, and the three-way cork connected with the atmosphere. A current of hydrogen is then passed through the generating flask, and when the air has been expelled, the flask is connected with the red-hot tube and hydrochloric acid is run in from a funnel. The hydrogen sulphide evolved is then passed through suitable absorbents. L. DE K.

**Detection and Estimation of [Traces of] Sulphuric Acid in Hydrofluoric Acid.** ERNST DEUSSEN (*Zeitsch. anal. Chem.*, 1907, 46, 320—323).—The sample is introduced into a platinum dish, nearly neutralised with sodium hydrogen carbonate, and evaporated to dryness. The residue is mixed with a little dry sodium carbonate and well powdered; its total weight should not exceed 0.5 gram. It is then placed on a filter paper 4 cm. square, and after mixing it with some filter-paper fibre, the whole is made into a cartridge, which is then surrounded by a trebly-wound coil of platinum wire. The paper is now heated with frequent rotation along the axis in the inner flame of

a light petroleum burner until the mass has fused. It is then dissolved in water, when it generally emits a faint odour of hydrogen sulphide. It is tested for sulphide by means of an acid solution of lead acetate. The test may be made quantitative by trying an experiment side by side with a sample containing about the same quantity of sulphuric acid; a mixture of sodium fluoride and sodium sulphate dissolved in water and then evaporated to dryness may be used.

L. DE K.

**Volumetric Estimation of [Combined] Sulphuric Acid in Waters.** ABRAM KOMAROWSKY (*Chem. Zeit.*, 1907, 31, 498—499).—A very slight modification of the original barium chromate method proposed by Andrews. The water is acidified with hydrochloric acid, heated to boiling, and some dry, pure barium chromate is added. When cold, the liquid is neutralised with ammonia and filtered from the barium sulphate and barium chromate. The alkali chromate left in solution, which represents the sulphuric acid, is then titrated by means of potassium iodide and sodium thiosulphate in the usual manner.

L. DE K.

**Determination of the Phosphoric Acid Soluble in Citric Acid in Basic Slag.** PAUL WAGNER, R. KUNZE, and W. SIMMERMACHER (*Landw. Versuchs-Stat.*, 1907, 66, 257—284).—The citric acid solution employed for extracting basic slag must contain 20 grams of the pure acid ( $1\text{H}_2\text{O}$ ) per litre, and the extraction is to be made at a temperature as near as possible to  $17.5^\circ$  in a rotating apparatus turning at the rate of 30—40 revolutions per minute for half an hour. A shaking apparatus must not be employed, and the extraction must not be prolonged for more than a few minutes beyond the half hour. The mixture is at once poured on to a folded filter large enough to contain the whole.

In the subsequent treatment, it is important not to carry the evaporation too far in getting rid of the hydrochloric acid, and the diluted residue must not be filtered until the whole of the silica is flocculated.

The direct precipitation method must be carried out immediately, or within an hour at the most, and the mixture of equal parts of magnesia mixture and ammoniacal citrate solution must be freshly made. The stirring apparatus must be worked at the rate of 250—300 turns per minute.

In the molybdate method, it is important to employ pure molybdic acid, and to discontinue the heating as soon as the desired temperature is reached.

When all precautions are taken, identical results are obtained by the method of the German Association, by Wagner's, Naumann's, and Lorenz's methods, and by the molybdate method. The direct precipitation method gives the correct results with slags which show only a very slight reaction with Kellner's test, but not otherwise. On the whole, it is considered preferable to separate the silica in all basic slag extracts by heating with citrate-magnesia mixture and to precipitate the phosphoric acid by adding ammonia.

N. H. J. M.

**Estimation of Traces of Arsenic Trihydride in the Atmosphere.** ALEXANDRE HÉBERT and F. HEIM (*Bull. Soc. chim.*, 1907, [iv], 1, 573—575).—The method employed is essentially that described by Dowzard (*Trans.*, 1901, 79, 715), the air being allowed to pass through a solution of cuprous chloride in hydrochloric acid and then to impinge on a paper impregnated with mercuric chloride, the depth of tint of the yellow stain produced serving to indicate the amount of arsenic trihydride present. T. A. H.

**Detection of Colloidal Silicic Acid.** HUGO HERMANN (*Zeit. anal. Chem.*, 1907, 46, 318—320).—Colloidal silica is soluble in a boiling solution of an alkali paratungstate forming a silicotungstate.

When 10 c.c. of a 0.1% solution of potassium silicotungstate are mixed with 1 c.c. of sodium acetate solution (15 grams of cryst. sodium acetate, 35 grams of water, 5 grams of 98% acetic acid) and then with 3 drops of a 5% caesium chloride, a distinct, crystalline precipitate is formed. L. DE K.

**Estimation of Potassium in Mixed Manures by the Modified Finkener Method.** HUGO NEUBAUER (*Zeitsch. anal. Chem.*, 1907, 46, 311—314).—Ten grams of the sample are boiled in a 500 c.c. flask with 300 c.c. of water for half an hour and neutralised with milk of lime with phenolphthalein as indicator. After a few minutes, the red colour is discharged by cautious addition of oxalic acid. When cold, the solution is diluted to the mark, well-shaken, and filtered. Twenty-five c.c. of the filtrate (0.5 gram of sample) are evaporated in a platinum dish, and the residue heated to expel ammoniacal salts. The mass is then dissolved in water containing a little hydrochloric acid, and the filtrate is evaporated with excess of platinic chloride. The residue is then treated as directed previously for potassium salts (*Abstr.*, 1900, ii, 759). Attention is called to the necessity of not heating the platinum compound too strongly when reducing it in a current of coal-gas so as to prevent fusion and consequent imperfect reduction. L. DE K.

**Detection of Sodium Hydrogen Carbonate in Milk by Means of Aspirin.** FRANCESCO FERRARI LELLI (*Chem. Zentr.*, 1907, i, 909; from *Arch. Pharmacol.*, 1906, 5, 645—648).—One to two c.c. of a saturated alcoholic solution of aspirin are added to 10 c.c. of milk diluted with its own volume of water, and heated for ten to twenty minutes in a water-bath at 60°. The opaque solution is filtered and mixed with 8 to 10 drops of a 10% ferric chloride solution. If sodium hydrogen carbonate is present, a copious, reddish-yellow precipitate is formed. L. DE K.

**Volumetric Methods for the Estimation of Lime and Magnesia in Water.** WILLIAM THOMAS BURGESS (*Analyst*, 1907, 32, 208—212).—*Estimation of Lime.*—A known quantity of ammonium oxalate is added to the water, the calcium oxalate is allowed to settle, and the excess of ammonium oxalate is ascertained by titration with permanganate. Two hundred c.c. of the water are treated with 50 c.c. of a solution containing 4 grams of ammonium oxalate, 8 grams of

ammonium chloride, and 4 c.c. of ammonia of D 0.88 per litre. A blank experiment, using 200 c.c. of distilled water and 50 c.c. of ammonium oxalate, is started at the same time. When the precipitate has subsided completely, 125 c.c. of the clear supernatant liquid are drawn off by means of a siphon, acidified, and titrated with potassium permanganate solution containing 1.128 grams per litre; 1 c.c. of this solution is equivalent to 0.001 gram of lime (CaO). The difference between the quantity of permanganate used for the water and for the blank experiment gives the amount of lime present. Fifty c.c. of the ammonium oxalate solution are sufficient for all waters with total solids up to 100 parts per 100,000.

*Estimation of Magnesia.*—A known excess of sodium hydroxide is added to the water, the precipitated magnesium hydroxide is allowed to subside, and the alkalinity of the clear water is titrated. The water is first titrated with  $N/10$  acid, using methyl-orange as indicator, and is then boiled to expel all carbon dioxide. The solution is then cooled, a known volume of  $N/5$  sodium hydroxide is added, for instance, 20 c.c. per 200 c.c. of water, and the mixture is diluted to a definite volume. A blank experiment is also started at the same time, and the difference between the alkalinity of the water and the control, after the magnesium hydroxide has settled, gives the quantity of the latter present.

W. P. S.

*Estimation of the Hardness of Water.* P. NAWIASKY and S. W. KORSHUN (*Arch. Hygiene*, 1907, 61, 348—354).—The temporary hardness is estimated by a method described originally by Pfeiffer, the water being titrated in the presence of alizarin; this indicator shows an alkaline reaction with the "bicarbonates" of the alkaline earths. One hundred c.c. of the water are titrated at a boiling temperature with  $N/10$  hydrochloric acid until the colour of the indicator changes from red to yellow; the quantity of the acid used is then calculated into degrees of hardness. It is necessary to perform the operation in a porcelain vessel, as the solubility of glass vessels tends to cause too high results. In order to estimate the total hardness, the volume of neutralised water remaining after the estimation of the temporary hardness is next treated with an excess of a solution consisting of equal parts of  $N/10$  sodium hydroxide and  $N/10$  sodium carbonate. The mixture is boiled for a few minutes, transferred to a 200 c.c. flask, diluted, after cooling, to the mark, filtered, and a portion of the filtrate titrated with  $N/10$  hydrochloric acid, using methyl-orange as indicator. The total quantity of  $N/10$  alkali used is calculated into degrees of hardness. The hardness due to magnesium salts may be estimated by treating the neutralised portion of the water with an excess of standardised calcium hydroxide solution, filtering, and calculating the quantity of calcium hydroxide used into magnesia.

W. P. S.

*Action of Concentrated Hydrochloric and Nitric Acids on Barium Chloride and Nitrate respectively.* DIOSCORIDE VITALI (*Boll. Chim. Farm.*, 1907, 46, 313—318).—The precipitation from solution of barium chloride by an excess of concentrated hydrochloric acid, and that of barium nitrate by concentrated nitric acid, may be

used for the quantitative separation and estimation of barium. Neither calcium nor strontium chloride is precipitated by hydrochloric acid, whilst lead and silver chlorides, which are thus precipitated, are insoluble in water.

T. H. P.

**Ignition of Barium Sulphate.** HENRI PELLET (*Ann. Chim. anal.*, 1907, 12, 186—188).—The author confirms the statement recently made by De Koninck that barium sulphate may be safely ignited with the filter in an open crucible, provided the temperature is not excessive, without fear of reduction (compare also Folin, this vol., ii, 123, 503). The author does not dry any precipitate previous to ignition; this not only saves time, but is often of real advantage, for instance, in the estimation of silica, finely-divided particles of which are apt to be carried away by the sudden heating.

L. DE K.

**Titration of Zinc.** FERNAND REPITON (*Ann. Chim. anal.*, 1907, 12, 183—186).—Ten c.c. of zinc chloride or sulphate solution containing exactly 0.1 gram of zinc are placed in a measuring flask, a measured quantity of ammonium chloride and acetate and ammonia is added, and a known volume of standard sodium sulphide is introduced. The liquid is then diluted to the mark, well shaken, and allowed to deposit for fifteen minutes. In another similar measuring flask, 10 c.c. of the prepared zinc solution are introduced and treated as just directed. Whilst waiting for the solutions to clear, the sodium sulphide is checked by means of standard iodine. Of both solutions, equal volumes are then filtered, and the excess of sodium sulphide in each is estimated with iodine solution. Before titrating with iodine, the liquids should be completely neutralised with acetic acid. The amount of zinc is then calculated readily.

L. DE K.

**Electrolytic Precipitation of Copper from an Alkaline Cyanide Electrolyte.** ANNA L. FLANIGEN (*J. Amer. Chem. Soc.*, 1907, 29, 455—459).—Copper may be deposited quantitatively by electrolysis in the presence of potassium cyanide. Addition of ammonium carbonate cannot be recommended, although free ammonia proved beneficial. Good results are also obtained by saturating the copper solution with hydrogen sulphide and then clearing the liquid by addition of potassium cyanide and a little free ammonia. The use of a rotating anode is recommended.

L. DE K.

**Volumetric Estimation of Mercury.** PHILIP W. ROBERTSON (*Chem. News*, 1907, 95, 253—254).—The solution, which should contain about 0.04 gram of mercury in the form of nitrate, is mixed with 10 c.c. of *N*/10 ammonium thiocyanate, and an excess of zinc sulphate is then added. This causes the precipitation of a double compound,  $\text{ZnHg}(\text{CNS})_4$ . The liquid is filtered, and the precipitate washed with dilute zinc sulphate solution. To the filtrate are added 10 c.c. of *N*/10 silver nitrate, and the excess of silver is estimated as usual by titration with *N*/10 ammonium thiocyanate, using ferric alum as indicator. One c.c. of thiocyanate = 0.005 of mercury.

L. DE K.



**Volumetric Estimation and Separation of Cerium by Means of Potassium Permanganate.** RICHARD J. MEYER and ALFRED SCHWEITZER (*Zeitsch. anorg. Chem.*, 1907, 54, 104—120).—Cerium salts are sometimes estimated by conversion into cerium peroxide,  $\text{CeO}_2$ , by potassium permanganate in the presence of a base, but as usually employed the reaction is not quantitative, owing more particularly to autoxidation. It is now shown that satisfactory results are obtained when the cerium solution, which must be approximately neutral, is run into permanganate solution (kept at 60—70°) containing suspended zinc oxide or magnesium oxide until the colour is just discharged.

In the presence of other earths, the results are somewhat higher than the theoretical values, and also than those obtained by von Knorre's method (*Abstr.*, 1898; ii, 311). The cause of this discrepancy has not been established satisfactorily; it is probably due to a slight induced oxidation of the other earths.

For the satisfactory separation of cerium from other earths, it is necessary to find by previous titration the amount of permanganate required to change it to the peroxide. If then it is desired to precipitate all the cerium, the calculated amount of permanganate and rather more than the calculated amount of sodium carbonate are added gradually, and the mixture heated at 60—70° for some time. If, on the other hand, the pure salt is required, the above process is modified by using rather less than the calculated quantity of sodium carbonate, the precipitation being then incomplete.

A method for the separation of cerium peroxide from precipitated manganese peroxide is also given.

The usual hydrogen peroxide and potassium carbonate tests do not detect traces of cerium in didymium and other rare earths. G. S.

**A New Test for Iron.** OSCAR LUTZ (*Chem. Zeit.*, 1907, 31, 570).—The solution to be tested for iron is mixed with a few drops of a solution of protocatechuic acid and then with sodium carbonate in excess. A more or less intense red coloration shows the presence of iron. If any coloured precipitate forms, the solution may be filtered. The presence of the more commonly occurring inorganic and organic acids does not interfere with the test. L. DE K.

**Colorimetric Estimation of Iron with Special Reference to Chemical Reagents.** HENRY N. STOKES and J. R. CAIN (*J. Amer. Chem. Soc.*, 1907, 29, 409—443).—The process may be summarised as follows: the iron is concentrated and freed from interfering substances by precipitation as hydroxide or sulphide, using a suitable substance, such as manganese or cadmium, to carry down mere traces, which is then dissolved in thiocyanic acid containing mercuric thiocyanate; the fading of the colour is prevented by the use of a persulphate.

The ferric thiocyanate is extracted from its aqueous solution by means of a mixture of amyl alcohol and ether (5:2), using two cylinders, one of which contains the iron to be determined; a standard iron solution is then added to both cylinders from two burettes, the

difference of the readings indicating the amount of iron sought. The final result is reached by averaging a series of readings.

A new form of colorimeter is described adapted for use in extracting liquids. L. DE K.

**Separation of Iron from the Other Members of the Iron Group.** RAGNVALD STOREN (*Zeitsch. anal. Chem.*, 1907, 46, 299—307).

Owing to the bulky nature of the ferric hydroxide obtained when iron is separated by a double ammoniacal precipitation from manganese or nickel and cobalt, the author has devised methods by which the iron oxide is separated in the anhydrous form.

Manganese, if not exceeding 2.5%, may be separated by fusing the substance with potassium hydroxide. On dissolving the fused mass in 25% potassium hydroxide solution, the manganese is dissolved as manganate, and may then be recovered in the usual manner. Nickel and cobalt may be separated from iron by heating the mixed sulphates at about 600°. The nickel and cobalt sulphates suffer no change, and may be extracted afterwards with hot ammonia, whilst the iron is left as oxide or basic sulphate.

For the estimation of nickel (in the absence of metals which interfere), the potassium cyanide process is recommended. L. DE K.

**New Method for the Estimation of Nickel.** OTTO BRUNCK (*Zeitsch. angew. Chem.*, 1907, 20, 834).—The hot and nearly neutral solution, which may also contain cobalt or zinc, is mixed with an excess of dimethylglyoxime dissolved in alcohol. The acid set free in the reaction is then neutralised with a very slight excess of ammonia. The precipitate is collected at once in a Neubauer crucible, washed with hot water, and dried at 110—120° for forty-five minutes; it then contains 20.31% of nickel. L. DE K.

**Estimation of Nickel and its Separation from Cobalt or Zinc.** HERMANN GROSSMANN and BERNHARD SCHÜCK (*Chem. Zeit.*, 1907, 31, 335—337).—The nickel solution is mixed with an excess of 10% dicyanodiamide sulphate solution, a little ammonium chloride is added, and then a large excess of ammonia. If cobalt is present, ammonium chloride and ammonia are added first, then a few c.c. of strong hydrogen peroxide, and then, after half an hour, the reagent. Ten per cent. solution of potassium hydroxide is now added in slight excess with vigorous stirring, and after remaining overnight the yellow nickel precipitate is collected on a filter, washed with ammoniacal water, and finally converted into sulphate by ignition and subsequent evaporation with nitric and sulphuric acids. The cobalt may be recovered from the filtrate by precipitation as sulphide, which may then be converted into sulphate.

Zinc, if present, may be recovered from the filtrate by precipitation as sulphide in presence of a little free acetic acid.

The reagent is also recommended as a qualitative test, as even extremely diluted nickel solutions give a yellow coloration. If cobalt is present, the supernatant liquid will be coloured more or less red.

L. DE K.

**Rapid Estimation of Nickel in Steel.** GEORGE T. DOUGHERTY (*Chem. News*, 1907, 95, 261—262, 268—269).—The process is based on the fact that iron may be precipitated free from nickel by means of ammonia in one single precipitation if only a very large quantity of ammonium chloride is added. One gram of steel is dissolved in 15 c.c. of nitric acid, D 1·2. (In presence of copper it is dissolved in 25 c.c. of hydrochloric acid and then boiled with 2·5 c.c. of nitric acid.) Two hundred and seventy c.c. of water containing 75 grams of ammonium chloride are added, the liquid is neutralised with ammonia, and 50 c.c. of ammonia are added in excess. After diluting to 500 c.c., 250 c.c. of the filtrate are first acidified with hydrochloric acid, then neutralised with ammonia and mixed with 5 c.c. of silver nitrate solution (0·1—200 c.c.), and then with 5 c.c. of 2% potassium iodide solution. The liquid is then titrated, until it just clears, with potassium cyanide solution (12 grams per litre), which has been checked with a solution of nickel nitrate containing 0·001 gram of the metal per c.c.

If copper is present in known quantity, it may be allowed for, but otherwise it should be removed from the ammoniacal solution by adding 14 c.c. of hydrochloric acid in excess, and then passing a current of hydrogen sulphide. The filtrate is then well boiled, again neutralised with ammonia, and titrated with cyanide as before.

L. DE K.

**Iodometric Estimation of Chromic Acid, Chloric Acid, Manganese Peroxide, and Lead Peroxide.** V. FARSE (Zeitsch. anal. Chem., 1907, 46, 308—310).—The substance is boiled with a mixture of 1—2 grams of potassium bromide, 80 c.c. of water, and 20 c.c. of sulphuric acid, and the bromine liberated is absorbed in a solution of potassium iodide contained in a (Meyer's) 10-bulb apparatus. The distilling flask is furnished with an elongated separating funnel, and during the heating a current of carbon dioxide is passed through the liquid. The iodine liberated is titrated with thiosulphate as usual.

L. DE K.

**Alkalimetric Method for the Estimation of Tungsten in Steel.** S. C. LIND and B. C. TRUEBLOOD (*J. Amer. Chem. Soc.*, 1907, 29, 477—481).—Two to ten grams of the sample are dissolved in 30 c.c. of nitric acid (D 1·2) with the aid of 1—2 grams of potassium chlorate. The residue left on evaporation is dissolved in 15—20 c.c. of hydrochloric acid, again evaporated, and redissolved in a little hydrochloric acid. The solution is diluted to 150—200 c.c., well boiled, and the residue washed (by decantation) with hot 5% acid until free from iron. It is then washed free from acid with a 5% solution of sodium nitrate to prevent tungstic oxide from passing through the filter. The residue and the filter, which is cut up into small pieces, are now introduced into a small Erlenmeyer flask and treated with excess of  $N/5$  potassium hydroxide, and, if necessary, heated for a few minutes on the steam-bath. After allowing the liquid to cool in the stoppered flask, the excess of alkali is titrated with  $N/5$  hydrochloric acid, using phenolphthalein as indicator. One c.c. of  $N/5$  alkali = 0·0184 gram of tungsten.

L. DE K.

**Electrolytic Estimation of Tin with the Use of a Rotating Anode.** LUTHER F. WITMER (*J. Amer. Chem. Soc.*, 1907, 29, 473—477).—The solution containing about 0.2—0.4 gram of tin in the form of stannic chloride is mixed with 15—20 c.c. of ammonium sulphide (D 0.985) free from polysulphide, and diluted to 100 c.c. A rotating anode is employed with a current of 5.5 amperes and 9 volts. The metal separates in a slightly crystalline, but perfectly adherent, form.

L. DE K.

**Electrolytic Separation of Tin and Arsenic.** ALEXANDER LAMPÉN (*Chem. Zentr.*, 1907, i, 1224; from *Chem. Ind.*, 30, 128—129).—The electrolytic separation of tin and arsenic depends on the fact that alkaline solutions of tin compounds are rapidly and quantitatively reduced by the current at a high temperature, whilst solutions of arsenic acid remain unchanged. The solution of the tin salt in potassium hydroxide should contain 0.1—0.2 gram of tin per 3.0—3.5 of potassium hydroxide; the presence of ammonium salts must be taken into account, since tin is not precipitated quantitatively from ammoniacal solutions. The solution, which should remain clear after diluting to 50 c.c. and boiling for five to ten minutes, is put into the electrolysing vessel, diluted to about 100 c.c., and electrolysed at 80°, using a current density of 0.6 ampere per 100 sq. cm. and an *E.M.F.* of 3.6—4.2 volts. Within half an hour, the temperature is raised to 80—85°, the current increased to 0.75 ampere, and the process continued for three to four hours. *b*-Stannic compounds must be converted into *a*-compounds. Large quantities of stannous salts should be oxidised to avoid the formation of a deposit which is not adherent. When arsenic is present, the end of the reaction is detected by using an auxiliary cathode on which no deposit of tin should be formed in fifteen minutes. The excess of alkali prevents the separation of stannic acid at the anode.

E. W. W.

**Colorimetric Estimation of Titanium.** JAMES H. WALTON, jun. (*J. Amer. Chem. Soc.*, 1907, 29, 481—485).—Titanium may be readily detected in ferruginous clays, &c., by fusing 1 gram with 8 grams of sodium peroxide. The fused mass is treated with 300 c.c. of cold water, filtered, and acidified with sulphuric acid. An approximately quantitative result may be obtained by comparing the coloration with that of a solution of titanium of known strength. The results, however, are below the truth, as a portion of the titanium is retained by the iron deposit. Satisfactory results may be obtained as follows. The substance is fused with sodium peroxide, the fused mass is dissolved in 200 c.c. of water, and, without filtering, 15 c.c. of sulphuric acid (D 1.4) and 6 c.c. of 50% phosphoric acid are added and the liquid is diluted to 250 c.c. The colour of this solution is then compared with that of standard solution of titanium prepared by fusing titanium peroxide with sodium peroxide, dissolving in water, and acidifying the solution with sulphuric and phosphoric acids. The addition of phosphoric acid is necessary as it affects the coloration.

L. DE K.

**Electrolytic Determinations and Separations with the Use of a Rotating Anode.** JULIA LANGNESS (*J. Amer. Chem. Soc.*, 1907, 29, 459—472).—A series of experiments showing the advantage of the rotating anode in the separation of gold from platinum, gold from palladium, copper from platinum, silver from platinum, silver from copper, silver and copper from platinum, silver from nickel, silver from zinc, and in the analysis of coins. As a rule, potassium cyanide is used as electrolyte. For details, the original communication should be consulted. A new form of dish anode is described. It consists of a platinum dish of the same general form as the cathode. It is about 7 cm. in diameter and 3 cm. deep, and its sides are provided with ten slits perpendicular to the edge, each slit being about 1.8 cm. long and 0.5 cm. wide. These openings, together with a circular opening 1.3 cm. in diameter in the bottom of the dish, ensure free circulation of the liquid. The dish is held in position by a stout platinum rod and is so adjusted that it is equidistant from the sides of the cathode.

During the rotation of the anode, the liquid is all contained within the space bounded by the cathode and the outer surface of the anode. Therefore the volume of the electrolyte should not exceed 65 c.c. With this apparatus, no splashing or loss of liquid takes place.

L. DE K.

**The Estimation of Chloroform in the Blood of Anæsthetised Animals.** G. A. BUCKMASTER and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1907, B, 79, 309—315).—Dumas' method as used by Nicloux gives satisfactory results for the estimation of small quantities of chloroform in air and in simple solution in such liquids as urine. In the case of the blood, if it has clotted, the results are too low; if clotting is prevented by oxalate, the results are better, but still somewhat too low. If clotting is prevented by hirudin, the figures came out correct, but only one experiment is given. It is inferred that the result would also be too low if the method was applied to organs and tissues.

W. D. H.

**Estimation of Higher Alcohols (Fusel Oil) in Distilled Liquors.** PHILIP SCHIDROWITZ (*J. Amer. Chem. Soc.*, 1907, 29, 561—566. Compare Abstr., 1906, ii, 584).—A reply to Lasche (*Lasche's Magazine*, Sept., 1906), who recommends the process devised by Röse. The author states that this process is not applicable to all kinds of distilled liquors and may give utterly untrustworthy results, whereas the Allen-Marquardt method is at present the only trustworthy method in existence.

L. DE K.

**Unification of Reducing Sugar Methods.** PERCY M. WALKER (*J. Amer. Chem. Soc.*, 1907, 29, 541—554. Compare Abstr., 1906, ii, 634).—Supplementary tables showing the relation between cuprous oxide (and copper) and anhydrous lactose, crystallised lactose with  $1\text{H}_2\text{O}$  and with  $\frac{1}{2}\text{H}_2\text{O}$ . Tables for dry and crystallised maltose are also given.

L. DE K.

**Detection and Estimation of Reducing Sugars.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1907, 3, 101—117).—In order to avoid

the injurious action of alkali hydroxides, the following solutions are recommended: (A) 69.3 grams of crystallised copper sulphate to 1000 c.c.; (B) 346 grams of Rochelle salt and 200 c.c. of dry sodium carbonate to 1000 c.c.; (C) 200 grams of potassium thiocyanate to 1000 c.c.; in some cases, such as the presence of traces of chloroform, 30 grams of potassium ferrocyanide, 125 grams of potassium thiocyanate, and 100 grams of dry sodium carbonate to 1000 c.c. are used.

The sugar solution to be titrated may contain from 0.1–2.2% of dextrose. The solutions are mixed in the order indicated in equal volumes, and to 30 c.c. are added 2.5–5 grams of dry sodium carbonate; this solution = 0.073 gram of dextrose. The liquid is now boiled and the sugar solution run in slowly until no further precipitate of cuprous thiocyanate is formed, and the liquid is perfectly decolorised.

For the detection of dextrose in urine, equal volumes of A and B are mixed, and the resulting liquid is diluted with three times its volume of water. Six c.c. of this are then heated with eight drops of urine.

L. DE K.

**Estimation of Reducing Substances in Normal Urine.** HILDING LAVESSON (*Biochem. Zeitsch.*, 1907, 4, 40–53).—The reducing substances in normal urine are traces of dextrose, isomaltose, dextrin-like substances, animal gum, glycuronic acid compounds, uric acid, and creatinine. Previous work on the estimation of the relationships between these substances in normal human urine are few and incomplete. In the present research, the following estimations were made: (a) total reduction; (b) reduction after fermentation; (c) uric acid by the Hopkins-Folin method, and (d) creatinine by Folin's methods. Under these conditions,  $a - b$  gives the dextrose, and  $b - (c + d)$  gives that due to other carbohydrates, glycuronic acid, and unknown substances. The analyses are given of the urines of sixty persons. In no case did the percentage of sugar reach 0.1%. The most striking result is the high value of the reduction due to the unknown residue; it varied between 37% and 67% of the total reduction.

W. D. H.

**Estimation of Fucose and Methylpentosan.** WILLY MAYER and BERNHARD TOLLENS (*Ber.*, 1907, 40, 2441–2442).—Fucose may be estimated in the same way as rhamnose (Ellett and Tollens, *Abstr.*, 1905, ii, 210), but since fucose is decomposed more slowly than rhamnose on distillation with hydrochloric acid, the furfuraldehyde produced is exposed longer to the decomposing action of the hydrochloric acid, and therefore a different equation must be employed in calculating the amount of fucose present from the weight of phloroglucide obtained.

W. H. G.

**Inversion of Sucrose by Acid Mercuric Nitrate.** C. B. COCHRAN (*J. Amer. Chem. Soc.*, 1907, 29, 555–556).—Wiley's acid mercuric nitrate process is recommended. Three c.c. of this reagent, when added to 100 c.c. of the sugar solution (condensed milk solution) at a temperature not exceeding 15°, yield a filtrate which contains the sucrose in an unaltered condition; this should be at once examined

in the polariscope. The usual inversion is then carried out by simply placing 50 c.c. of the liquid in a flask and heating in a boiling water-bath for exactly seven minutes. The difference in the two polarisations is due to the sucrose only, as lactose suffers no inversion in this way. For the calculation of the sucrose, the following modified Clerget formula is then applied:  $\text{sucrose} = 100D/132.68 - t/2$ , in which  $D$  is the difference between the two polarisations, and  $t$  the temperature above  $20^\circ$ .  
L. DE K.

**Estimation of Lactose and Butter Fat in Milk Chocolate.** WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1907, 29, 556—561).—A convenient quantity of the sample is repeatedly centrifugalised with light petroleum, and the fat left on evaporation is treated by the Reichert-Meissl process for butter content.

The residue is then dissolved in water and clarified with basic-lead acetate, the excess of which is removed by means of potassium sulphate. The liquid is examined in the polarimeter. Another portion is inverted by means of hydrochloric acid (German official method), the acid is nearly neutralised, and another reading is made. After allowing for dilution, the sucrose is calculated by the usual formula.

Lactose is estimated by polarising the neutralised inverted solution at  $86^\circ$ , and multiplying the corrected reading by 1.11. L. DE K.

**New Reaction of Formaldehyde, Applicable in Pharmacology.** EMILIO GABUTTI (*Boll. Chim. Farm.*, 1907, 46, 349—351).—A solution of carbazole in concentrated sulphuric acid gives an intense blue coloration with small, or a greenish-blue precipitate with larger, quantities of formaldehyde. This coloration, which is formed with cold or hot aqueous or alcoholic solutions of formaldehyde, persists for some time, resists the action of water and, to some extent, that of fixed alkali, but is destroyed by ammonia. One part of formaldehyde per 10,000 can be detected in this way. The test cannot be applied to solutions containing nitrates or other oxidising agent. Of a number of other aldehydes examined, none gave the blue coloration, acetaldehyde yielding a yellow colour which changes to yellowish-red.

The test may be used directly to detect formaldehyde in milk, a few drops of which are added to a solution of carbazole in an excess of sulphuric acid; if the aldehyde is absent, a more or less intense red coloration appears. The better plan, however, is to test the liquid obtained by distilling the exactly neutralised milk in a current of steam.

Meat or other food-stuff should be either macerated for some time with distilled water, and the whole then distilled or extracted with absolute alcohol, the distillate or extract being tested with the carbazole solution.  
T. H. P.

**Detection of Acetone in Urine.** PAUL BORISCH (*Pharm. Centr.-h.*, 1907, 48, 181—184, 206—210, 220—226, 245—252).—A criticism of the various recorded tests for acetone in urine. For details, the

original paper should be consulted. If no red ring is obtained by Frommer's salicylaldehyde test, acetone is sure to be absent. If a strong reaction is obtained, Legal's nitroprusside test, Penzoldt's indigo test, or Fröhmer's hydroxylamine test should be applied. In order to avoid mistaking acetoacetic acid for acetone, the acidified urine is shaken with ether, which is then in turn shaken with water. The aqueous layer is divided into two portions, one of which is tested for acetoacetic acid with ferric chloride. If this gives a red coloration, the other portion is warmed to expel ether and then tested by Lieben's iodoform, or Gunning's tincture of iodine and ammonia process. If the urine is highly coloured, the ether process is resorted to, or the urine may be submitted to distillation and the various tests applied to the distillate. L. DE K.

**Estimation of Acetone in Urine.** W. C. DE GRAAFF (*Pharm. Weekblad*, 1907, 44, 555—561. Compare Kraemer, Abstr., 1880, 826; Messinger, Abstr., 1889, 313; Strache, Abstr., 1892, 546, 1530; Bamberger and Sternitzki, Abstr., 1893, i, 520; Supino, Abstr., 1893, ii, 250; Argenson, Abstr., 1897, ii, 467; Alberda van Ekenstein and Blanksma, Abstr., 1904, i, 98, and 1905, i, 474).—The author reviews the application of the *p*-nitrophenylhydrazone method to the estimation of acetone in urine. A. J. W.

**Separate Estimation of Acetone and Acetoacetic Acid in Diabetic Urines.** OTTO FOLIN (*J. Biol. Chem.*, 1907, 3, 177—182).—The joint acetone and acetoacetic acid are found by the Messinger-Huppert method. The acetone may then be estimated separately as follows: 20—25 c.c. of the urine are placed in an aerometer cylinder and 0.2—0.3 gram of oxalic acid or a few drops of 10% phosphoric acid, 8—10 grams of sodium chloride, and a little petroleum are added. A fairly strong current of air is now passed so as to remove the acetone, which is then absorbed in the usual apparatus in 150 c.c. of water mixed with 10 c.c. of 40% potassium hydroxide and an excess of standard iodine solution. The liquid is acidified with 10 c.c. of hydrochloric acid and then titrated as usual with standard thiosulphate.

If desired, acetone and ammonia may be determined in a single operation, the ammonia being absorbed in a separate receiver, but the author does not recommend that course. L. DE K.

**New Colour Reaction for Lignocelluloses.** EUGÈNE GRANDMOUGIN (*Ber.*, 1907, 40, 2453).—A claim for priority (see *Zeitsch. Farb. Ind.*, 1906, 5, 321) against Wheller (this vol., ii, 511). Diazotisation and methylation of the amino-group prevents the formation of the coloration; thus, diazobenzene salts, *p*-nitrodiazobenzene salts, and dimethylaniline give no coloration, whilst *p*-nitrodimethylaniline gives only a slight yellow coloration with lignocellulose. W. H. G.

**Volumetric Estimation of Tartaric and Malic Acids by Means of Permanganate.** W. MESTREZAT (*Ann. Chim. anal.*, 1907, 12, 173—181).—Fifty c.c. of liquid containing 0.1—0.15 of the acid are mixed with 10 c.c. of 20 vol.% sulphuric acid, heated to boiling, and



titrated with  $N/5$  permanganate. The precipitated manganese oxides are dissolved by adding 20 c.c. of  $N/5$  oxalic acid and the titration is then continued. The oxygen taken up is somewhat higher than it should be, assuming that the acids yield formic and carbonic acids. One litre of  $N/5$  permanganate = 4.37 grams of tartaric and 3.042 grams of malic acid. The author has therefore worked out a process which guarantees an almost complete oxidation, carbon dioxide being the sole end product. The boiling solution is mixed first with a decided excess of permanganate, slight excess of sodium carbonate is then added, and the boiling is continued with addition of some more permanganate. Ten c.c. of dilute sulphuric acid are added and the liquid is cleared by addition of 20 c.c. of  $N/5$  oxalic acid. The titration is then continued. One litre of  $N/5$  permanganate = 3.06 grams of tartaric and 2.35 grams of malic acid. These figures are a little less than those required by theory, as a little aldehyde seems to be formed in the reaction and is lost by evaporation.

L. DE K.

**A New Method of Separation and Estimation of the Organic Acids in Fruits and Vegetables.** JACQUES M. ALBAHARY (*Compt. rend.*, 1907, 144, 1232—1233).—The substance to be analysed is weighed in its natural condition, then dried to constant weight at  $100^{\circ}$ , finely powdered, and extracted in a Soxhlet apparatus (1) with dry chloroform, which removes the fats, most of the colouring matter, and some alkaloids; (2) with anhydrous ether, which dissolves small quantities of the acids; (3) with 90% alcohol, which extracts the remainder of the acids. The residues from the evaporation of extracts (2) and (3) are together dissolved in water and the solution diluted to 100 c.c., of which 10 c.c. are titrated against  $N$ -soda. The residue remaining after the above extractions is heated with alcohol containing hydrogen chloride in a reflux apparatus in order to remove acids present in the substance in the form of salts. The filtrate (+ washings) from this extraction are neutralised with ammonia, most of the alcohol is distilled off, and the residue added to the solution of the free acids, previously neutralised with ammonia. The acids are precipitated in the form of their lead salts, from which lead malate is dissolved by acetic acid and estimated. The residue is suspended in water and the lead precipitated by hydrogen sulphide. Oxalic acid in the filtrate is removed and estimated as calcium oxalate, then the tartaric acid is removed and estimated as potassium tartrate, and the succinic and citric acids in the filtrate estimated separately as basic ferric succinate and barium citrate respectively.

E. H.

**Rapid Detection of Uric Acid in Sediments or Calculi.** E. LETURC (*Ann. Chim. anal.*, 1907, 12, 194—195).—A small particle of the substance to be examined is heated in a porcelain capsule with 1 c.c. of water until dissolved, 2 c.c. of Moreigne's liquid are added, and then 1—2 drops of aqueous sodium hydroxide. If uric acid is present, the liquid at once assumes a splendid blue colour.

Moreigne's test solution is prepared by boiling 20 grams of pure sodium tungstate with 10 grams of phosphoric acid ( $D\ 1.13$ ) and 100 c.c. of water for twenty minutes, and replacing the evaporated water. The

solution which has become alkaline is then acidified with hydrochloric acid. L. DE K.

**Estimation of Humic Acids in Soils.** GERRIT H. COOPS (*Chem. Weekblad*, 1907, 4, 315—321).—About 10 grams of the soil are boiled repeatedly with absolute alcohol. The bulk of the alcohol is recovered by distillation and the original volume is then restored by addition of water (Fresenius's method). The solution containing the soluble humic acids is filtered off from the waxy and resinous matters and titrated with  $N/10$  barium hydroxide. The precipitate formed, which may be converted into barium sulphate, represents those humic acids which form insoluble barium compounds. The filtrate on addition of sulphuric acid yields a further quantity of barium sulphate representing soluble barium salts of humic acids.

The residue from the alcoholic extraction contains other humic acids. It must be remarked, however, that humic compounds are present, which under the influence of alkalis gradually yield additional humic acids. The mass is now heated with addition of a little water on the water-bath for half an hour, with careful addition of  $N/10$  potassium hydroxide until neutral. The solution is filtered and the residue washed a few times (this is much assisted by centrifugal action), and then digested with an equivalent amount of  $N/10$  sulphuric acid; the two extracts are then united. By way of a check, one-half of the solution is mixed with a saturated solution of potassium sulphate, which precipitates certain humic acids, and the filtrate titrated with  $N/10$  potassium hydroxide. The other half is well shaken with ether, which removes any colloidal silica as an emulsion. After submitting to centrifugal action, the bottom layer may be siphoned off. It is divided into three portions. One of these is mixed with a saturated solution of potassium sulphate, and the filtrate is titrated with  $N/10$  potassium hydroxide. The second portion is titrated with  $N/10$  barium hydroxide. The soluble and insoluble barium salts formed may then be converted into sulphate and weighed. The last portion is carefully neutralised with  $N/10$  potassium hydroxide and precipitated with ferrous ammonium sulphate. The precipitate is collected and weighed, and, after allowing for the iron oxide contained therein, it represents gallic acid derivatives. All results are finally calculated on air-dry and ash-free soil. L. DE K.

**Hydrolysis of Sodium Palmitate.** DAVID HOLDE and F. SCHWARZ (*Ber.*, 1907, 40, 2460—2462. Compare this vol., i, 176).—In reply to Cohn (this vol., ii, 409), the authors still maintain that sodium hydroxide cannot be titrated accurately in the presence of sodium palmitate with phenolphthalein as indicator. W. H. G.

**Estimation of "Dry Extract" of Milk.** G. HINARD (*Bull. Soc. chim.*, 1907, [iv], 1, 558—559).—The author finds that if a few drops of formalin are added to milk before coagulation with acetic acid, the "dry extract" obtained on evaporation is lighter in colour and shows less change in weight on continued heating than when acetic acid alone is used. Some of the formaldehyde no doubt remains combined

with the nitrogenous matter of the milk, but if the estimations are carried out under comparable conditions, concordant results are obtained. Commercial formalin leaves a small residue when dried at 95–100°, and a correction for this is necessary. T. A. H.

**Estimation of Urea in Normal Urine and in Urine containing Sugar.** BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1907, 117, 275–290. Compare Pflüger and Bleibtreu (Abstr., 1890, 308; Schöndorff, Abstr., 1896, ii, 131).—Mainly a reply to criticisms on the method already described (*loc. cit.*). It is absolutely essential to test the phosphotungstic acid before it is used, as there are so many different acids and most commercial products are mixtures; some of the acids precipitate urea, others do not. If the acid causes the precipitation of even a small portion of the urea, it is useless. In the conversion of the urea in the filtrate into ammonia, it is necessary to use an excess of phosphoric acid; this can easily be attained by adding 10 grams of crystallised phosphoric acid in each determination. Landau's method of treating the filtrate directly with phosphoric acid without previously adding calcium hydroxide, allowing to remain and filtering, is not to be recommended, as the percentage of urea comes too high.

When oxyproteic acid is present, the urea-nitrogen, as determined by the phosphoric acid, comes about 1% too high.

Correct results for urea-nitrogen may be obtained with urines rich in sugar provided the urine is diluted until the percentage of sugar is 1, and also that an excess of calcium hydroxide is avoided. J. J. S.

**Detection of Tryptophan and Phenylalanine.** M. MAYEDA (*Zeitsch. physiol. Chem.*, 1907, 51, 261–263).—Picric acid and picrolonic acid are recommended for the isolation of tryptophan and phenylalanine. In both cases the picrolonates are the more insoluble.

*Tryptophan picrate*,  $C_{11}H_{12}O_2N_2 \cdot C_6H_3O_7N_3$ , crystallises in tufts of lustrous needles or plates, m. p. 195–196° (decomp.); the *picrolonate*,  $C_{11}H_{12}O_2N_2 \cdot C_{10}H_8O_5N_4$ , crystallises in tufts of orange-red needles, m. p. 203–204° (decomp.).

*Phenylalanine picrate*,  $(C_9H_{11}O_2N)_2 \cdot C_6H_3O_7N_3$ , crystallises in sulphur-yellow needles, m. p. 173° when freshly prepared; the *picrolonate*,  $C_9H_{11}ON_2 \cdot C_{10}H_8O_5N_4$ , forms tetragonal plates or four-sided prisms, m. p. 238° when freshly prepared. W. D. H.

**A Characteristic Reaction of Adrenaline.** ALEXANDER GUNN and EDWARD FRANK HARRISON (*Pharm. J.*, 1907, 78, 718).—On treating adrenaline with sodium or potassium hydroxide, an odour resembling that of phosphine is produced and the mixture is coloured reddish-brown. The test is best applied by placing a few drops of a 0.1% adrenaline solution in a small porcelain crucible and adding five drops of 10% sodium hydroxide solution. The solution becomes coloured gradually, and the odour is fully developed in about one minute. One drop of adrenaline solution gives a marked odour, and probably still smaller amounts can be detected by the test. No trace of phosphorus was found in the preparations examined.

W. P. S.

**Use of Picrolonic Acid (Dinitrophenylmethylpyrazolone) for Evaluating Narcotic Drugs, &c.** HERMANN MATTHES and O. RAMMSTEDT (*Arch. Pharm.*, 1907, 245, 112—132).—Picrolonic acid forms with bases compounds that crystallise well and are insoluble in most solvents. In consequence, use has been made of it for the characterisation of bases (Knorr, *Abstr.*, 1897, i, 314); for this purpose it is superior to picric acid.

In the paper under consideration, a detailed account is given of attempts to estimate alkaloids in official preparations of *Nux vomica* (strychnine and brucine together), *Hydrastis* (hydrastine), and *Jaborandi* (pilocarpine); the molecular weights and melting (and decomposing) points of the picrolonates concerned are: brucine, 658, 227°; strychnine, 598, 286°; hydrastine, 647, 225°; pilocarpine, 472, 200—205°. As a rule, the preparation was shaken with a mixture of ether and chloroform and 33% aqueous sodium carbonate, or with a mixture of ether and light petroleum and aqueous ammonia; an aliquot part of the ethereal solution was filtered, concentrated by evaporation, and mixed with *N*/10 alcoholic picrolonic acid; after twenty-four hours the precipitated picrolonate was collected on a Gooch filter, washed with a little mixture of alcohol and ether (1:3), dried for thirty minutes at 110°, and weighed. The results were usually less than those obtained by the ordinary methods by about 5% of the total amount.

A detailed description is given of the best method of preparing picrolonic acid (dinitrophenylmethylpyrazolone), namely, by nitrating phenylmethylpyrazolone, &c.

C. F. B.

**Alkaloid Reactions [Papaverine].** C. REICHARD (*Pharm. Centr.-h.*, 1907, 48, 288—290, 313—315, 334—336).—The author has tried the behaviour of papaverine towards a very large number of reagents. A few of these may be mentioned as being more or less characteristic for this alkaloid. A little papaverine and a crystal of sodium ortho-arsenate when moistened with a drop of sulphuric acid and gently heated turns yellow, yellowish-green, dark green, and finally a dark greenish-black, particularly if heated somewhat more strongly. This reaction distinguishes papaverine from morphine and thebaine. When evaporated to dryness with potassium hydroxide solution, the mass turns yellow and then yellowish-green, and emits a blossom-like odour.

A mixture of the alkaloid and mercurous nitrate when moistened with sulphuric acid turns brownish-yellow which fades a little on exposure to air. In these circumstances, papaverine, also narceine and narcotine, may be distinguished from thebaine, which turns black.

L. DE K.

## General and Physical Chemistry.

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**Pure Temperature Radiation and the Application of Kirchhoff's Law.** CARL FREDENHAGEN (*Physikal. Zeitsch.*, 1907, 8, 407—415. Compare this vol., ii, 146).—In reply to Reinganum (*Physikal. Zeitsch.*, 1907, 8, 182) the author maintains the statement previously made on the basis of experiments that iodine vapour has a perfectly continuous emission spectrum when heated so that its temperature is homogeneous. Kirchhoff's law is not applicable to the emission and absorption of iodine vapour, for when light passes through it the vapour begins to fluoresce and therefore undergoes changes other than a mere rise in temperature. The selective absorption of iodine vapour at the ordinary temperature is therefore not a temperature absorption. The absorption is accompanied by a decomposition of iodine molecules, the light energy being used up by the dissociation process. The energy which becomes free on the reunion of the dissociated atoms is then liberated in the form of light waves. According to this view, the absorption and fluorescence spectrum of iodine vapour should be identical, which is actually the case according to R. W. Wood's experiments. The changes represented by the equation  $I_2 \rightleftharpoons 2I$  are therefore supposed to be the cause of the absorption and selective emission of iodine vapour observed by several experimenters.

The Bunsen flame reactions are similarly considered by the author to be reaction spectra and not temperature spectra. Since the ordinary Bunsen flame reactions are always obtained in oxygen flames, but not in oxygen free flames, such as the hydrogen chlorine flame, it is supposed that the spectral reaction is the union of the metals with oxygen.

H. M. D.

**Ultra-violet Emission of Carbon in Certain Flames.** ALESSANDRO AMERIO (*Atti R. Accad. Sci. Torino*, 1907, 42, 673—676. Compare Abstr., 1906, ii, 440).—The flames of illuminating gas and of acetylene have an appreciable emission in the ultra-violet portion of the spectrum which, with acetylene, reaches beyond  $\mu = 0.31$ . In all cases, the more highly refracted part of the spectrum exhibits well marked maxima resembling very narrow bands, which are clearer if the flame is surrounded by a silvered tube, although the remainder of the emission spectrum does not differ appreciably from that given by a free flame.

The emission of carbon in these flames may be divided into two parts corresponding with the two states through which it passes after liberation from the hydrocarbons. The first of these, due exclusively to carbon existing in the interior of the flame, is a continuous temperature spectrum. The second, which is due possibly to the carbon in the act of burning in the mantle of the flame, or to the products of its combustion (compare Huggins, Abstr., 1882, 250), is a band spectrum, and its relatively high intensity may depend either on

the high temperature of the mantle of the flame or on the chemical excitation of the reaction.

T. H. P.

**Cause of Emission of Bunsen Flame Spectra.** CARL FREDENHAGEN (*Ber.*, 1907, 40, 2858—2861; *Physikal. Zeitsch.*, 8, 404—407. Compare Abstr., 1906, ii, 409).—A reply to Baur's criticism (*Kurzer Abriss der Spektroskopie und Colorimetrie*, p. 31). In support of his contention that the metallic spectra obtained in the ordinary Bunsen flame are oxide spectra, the author describes a slight modification of Smithells' experiment (*Trans.*, 1892, 61, 204). The modified form of Bunsen burner is fed simultaneously with lithium and copper by employing Beckmann's method (this vol., ii, 209); it is found that the outer zone of the flame is coloured green, whilst the inner zone is coloured red. The explanation of this is, that the copper is oxidised in the outer zone and not in the inner, whilst the lithium, having a greater affinity for oxygen than hydrogen, is oxidised in the inner zone.

W. H. G.

**Cathodic Phosphorescence of Complex Systems. Paralyzing Action of Certain Exciting Agents of the Rare Earth Series on other Exciting Agents of the Same Series.** GEORGES URBAIN and CLAIR SEAL (*Compt. rend.*, 1907, 144, 1363—1366).—Since phosphorescence is due to cathodic rays it seems likely that in a solid solution coloured substances, which exert a paralyzing action, absorb the phosphorescent radiations produced by the generation of negative charges, but since certain colourless substances, themselves capable of producing phosphorescence, are also able to mask the phosphorescence produced by some other substances, it is obvious that the paralysis of phosphorescence cannot be wholly due to this absorbent action.

Spectroscopic observations of ternary mixtures containing (a) either the black oxide of praseodymium or terbium, (b) a colourless rare earth oxide, and (c) lime (added as a diluent) show that (1) the coloured oxide diminishes the phosphorescence due to the other oxide present, and that in this respect the oxide of terbium is more efficient as a paralyzing agent than that of praseodymium. (2) Samaria and dysprosia mask the phosphorescence of the black oxide of praseodymium, but to a less extent than the black oxide of terbium. (3) The optimum of phosphorescence due to each exciting agent is almost the same as for binary mixtures with the same diluent, but is always less luminous. (4) The changes due to dilution are the same as for binary mixtures.

The salts of praseodymium and of terbium, as distinguished from the black oxides referred to above, behave in ternary mixtures as colourless substances, and for such mixtures the observations 3 and 4 mentioned above hold, but the salts of praseodymium no longer mask the phosphorescence due to samarium or dysprosium, whilst the three latter, on the contrary, not only mask enormously that due to praseodymium, but also that due to other rare earths. This observation explains the failure to detect in the phosphorescent spectrum of chlorophane the bands due to terbium and dysprosium, although these

are always present in small quantity. In confirmation of this, a synthetic chlorophane, giving the characteristic phosphorescent spectrum of this mineral, has been prepared by adding a small quantity of the mixture of crude rare earths extracted from gadolinite to non-phosphorescent lime, converting the mixture into fluorides, and melting this at a high temperature.

T. A. H.

**Magnetic Rotation of Sodium Vapour at the *D* Lines.** ROBERT W. WOOD (*Phil. Mag.*, 1907, [vi], 14, 145—152. Compare Abstr., 1906, ii, 821).—More accurate measurements have been made of the magnetic rotation of the plane of polarisation in the vicinity of the *D* lines. The sodium vapour used as the medium was contained in a highly exhausted porcelain tube heated in an electrical furnace. Sunlight was used as the source of light and the observed rotations ranged from  $90^\circ$  to  $1200^\circ$ . It was found possible to maintain the condition of the sodium vapour constant for a sufficient length of time to obtain a photographic registration of the phenomenon, and the wave-length measurements were made from the photographs. The relationship between rotation and wave-length is shown by means of a graphic representation.

The rotation values in the region outside the *D* lines agree with Drude's formula based on the Hall effect, but this formula does not hold at all for the region between the *D* lines, the observed rotation at the centre being much larger than the calculated value.

H. M. D.

**Significance of the Presence of Oxygen in the Photochemical Reactions which take place in Eder's Solution and in Solutions of Ferric Salts.** A. JODLBAUER (*Zeitsch. physikal. Chem.*, 1907, 59, 513—531. Compare Jodlbauer and von Tappeiner, Abstr., 1905, ii, 565).—The decomposition of Eder's solution (mercuric chloride + ammonium oxalate) under the influence of light is about eighty times more rapid in the absence of oxygen than it is when the solution is saturated with oxygen. The action is the same in both cases; calomel, carbon dioxide, and ammonium chloride are produced in a constant ratio.

The photochemical decomposition of ferric oxalate is also retarded by the presence of oxygen, in so far at least as this decomposition is measured by the amount of ferrous oxalate precipitated. The amount of carbon dioxide liberated is, however, pretty much the same whether oxygen is present or not. It is probable that, when oxygen is present, some intermediate product, soluble in water, is formed, but no clue to the nature of this intermediate product has yet been obtained. The separation of carbon dioxide from ferric oxalate solutions exposed to light begins with the exposure, but the precipitation of the ferrous salt is preceded by an apparent induction period.

The amount of ferrous salt precipitated when ferric tartrate solutions are exposed to light is greater in the absence than in the presence of oxygen; the amount of carbon dioxide liberated is, however, greater in the presence than in the absence of oxygen. This result is to be explained by the formation of an intermediate oxidation product which

remains in solution, and in support of this view it is shown that there is an actual consumption of oxygen during the exposure to light.

Whereas the decomposition of Eder's solution is accelerated by certain fluorescent substances (*loc. cit.*), no such effect has been observed with ferric oxalate and tartrate solutions, probably because fluorescent substances, when added to these solutions, lose their fluorescence.

Discrepancies in photometric measurements made with Eder's solution are to be attributed to the smaller or greater quantity of oxygen which has been absorbed by the solution. J. C. P.

**Secondary Radiation from a Plate Exposed to Rays from Radium.** A. STANLEY MACKENZIE (*Phil. Mag.*, 1907, [vi], 14, 176—187).—A comparison has been made of the secondary radiation emitted from the back and front sides of a plate exposed to rays from radium, the arrangement of the apparatus being such as to keep the various types of rays as distinct as possible from each other. The intensity of the radiation was determined by conductivity measurements. Using different thicknesses of lead plate to partially absorb the primary radiation, it is found that the most easily absorbed rays are most effective in producing secondary air-rays. The penetrability of the air-rays has been examined, and it is found that about five-sixths of the radiation is readily absorbed, the remaining one-sixth being of a very penetrating type.

In examining the "reflected rays" from the front surface of a lead plate, various thicknesses were used in order to ascertain when the maximum intensity of reflected radiation is reached. In the case of the  $\beta$ -rays, this is reached with a plate 0.25 mm. thick, but 6—7 mm. are required before the maximum for the  $\gamma$ -rays is attained. From this the conclusion is drawn that some of the secondary rays produced by the  $\gamma$ -rays in lead are of a highly penetrating character.

In the case of the "transmitted rays" from the back surface of a lead plate, it is found that the  $\beta$ -radiation decreases with increasing thickness of the plate, but is still emitted in appreciable amount from a plate 15.6 mm. thick. The ionisation due to the  $\gamma$ -rays increases until the thickness of the plate reaches 0.75 mm., and then decreases steadily. A similar phenomenon was observed in the absorption of the secondary air-rays, the probable explanation being that a secondary radiation is set up, the ionising activity of which is more than sufficient to make up for the absorption of the original rays.

H. M. D.

**Absorption of  $\alpha$ -Rays in Metals.** EDGAR MEYER (*Physikal. Zeitsch.*, 1907, 8, 425—430. Compare this vol., ii, 521).—Further evidence is brought forward in support of the view that the difference in the absorption, which is found when  $\alpha$ -rays pass through two plates of different metals in opposite directions, is due to the loss of velocity which the rays experience in passing through the metals, and not to diffuse scattering of the rays in the metals. Since, according to Kučera and Masek, the supposed scattering increases with the atomic weight of the metal, the author has made experiments with gold and silver, for



which the scattering should be considerable, and it is shown that the absorption for  $\text{Au} \rightarrow \text{Ag}$  and  $\text{Ag} \rightarrow \text{Au}$  can be calculated if the absorption of the separate metals in its dependence on the velocity of the rays or on the distance of the absorbing metal from the source of the rays is known. The agreement between found and calculated values is not so good for the pair—aluminium and gold; the calculated values being too high for  $\text{Au} \rightarrow \text{Al}$  and too low for  $\text{Al} \rightarrow \text{Au}$ . The author concludes that the assumption of a diffuse scattering of the rays in metals is unnecessary.

H. M. D.

**$\beta$ -Rays from Potassium.** NORMAN CAMPBELL (*Proc. Camb. Phil. Soc.*, 1907, 14, 211—216. Compare Campbell and Wood, this vol., ii, 217).—Observations of the deflection in an electrostatic field of the rays emitted by potassium salts show them to be  $\beta$ -rays of an average velocity less than that of the  $\beta$ -rays of uranium. It has also been proved beyond doubt that they can affect a photographic plate.

W. H. G.

**The First Decomposition Products of Actinium (Emanium). A New Emanation. Formation of Helium from Actinium.** FRIEDRICH GIESEL (*Ber.*, 1907, 40, 3011—3017. Compare Abstr., 1904, ii, 462, 800; 1905, ii, 220).—Radioactinium appears to resemble the metals of the alkaline earths. Finely-divided sulphur may be used for the precipitation of radioactinium, its action being possibly due to its forming sulphuric acid, which then causes the precipitation. The observation of Debierne that actinium is closely related to thorium is incorrect. Actinium is not precipitated together with thorium from a mixture of the rare earths in pitchblende, but remains with the cerium earths, more particularly with lanthanum.

Those actinium preparations of the author, which were strongly radioactive, were not free from  $\beta$ -rays.

Actinium  $X$  practically is not precipitated from solutions by sulphuric acid, which can, accordingly, be used to separate it from actinium. It may also be separated from actinium by means of ammonia. The period of half decay of actinium  $X$  is eight to nine days.

The author was unable to confirm Boltwood's contention that radium is slowly formed from actinium. A strongly radioactive emanium preparation, which had been kept for four years, was dissolved in hydrochloric acid, and sulphuric acid then added. If radium were present, it would have been in the precipitate obtained. The amount obtained was too small for spectrographic investigation, but was exceedingly active. The activity, however, did not increase as it would have done had radium been present, but decreased at a rate characteristic for radioactinium. The actinium emanation decomposes to give a new emanation, which, from the observations quoted, must have an extraordinarily long life.

The author confirms Debierne's observation that actinium may be converted into helium.

A. McK.

**Specific Resistance and Temperature-Coefficient of Tantalum.** MARCELLO VON PIRANI (*Zeitsch. Elektrochem.*, 1907, 13, 344—345).—Tantalum wires of different diameters, which gave different values for the specific resistance, were heated in a high vacuum at about 1900° for one hundred and two hundred hours; after this treatment all gave the same value. The specific resistance is 0.146 and the temperature-coefficient between 0° and 100°, 0.33%. H. M. D.

**The Potentials of Iron and the Passivity of the Metal.** FRITZ HABER and WILLIAM MAITLAND (*Zeitsch. Elektrochem.*, 1907, 13, 309—310).—The potential difference observed by Faust (this vol., ii, 426) between spongy iron and concentrated potassium hydroxide solutions ( $-1.13$  volt compared with the  $N/10$  calomel electrode) has never been observed with massive iron. The authors find, however, that by using boiling  $11N$ -potassium hydroxide solution a potential difference of  $-1.3$  volt is obtained, owing to the fact that the hot potassium hydroxide solution dissolves the film of iron oxide on the surface of the metal; this does not occur with the cold solutions which have always been used previously. The same result is obtained by acting on the iron with dilute acid until the solution is free from oxygen and then adding excess of concentrated alkali hydroxide solution.

T. E.

**Polarisation Voltages of Silver Nitrate Solutions.** J. A. WILKINSON and H. W. GILLET (*J. Physical Chem.*, 1907, 11, 382—391).—The "polarisation voltages" of the solutions in question were determined by polarising the electrodes (which were of platinum) by means of a direct current, then breaking the charging current, and short circuiting the cell through a high resistance voltmeter. The polarisation voltage is the same as the decomposition voltage when the reaction is reversible.

The effect on the polarisation voltage of varying independently the temperature and the concentrations of nitric acid, of silver nitrate, and of water has been determined. The polarisation voltage is diminished both by increasing the proportion of water and by decreasing the nitric acid concentration, whilst it is increased by diminishing the silver nitrate concentration. By thus altering the conditions, the polarisation voltage may be made to vary from 0.625 to 1.05 volts. From the results of measurements against a mercurous sulphate electrode, it is shown that the addition of nitric acid slightly diminishes the potential difference between silver and the solution, whilst it increases in a marked way that between the solution and the peroxide electrode.

The polarisation voltage increases slightly with rise of temperature, the temperature-coefficient being about 0.0008 volt per degree.

G. S.

**The Electrolytic Dissociation of Fused Salts.** KURT ARNDT (*Ber.*, 1907, 40, 2937—2940).—Attempts to calculate the degree of electrolytic dissociation of fused salts by comparing the conductivity of a solution of known strength and the conductivity at infinite dilution

have failed hitherto because a suitable solvent could not be found. The author has discovered that boric anhydride is convenient as it has  $K=0.000021$  at  $900^{\circ}$ , and the electrolyte chosen was sodium metaphosphate, which dissolves in the anhydride in all proportions. The more dilute solutions are viscous and the low conductivities obtained must be due partly to the decreased mobility of the ions, and the degree of dissociation is therefore obscured from this cause.

In order to allow for this, the viscosities of the solutions at  $900^{\circ}$  were measured, and it was found that the product of the viscosity and equivalent conductivity was a constant for all concentrations from 0.5—100%. This shows that the equivalent conductivity is independent of the concentration and is explained by assuming that the sodium metaphosphate is completely dissociated in the molten state.

The conductivities of potassium and sodium chlorides are linear functions of the temperature, and from the behaviour of silver chloride dissolved in molten alkali chloride the author considers that fused univalent salts are completely dissociated.

W. R.

**Anodic Disturbances in Electrolysis of Molten Liquids.** KURT ARNDT and K. WILLNER (*Ber.*, 1907, 40, 3025—3029).—The electrolysis of fused salts is not simple, and the changes occurring at the anode have been little investigated. The chlorides of barium, strontium, and calcium were examined, and the apparatus used was either a porcelain crucible heated in a Kryptol furnace, or an iron crucible lined with chamotte in which the contents were melted by an arc. The cathode was a thick iron wire, the anode a carbon rod. In electrolysis either barium or strontium chlorides, a few minutes after the current has been passing the resistance suddenly increases, the tension in the case of barium rising from 6—10 volts to 30—60. The carbon anode is surrounded by a small blue circle of light, the evolution of chlorine stops, and there is a considerable movement in the mass. With calcium chloride, the electrolysis goes quite quietly, and this observation disproves the assumption that these sudden increments in the voltage are due to gas layers, as in all these cases chlorine is the gas at the anode. That it is not due to the lower temperature of the calcium chloride bath ( $\text{CaCl}_2$ ,  $774^{\circ}$ ;  $\text{SrCl}_2$ ,  $873^{\circ}$ ;  $\text{BaCl}_2$ ,  $950^{\circ}$ ) was shown by the fact that the resistance at  $1100^{\circ}$  is less than at the lower temperature. That it cannot be the result of the formation of a layer of badly conducting oxide is rendered evident by the solubility of the oxides in their fused chlorides, increasing from calcium to barium (Arndt, this vol., ii, 167). No carbide could be recognised, but small quantities of silicic acid were found enveloping the anode, derived from the porcelain or chamotte by the action of the barium or strontium oxide. Silicic acid is therefore the cause of the anodic disturbances.

Metallic strontium is easily obtained by using an iron trough; the current required is 35 amperes at 13 volts.

W. R.

**Ionisation in Solutions and Two New Types of Viscosity.** WILLIAM SUTHERLAND (*Phil. Mag.*, 1907, [vi], 14, 1—35).—The theory of the conductivity of electrolytic solutions given previously

(Abstr., 1902, ii, 300) is further elaborated. The author considers that the fraction which is usually taken to represent the degree of ionisation of an electrolyte has its origin in a resistance which the ions offer to one another's motion, because of their forming with the solvent, through their electric action on one another, a medium which offers a special viscous resistance to the motion of each individual ion. Each ion further causes electric induction through the surrounding solution, and with this is associated another type of viscosity. These and the ordinary viscosity of the solution give three resistances which oppose the motion of the ions. By equating them with the electrical driving force, a formula is obtained for the molecular conductivity, which is found to agree with results for both aqueous and non-aqueous solutions at low and high temperatures.

By taking into account the electrical and dynamical complicating factors in the above manner, the conclusion is drawn that the ionisation of all ordinary electrolytic solutions, aqueous or non-aqueous, is complete at all concentrations. The weak acids which satisfy the dilution law, and acids which, like sulphuric acid, can ionise in two or more different ways are exceptions. The so-called degree of ionisation is a measure of the mobility of the ions, and the author considers that the literature of ionisation must be reinterpreted. Incidentally it is shown that the theory of conductivity is in harmony with that previously given for the diffusion of non-electrolytes, and that both can be used for calculating molecular and atomic sizes leading to values in the case of hydrogen in agreement with the value obtained on the basis of the kinetic theory.

H. M. D.

**Ionic Mobilities in Water.** FRIEDRICH KOHLRAUSCH (*Zeitsch. Elektrochem.*, 1907, 13, 333—344).—A critical consideration of the values obtained for the mobilities of ions in water at 18° from conductivity and transport measurements. In Drucker's recent recalculation of the ionic mobilities, it was assumed that the dissociation of salts containing univalent ions is complete at a concentration of 0.0001 gram-equivalent per litre, and that salts containing bivalent ions also are ionised practically completely at this concentration. The author maintains that this assumption is unjustified and that the conductivity at infinite dilution ( $\Lambda_\infty$ ) is given by the formula  $\Lambda_\infty - \Lambda = P\eta^{\frac{1}{2}}$ , in which  $P$  is a constant and  $\Lambda$  the conductivity of a very dilute solution of concentration  $\eta$ . By means of a modified formula, the value of  $\Lambda_\infty$  can be calculated from the conductivity of more concentrated solutions.

The calculated value of  $\Lambda_\infty$  exceeds the conductivity found experimentally for 0.0001 equivalent solutions by 0.75—1% in the case of salts containing univalent ions, by 1.3—2% for salts containing uni- and bi-valent ions, and by 4—5% for the sulphates of the bivalent metals.

A comparison of the conductivities and migration ratios of pairs of salts containing univalent ions indicates that these agree completely with the theory of independent ionic mobilities. In the case of salts containing uni- and bi-valent, and still more in the case of those with two bivalent ions, the deviations exhibited, when pairs of salts are so

compared, are much greater, and it is not yet possible to give more than approximate values for the mobilities of the bivalent ions. Whether the deviations are to be ascribed to non-compliance of multivalent electrolytes with theory, or to errors of measurement of conductivity and migration ratio in the case of these salts, cannot yet be decided.

H. M. D.

**Relation of the Electrolytic Solution Pressures in Different Solvents.** EMIL ABEL (*Zeitsch. Elektrochem.*, 1907, 13, 305—307).—A theoretical note referring to previous publications (Abstr., 1906, ii, 722, 827).

T. E.

**Periodic Phenomena in the Electrolysis of Nickel Salts.** ALFRED THIEL and A. WINDELSCHMIDT (*Zeitsch. Elektrochem.*, 1907, 13, 317—325. Compare Abstr., 1906, ii, 827).—The authors give a detailed account of the periodic variations of current strength and potential difference which have been observed in the electrolytic estimation of nickel by the ammonia and the oxalate methods. In ammonia solution containing ammonium sulphate or chloride, periodic variations have been observed (at temperatures between 15° and 70°) between potential differences of 2·2 and 4·8 volts, and current strengths of 0·5—2·0 amperes. The amplitude of the variations is independent of the temperature and the current strength, and usually amounts to 0·1 to 0·2 volt, although variations of 0·4 volt are occasionally observed. The periodicity does not commence until the solution contains but a very small quantity of nickel, and if the ammonia concentration is too low or too high, no periodicity is observed. An apparatus for continuous registration of the periodic variations has been used, and curves are recorded which show the entire series of variations in a given experiment.

To explain the phenomena, it is assumed that the nickel in solution is chiefly present in the form of a complex ion,  $\text{Ni}(\text{NH}_3)_x^{++}$ , and a small proportion as  $\text{Ni}^{++}$ . The latter is oxidised at the anode to the hydroxide,  $\text{Ni}(\text{OH})_2$ , which is deposited on the anode surface. This hydroxide is then dissolved by the ammonia and the nickel converted into the complex ion,  $\text{Ni}(\text{NH}_3)_x^{++}$ , the ammonia being oxidised with evolution of nitrogen. That the variations are confined to the anode has been proved by direct experiment, and the alterations in the potential difference at the anode are attributed to the alternate covering of the anode with nickelic hydroxide and the dissolving of this by the ammonia.

The periodicity in the oxalate solution is of a somewhat different character. It commences soon after the current is passed through the solution, the concentration of the nickel being much larger than in the ammonia solution, and ceases when the solution still contains appreciable quantities of nickel. The periods are most sharply defined when the current strength is about 1·0 ampere. An explanation of the phenomena in the oxalate solution is not attempted.

H. M. D.

**Behaviour of the Electric Arc in Various Gases.** A. GRAU and FRANZ RUSS (*Zeitsch. Elektrochem.*, 1907, 13, 345—348).—An arc

was established between platinum electrodes enclosed in a water-cooled quartz tube through which various gases were passed, and the relationship between the potential difference and the current was determined. In all the experiments the length of the arc was 5 cms. The data are plotted with current strengths as abscissæ and potential differences as ordinates. For the different gases, different curves are obtained, the following order being obtained when the gases are arranged in the order of increasing potential difference: nitrogen, air (carbon monoxide), sulphur dioxide, oxygen, carbon dioxide, and hydrogen. Addition of small quantities of other gases to oxygen and carbon dioxide has been found to displace the potential current curves considerably.

The rate of fall of the potential with increasing current strength is much greater for carbon dioxide than for the other gases examined, and this is attributed to the greater dissociation of the dioxide according to  $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$  with increasing watt-consumption.

At the temperature of the arc, sulphur dioxide is decomposed with the separation of sulphur.

H. M. D.

*cycloHexane as a Cryoscopic Solvent.* I. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 924—929).—The molecular elevation of the boiling point of *cyclohexane*, determined by means of solutions of naphthalene, diphenyl, *p*-xylene, *m*-xylene, dibenzyl, and cymene, is found to have the value 203.0.

The following compounds have abnormal molecular weights in boiling *cyclohexane*: benzene, 99—102 (78); phenol, 240—316 (94); aniline, 105—136 (93); pyridine, 109—115 (79); *cyclohexanol*, 775—1609 (100); *cyclohexanone*, 461—527 (98); piperidine, 695—716 (85); thiophen, 106—113 (84); pyrrole, 84—113 (67); pyrrolidine, 73—111 (71).

The following conclusions are drawn. The principal condition for substances to form mixed crystals is that they resemble one another in molecular constitution and not in chemical characters. As regards the property of crystallising together, a ring containing five atoms corresponds with one containing six. In general, in a closed chain, the group  $\cdot\text{CH}_2\cdot$  may be replaced by  $\cdot\text{CH}(\text{OH})\cdot$  or  $\cdot\text{CO}\cdot$  or  $\cdot\text{NH}\cdot$ , or the group  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  by  $\cdot\text{CH}:\text{CH}\cdot$  or  $\cdot\text{N}:\text{CH}\cdot$  or  $\cdot\text{NH}\cdot$  or  $\cdot\text{S}\cdot$ , without alteration of the configuration of the molecule. Cyclic compounds and nuclei of the benzene type give solid solutions with related cyclic compounds, which are completely hydrogenated when the first are dissolved in the second, but probably not when the second are dissolved in the first. The latter point is under investigation.

T. H. P.

**Determination of the Reciprocal Actions of Substances in Solution by their Vapour Pressures.** DMITRI P. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 315—342. Compare this vol., ii, 334).—In normal solutions the equation representing the relation of the partial pressure of one of the components to the constitution of

the solution is  $p = Px \pm KPx(1-x)^2$ , and for infinite dilution,  $dp/dx = P$ , from which it is evident that the depression is independent of  $K$ ; but where the form of the equation is:  $p = Px + KPx^n(1-x)$ ,  $dp/dx = P - KP$  (for  $x=1$ ), hence the depression will be abnormal and will depend on  $K$ , in general the calculated molecular weight  $M_v$  will be equal to  $M.1/1-K$ . The behaviour of *n*- and *iso*-butyric acids, or associated liquids, in solutions of ethyl bromide, ethyl alcohol, methyl and ethyl formates, &c., has been compared with the behaviour of chemically more active, but less dissociated, substances, such as mono-, di-, and tri-chloroacetic acids in the same solvents. All these substances give abnormal depressions in each solution, whilst the equation to be applied varies with the solvent employed. The relation  $p/1/2P$  in different solvents varies in the same direction for all the solutes investigated, but is the more marked, the more chemically active the solute employed; further, the change in vapour pressure produced by the solution of, say, dichloroacetic acid varies greatly for different solvents, but for solvents of analogous constitution, such as methyl and ethyl formates, the changes produced are very nearly identical. Thus the behaviour of a substance in solution depends far more on its chemical nature and that of the solvent than on the degree of association of the solute in the pure state. Probably unstable complex compounds are formed. This hypothesis finds confirmation in the behaviour of aromatic amines and acids (Abstr., 1893, ii, 356; 1894, ii, 51), the ionising and polymerising properties of water and of nitrogen (Brühl, Abstr., 1899, ii, 10), &c. The properties of solutions of methyl ether in strong acids indicate that the complex molecules formed are not of Baeyer's type  $R_2O < \frac{H}{X}$  (Abstr., 1902, i, 355), but of the type  $HX = OR_2$

(where  $X$  is a halogen or an acid group containing oxygen), that is, the complex molecule is formed by the exercise of the higher valency of both the acid and ether oxygen atoms. For most normal liquids the equations for each component are symmetrical, that is, if one is represented by  $p'/P' = x + K_{11}(1-x)^2x$ , then for the other component  $p''/P'' = 1 - x + K_{11}(1-x)^2x^2$ , but the equations for associated substances usually contain more than one constant, and the relation of solute to solvent is far more complicated. Thus, for a solution of acetone in chloroform, the equation of the associated component, acetone, can be represented thus:  $p/P = x - K_{11}(1-x)^2x$ , whilst that of chloroform is  $p = Px - \frac{1}{2}x(1-x)(1-x^3)$ . Where both liquids are associated, the relations of the two are still more complicated. In the critical regions such solutions are also not symmetrical, the amount of the non-associated component varying between  $x' = \frac{1}{2}$  and  $x' = \frac{2}{3}$ , and its critical pressure between  $P'$  and  $\frac{8}{9}P'$ ; whilst the associated component varies between  $x'' = \frac{1}{2}$  and  $x'' = \frac{1}{3}$ , the critical equation will be  $p = P + K_{11}P''(1-x)^3x$  and the partial pressure at the critical point will be  $p_{kp} = P(3x^2_{kp})/(4x_{kp} - 1)$ . The thermodynamic relations between a liquid and gaseous phase in equilibrium with each other are also in agreement with the relations of solute and solvent deduced by the author. The addition of a third substance, soluble in one component and not in the other, also disturbs the symmetrical relations of the two components (compare Wrevsky, Abstr., 1901, ii, 56). Z. K.

**Adiabatic Determination of the Heats of Combustion of Organic Substances, Especially of Sucrose and Benzene.**

THEODORE W. RICHARDS, LAWRENCE J. HENDERSON, and HARRY L. FREVERT (*Zeitsch. physikal. Chem.*, 1907, 59, 532—552).—The adiabatic method of calorimetry suggested by Richards, Henderson, and Forbes (Abstr., 1905, ii, 677) has been improved and tested in detail with satisfactory results. With a calorimeter constructed on this principle and fully described in the paper, the relative heats of combustion of sucrose and benzene have been determined. In the latter case, a small sealed tube, almost completely filled with benzene, was put in the explosion bomb along with a small known quantity of sugar, and was subsequently burst by the combustion of the sugar. Many experiments were made, and it was found that the combustion of benzene produces at least 2·534 times as much heat as that of an equal weight of sucrose. The words "at least" have reference to the fact that the oxygen used contained a little nitrogen, and the presence of nitrogen was found to lead to a slightly lower value for the heat of combustion of benzene, although no such influence could be detected in the case of sucrose. J. C. P.

**Heat of Formation of Phosphorus Nitride.** ALFRED STOCK and FRANZ WREDE (*Ber.*, 1907, 40, 2923—2925. Compare this vol., ii, 541).—The combustion of phosphorus nitride with dry oxygen under a pressure of 50 atmospheres in a Kroecker bomb leads to the formation of nitrogen, phosphoric oxide, and a minute quantity of nitric oxide. The last substance is estimated by condensing the gaseous products in liquid air, allowing the oxygen and nitrogen to boil away, and then slowly evaporating the nitric oxide and passing it into standard potassium hydroxide.

The heat of combustion is 473·2 Cal. at constant volume, and 474·7 Cal. at constant pressure. The heat of combustion of colourless phosphorus is 370·8 Cal., and of the red variety, 363·4 Cal. at constant pressure (compare Giran, Abstr., 1903, ii, 270); hence the heat of formation of the nitride is 81·5 or 70·4 Cal., calculated for colourless and red phosphorus respectively. C. S.

**Calculation of Physico-chemical Constants.** H. STANLEY REDGROVE (*Chem. News*, 1907, 95, 301—302).—In a previous paper (this vol., ii, 446) it has been suggested that in certain physical properties, such as the heat of combustion, the single carbon linking exerts a specific influence, just as the double and triple linkings are usually assumed to do, and that the atomic constants for hydrogen in  $H_2$  are different from those for hydrogen in hydrocarbons. Although the actual values of these linkings cannot be obtained, certain so-called "fundamental constants" have been calculated, and the values of the heats of combustion obtained with the help of these constants are compared with the values actually found by Thomsen, the agreement, in general, being excellent.

The suggestion of Le Bas (*Proc.*, 1907, 23, 134) that the quotient of the molecular heat of combustion of hydrocarbons by the "valency number" is constant does not hold when saturated and unsaturated hydrocarbons are compared. G. S.



**Application of the Method of Limiting Densities to Liquefiable Gases.** PHILIPPE A. GUYE (*Compt. rend.*, 1907, 144, 1360—1363. Compare this vol., ii, 437).—The author has calculated the value of  $R$  from the relation  $R = M/L(1 - A_0^1)$  for the five gases, carbon dioxide, nitrous oxide, hydrogen chloride, ammonia, and sulphur dioxide. The values of  $L$  (weight of a litre of gas at  $0^\circ$  under 1 atmosphere pressure where  $\text{lat.} = 45^\circ$  and  $h = 0$ ) adopted are 1.9768, 1.9777, 1.6398, 0.7708, and 2.9266 respectively. The term  $A_0^1$ , representing the variation of the gas from Boyle's law between 0 and 1 atmosphere, may be evaluated either by linear extrapolation, which Jaquerod and Scheuer have shown (*Compt. rend.*, 1905, 140, 1384) is not strictly applicable to such compressible gases as ammonia or sulphur dioxide, or by the method of parabolic extrapolation suggested by D. Berthelot (this vol., ii, 154). The values of  $M$  (molecular weight) were calculated from the atomic weights, and it is pointed out that those for chlorine and sulphur are not quite certain.

The values of  $R$  thus obtained are not constant, whichever method of evaluating  $A_0^1$  is adopted; they vary 1/930 between the gases carbon dioxide and ammonia, and increase with the critical temperature ( $T_c$ ) of the gas. This variation is almost regular, and has the value  $\pm 2/10,000$  (approx.) for the relation  $R = 22410 + 15 \times 10^{-8} (T_c - 273)^2$ . Using the value 22,410 for the gas constant,  $R$ , the calculated values of  $M$  are always less than those deduced from the atomic weights determined experimentally.

If Berthelot's method of evaluating  $A_0^1$  is correct, there can be no gas constant for perfect gases, and the validity of this hypothesis will be discussed in a subsequent paper.

T. A. H.

**Arsenic and Methylarsonic Acids.** E. BAUD and A. ASTRUC (*Compt. rend.*, 1907, 144, 1345—1347. Compare Abstr., 1904, ii, 644).—From determinations of the heats of solution of arsenic and cacodylic acids and of their anhydrous sodium salts, and of the heats of neutralisation of the acids in solution by one, two, or three molecules of sodium hydroxide, the following heats of reaction have been calculated:  $\text{H}_3\text{AsO}_4$  (solid) + Na (solid) = H (gas) +  $\text{NaH}_2\text{AsO}_4$  (solid) + 57.15 Cal.  $\text{NaH}_2\text{AsO}_4$  (solid) + Na (solid) = H (gas) +  $\text{Na}_2\text{HAsO}_4$  (solid) + 45.87 Cal.  $\text{Na}_2\text{HAsO}_4$  (solid) + Na (solid) = H (gas) +  $\text{Na}_3\text{AsO}_4$  (solid) + 40.76 Cal.  $\text{HMe}_2\text{AsO}_2$  (solid) + Na (solid) = H (gas) +  $\text{NaMe}_2\text{AsO}_2$  (solid) + 41.72 Cal. From these and the results already recorded for methylarsonic acid (*loc. cit.*), it appears that the fixation of a methyl group to an atom of arsenic diminishes the heat of neutralisation by 3.22 Cals., and the fixation of a second methyl group lowers it by an almost equal quantity, 2.98 Cals. These values are in accordance with de Forcrand's rule (Abstr., 1900, ii, 526, 527, 528), whence the calculated mean acidity for methylarsonic acid is 44.742 (found, 44.70), and that for cacodylic acid, 41.564 (found, 41.72).

T. A. H.

**Adsorbent Action of Lead Sulphide.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1907, 245, 259—261).—Mannitol, dextrose, tartaric acid, salicin, codeine, amygdalin, and caffeine were dissolved separately in fifty to one hundred times their weight of 3.3% lead acetate

solution, and the solutions were precipitated with hydrogen sulphide; the percentage carried down by the precipitate of lead sulphide increased from 0 (first three) to 4.5 in the order named. The material adsorbed is easily removed from the precipitate by washing.

C. F. B.

**Curved Capillary Layer and the Theory of Boiling.** GERRIT BAKKER (*Zeitsch. physikal. Chem.*, 1907, 59, 638—639).—Some remarks and corrections on the author's former paper (this vol., ii, 434).

**Tension at the Boundary of Two Layers.** G. N. ANTONOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 342—353. Compare this vol., ii, 334).—An improved form of the method employed by Guthrie (*Ann. Phys. Chem.*, 1867, [ii], 131, 129) for the determination of the tension at the boundary of two layers is described. The systems formed by water with the following liquids: benzene, ether, chloroform, and isobutyl and isoamyl alcohols, have been investigated, and although, as Quincke (*ibid.*, 1824, [ii], 1, 139) has pointed out,  $\alpha_{1,2}$ , the tension at the boundary of the two layers, cannot be calculated from the surface tensions of the two pure liquids, it is always equal to the difference between the surface tensions of the two phases formed by the liquids, provided the temperature is such as to ensure equilibrium between the layers. The changes in the surface tension of solutions cannot be explained on the purely mechanical principles applied by Packels (*ibid.*, 1899, [iii], 67, 668), for they are really caused by the chemical changes accompanying the formation of solutions.

Z. K.

**Diffusion of Metals in Mercury.** MAX VON WOGAU (*Ann. Physik.*, 1907, [iv], 23, 345—370).—The diffusion constants of a number of metals in mercury have been determined by the method which Graham used in studying the diffusion of salts in solution. Diffusion constants have been determined for the first time for lithium, sodium, potassium, rubidium, caesium, calcium, strontium, barium, tin, and thallium in mercury, and the temperature-coefficient of the diffusion constant has been determined for zinc, cadmium, and lead. The properties of amalgams of the alkali metals, of metals of the alkaline earths, and of thallium (1) in relation to their electromotive behaviour, and (2) in regard to their rate of diffusion, can be interpreted on the view that these metals when dissolved in mercury are in the monatomic condition.

J. C. P.

**Osmosis between Mineral Acids and Organic Salts.** J. P. MOSESHVILI (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 423—426).—The substances investigated were hydrochloric, nitric and sulphuric acids with sodium and barium acetate, using parchment as the semi-permeable membrane. The rate of osmosis of the mineral acids towards both water and the organic salts varies directly with the electrical conductivity of the acid, and is but little affected by the employment of very weak solutions of the organic salt. From these and other experiments, it is evident that the osmosis of substances

which react with one another proceeds according to the same laws as those for indifferent substances. Z. K.

**Osmotic Pressure of Colloids and the Action of Electrolytes on the Osmotic Pressure of Protein Solutions.** RALPH S. LILLIE (*Proc. Amer. physiol. Soc.*, 1907, xvi.; *Amer. J. Physiol.*, 19).—The osmotic pressure of solutions of egg-albumin and gelatin depends on the nature of concentration of the electrolytes in solution. Salts depress it, the degree of action depending on the character of the ions. Solutions of salts of the alkali metals depress to a less degree than those of the alkali earths, and these to a less degree than those of the heavy metals. The nature of the anions is also important; in general, the decreasing depressant action is  $\text{SO}_4 < \text{Cl} < \text{NO}_3 < \text{Br} < \text{I} > \text{CNS}$ . Salts with multivalent anions usually depress osmotic pressure more than those with univalent anions. The presence of non-electrolytes has little or no effect. The osmotic pressure of gelatin, but not of albumin, is greatly increased by the addition of small quantities of either acid or alkali. W. D. H.

**Atomic Energy of Gases.** HOLLAND CROMPTON (*Zeit. physikal. Chem.*, 1907, 59, 635—637).—If  $\lambda$  represents the ratio of the energy of a single atom to the molecular energy, then  $\lambda$  may be calculated by the formula  $\lambda = (C_p - 5)/3n$  or  $\lambda = (C_v - 3)/3n$ , where  $n$  is the number of atoms in the molecule. According to theory,  $\lambda$  must be less than 1, but the foregoing formulæ have for some substances given values greater than 1. This discrepancy is attributed by Ensrud (this vol., ii, 249) to incomplete vaporisation of the substances in question, but the author points out that it may be accounted for also by the variation of the specific heat with temperature. J. C. P.

**Composition of Solid Phases in Four-Component Systems.** JAMES M. BELL (*J. Physical Chem.*, 1907, 11, 394—395).—Schreinemakers (*Abstr.*, 1893, ii, 250) has pointed out how the composition of a solid phase in a three-component system which cannot be separated completely from the mother liquor can be determined indirectly, and the author now shows how by a slight modification the method may be extended to a four-component system. The method is applied in a subsequent paper. (See this vol., ii, 648). G. S.

**Polymorphic Transformations of Isomorphous Mixtures of Three Substances.** FRÉDÉRIC WALLERANT (*Compt. rend.*, 1907, 144, 1373—1374).—The sum of the distances between any point in an equilateral triangle and the three sides is constant. If a point be selected, so that the distances between it and the three sides taken in turn are proportional to the amounts of the three constituents in a mixed crystal, and from this point a perpendicular to the plane of the triangle is drawn, proportional to the temperature of transformation, a method of graphically representing the condition of a crystallising mass composed of three substances is obtained. As the composition changes, a segment of the surface between the three faces of the tetrahedron of which the equilateral triangle is the base will be

marked out, which will separate the zones of stability of two crystalline forms. The subject has been investigated experimentally for mixtures in varying proportions of cesium, thallium, and ammonium nitrates. When the three nitrates are melted and the fused mass cooled, magmas of cubical crystals separate, and these undergo various transformations depending on the relative proportions in which the three salts are present. Usually they become rhombohedra. These, when thallium nitrate is predominant, become orthorhombic at 80°. When ammonium nitrate is present in considerable quantity, the cubical crystals become quadratic, and where this salt is present in large amount, they become successively monoclinic and orthorhombic. In the graphic representation, the zones of stability for these various forms are separated by lacunæ, which represent the change of the cubical crystals into conglomerates of two forms of mixed crystals. A figure showing the distribution of the zones of stability and of the lacunæ is given in the original.

T. A. H.

**Relations between the [Equilibrium] Diagram of Binary Alloys and their Malleability.** LEON GUILLET (*Compt. rend.*, 1907, 144, 1273—1275).—Six cases are described. (1) In which the metals are deposited in the pure state. The *liquidus* consists of two branches of a curve with a eutectic point, the *solidus* of a horizontal line. If both metals are malleable, so are all their alloys (Pb-Cd); if one metal is malleable and the other non-malleable, the malleability of the alloys depends on that of the eutectic, that is, they will be malleable if the eutectic point more nearly approaches the side of the malleable metal (Pb-Sb) and *vice versa* (Pb-Bi); if neither metal is malleable, neither are their alloys. (2) In which the metals are only miscible in the solid state in the neighbourhood of the pure metals. The *liquidus* is similar to that of case (1), the *solidus* consists of a horizontal line and two branches of curves. If one of the metals is malleable, solid solutions containing much of it are always malleable. The malleability of other alloys follows the same laws as in the first case, but here the eutectic consists of two solid solutions. (3) The metals form compounds or solid solutions having constant solidifying points. The *liquidus* possesses one or several maxima, the *solidus* indicates solid solutions or compounds corresponding with these maxima. All the alloys containing the pure solid solution or those corresponding with pure compounds are non-malleable (Ni-Sn, Ni-Sb, &c.); only the alloys at the extremities of the diagram are malleable. (4) The metals form compounds or solid solutions which when pure decompose before liquefying. The *liquidus* exhibits one or more transition points, the *solidus* indicates a solid solution which is always non-malleable. Very small proportions of this solution are sufficient to render any of the alloys non-malleable (Cu-Cd). An alloy consisting of two solid solutions, one rich in a malleable metal, is only malleable when the amount of the second solution is small (Cu-Zn, Cu-Sn). (5) The metals are miscible in all proportions. Both *liquidus* and *solidus* consist of a single curve. The single solid solution is malleable if one metal is malleable. From this the conclusion is drawn that two isomorphous metals are either both malleable (Au-Ag, &c.) or both non-malleable

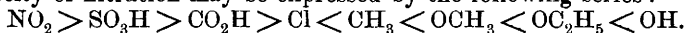
(Bi-Sb). (6) The alloys undergo transformations in the solid state, which are indicated by the diagram. The author concludes that the malleability of alloys can be determined by analysis of their equilibrium diagrams.  
E. H.

**Influence of Salt Solutions on the Velocity of Chemical Reaction.** ALBERT J. J. VANDEVELDE (*Chem. Weekblad*, 1907, 4, 381—385).—The author has found from experiments on the action of zinc on solutions of copper sulphate, cupric chloride, copper sulphate + sodium chloride, cupric chloride + sodium sulphate, sulphuric acid + sodium chloride, hydrochloric acid + sodium sulphate, sulphuric acid + sodium nitrate, nitric acid + sodium sulphate, hydrochloric acid + sodium nitrate, and nitric acid + sodium chloride, that the velocity of reaction is uninfluenced by the degree of ionisation, but depends on the nature of the ions present. It is increased by Cl-ions, and retarded by  $\text{SO}_4$ -ions.  
A. J. W.

**Kinetics of the Nitration Reaction. II.** HAAVARD MARTINSEN (*Zeitsch. physikal. Chem.*, 1907, 59, 605—634. Compare Abstr., 1905, ii, 149).—Two very suitable substances for a study of the rate of nitration in concentrated sulphuric acid are *p*-chloronitrobenzene and 4:6-dinitro-*m*-xylene. They are fairly soluble and are nitrated slowly, so that the course of the reaction can be conveniently determined with the aid of the nitrometer. The rate of nitration was determined for these and other aromatic substances (1) in 95%  $\text{H}_2\text{SO}_4$ ; (2) in 100%  $\text{H}_2\text{SO}_4$ . When the substance to be nitrated is an alkyl, halogen, nitro-, hydroxy-, or hydroxyalkyl-derivative of benzene, the rate of nitration is on the average three times as rapid in the 95% acid as in the 100% acid. When the substance to be nitrated is a carboxyl or sulphonic derivative, the ratio of the rates of nitration in these two media is much higher and more variable. For the first-named set of benzene derivatives, the rate of nitration becomes three times as great with a rise of temperature from 25° to 35°.

A considerable addition of phosphoric oxide to the 95% acid exerts no effect on the rate of nitration.

The relative influence of the various substituent groups on the velocity of nitration may be expressed by the following series:



Chlorine is put in the middle because it sometimes accelerates and sometimes retards nitration. Those groups to the left of chlorine retard nitration, and the further to the left the greater is the retarding influence. Those groups to the right of chlorine are found to accelerate nitration, and the further to the right the greater is the accelerating influence. It is noteworthy that when a substance with a retarding substituent group is nitrated, the nitro-group takes up the meta-position; when a substance with chlorine or an accelerating substituent group is nitrated, the nitro-group takes up the ortho- or the para-position.  
J. C. P.

**New Type of Catalysis. Acceleration by Chromic Acid of the Reaction between Bromic and Hydriodic Acids.** ROBERT H. CLARK (*J. Physical Chem.*, 1907, 11, 353—362. Compare this vol., ii, 77).—It was shown by Ostwald (Abstr., 1888, 1024) that the

rate of liberation of iodine in the reaction between bromic and hydriodic acids is accelerated by the addition of chromic acid to a much greater degree than corresponds with the simultaneous reduction of the latter, and that the acceleration is proportional to the concentration of chromic acid. The author has now confirmed and amplified these observations, and shows that the rate of reaction is proportional to the bromate and to the iodate concentration and to the  $n$ th-power of the acid concentration (hydrogen chloride being used). In the absence of chromic acid  $n=2$ , but as the chromate concentration increases,  $n$  gradually diminishes to unity.

To account for these results, it is suggested that two simultaneous and independent reactions are taking place, the rate of the former being proportional to the bromate and to the iodide concentrations, and to the square of the acid concentrations, and that of the latter to the bromate, iodide, chromate, and acid concentrations, without reduction of the chromate. The temperature-coefficient of the first reaction is 1.85, that of the latter, 1.19 for a rise of  $10^\circ$ .

The rate of oxidation of hydriodic and hydrobromic acids by the oxy-acids of halogens, other than that of hydriodic by bromic acid, is not affected by the presence of potassium dichromate. G. S.

**Dissociation of Sulphuric and Arsenic Acids.** ROBERT LUTHER (*Zeitsch. Elektrochem.*, 1907, 13, 294—297).—Using the most trustworthy measurements of the freezing points and electrolytic conductivities of solutions of sulphuric and arsenic acids, the author draws the following conclusions: the mobility of the ion  $\text{HSO}_4'$  is almost the same as that of  $\frac{1}{2}\text{SO}_4''$ , that is, at  $15^\circ$ , 62.5, at  $18^\circ$ , 67, and at  $25^\circ$ , 78. The first dissociation of sulphuric acid,  $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4'$ , is similar to that of the strongest monobasic acids. The second dissociation,  $\text{HSO}_4' \rightleftharpoons \text{H}^+ + \text{SO}_4''$ , takes place in accordance with the expression  $[\text{SO}_4''][\text{H}^+]/[\text{HSO}_4'] = 0.013$  approximately. Temperature has no appreciable influence on the value of the constant. The dissociation of arsenic acid,  $\text{H}_3\text{AsO}_4 \rightleftharpoons \text{H}_2\text{AsO}_4' + \text{H}^+$ , is expressed by the formula  $[\text{H}_2\text{AsO}_4'][\text{H}^+]/[\text{H}_3\text{AsO}_4] = 0.005$ . T. E.

**Hydrolysis of Salts.** AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1907, 144, 1284—1285).—Tortelli's classification of the rosaniline hydrochlorides as salts because of the complete precipitation of the chlorine they contain by silver nitrate (Abstr., 1895, i, 540) is invalid, since some esters, for example, triphenylchloromethane, undergo the same reaction. With other esters, the reaction takes place at rates varying with the ester, previous hydrolysis being necessary. This slow hydrolysis is also observed with Scheurer-Kestner's iron acetochlorides (*Bull. Soc. chim.*, 1863, i, [i], 5, 343), Recoura's chromium sulphates (Abstr., 1892, 411, 783; 1893, ii, 470), and with the triphenylmethane methiodides (Abstr., 1896, i, 376). Thus there are both esters and salts which hydrolyse slowly, and as there are esters which are hydrolysed instantaneously, there should be salts which hydrolyse equally rapidly. In fact, the author considers that all salts of which the aqueous solutions obey Berthollet's laws are completely hydrolysed in solution. This view is supported by the facts that (1) the clear

concentrated solutions of many salts become cloudy on dilution owing to the separation of base, acid, or basic salt; (2) in solutions of other salts hydrolysis is revealed by separation of acid and base by diffusion; (3) the hydrochlorides of methylene-blue, hexamethyl-violet, and malachite-green are hydrolysed by water; and (4) for other salts, such as sodium chloride, the separation of the products of hydrolysis of which is prevented by their solubility, complete hydrolysis agrees with the so-called abnormal osmotic pressures, cryoscopic and ebullioscopic constants exhibited by them.

The author considers that the substances resulting from the action of an acid on an alcohol or a base, on dissolution, undergo quickly or slowly the inverse reaction, and that this breaking up of the molecule renders the ionic dissociation hypothesis useless for esters and salts.

E. H.

**Hydrolysis of Esters of Multivalent Alcohols.** ROBERT KREMANN (*Zeitsch. Elektrochem.*, 1907, 13, 307).—The measurements of the rate of hydrolysis of the glycol acetates, made by J. Meyer (this vol., i, 462), are in good agreement with the theory given by Abel (*Abstr.*, 1906, ii, 731).

T. E.

**Boundary between the Solid and Liquid Conditions in Gelatin Solutions.** C. ROHLOFF and SHINJO (*Physikal. Zeitsch.*, 1907, 13, 442—446).—The elasticity of gelatin solutions of various strengths has been measured with an apparatus in which the gelatin was contained between two concentric spheres, the inner of which was suspended by a wire attached to a torsion head. The movement of the inner sphere, resulting from a turn of the torsion head, was observed by means of a scale and reflecting mirror. The data obtained indicate that the coefficient of elasticity of gelatin solutions increases with time, and this is supposed to be due to changes in constitution of the jelly. If curves are plotted to show the variation of the elasticity with the concentration, evidence is obtained that at a concentration of 0.18% of gelatin the elasticity is zero and solidification of the solution does not occur.

H. M. D.

**Formation and Transformation of Mixed Crystals and Double Salts in the Binary Systems of the Dimorphous Sulphates of Lithium, Sodium, Potassium, and Silver.** RICHARD NACKEN (*Jahrb. Min. Beil.-Bd.*, 1907, 24, 1—68).—By an optical method, as well as by a study of cooling curves, it has been shown that the sulphates of lithium, sodium, potassium, and silver all undergo reversible transformation. The transition temperatures are as follows: lithium sulphate (m. p. 843°), 573°; sodium sulphate (m. p. 883°), 234°; potassium sulphate (m. p. 1076°), 595°; silver sulphate (m. p. 651°), 412°. The systems  $\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4 + \text{K}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4$  have been studied in detail, and the corresponding temperature-concentration diagrams have been drawn. From these the existence of the following compounds has been deduced:  $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ ;  $2\text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4$ ;  $2\text{Li}_2\text{SO}_4 \cdot 3\text{Ag}_2\text{SO}_4$ ;  $\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ;  $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4 \cdot 3\text{Ag}_2\text{SO}_4$ .

The first three of these compounds separate as such from the corresponding fused mixtures; the last three are produced from isomorphous mixtures which have been formed in the primary crystallisations. Of the foregoing compounds, the only one which is dimorphous is  $\text{Li}_2\text{SO}_4, \text{K}_2\text{SO}_4$ , which has a transition temperature at  $435^\circ$ .

Continuous freezing point curves have been recorded for the systems  $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$ ;  $\text{Na}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4$ ;  $\text{K}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4$ .

Further, the compounds  $2\text{Li}_2\text{SO}_4, 3\text{Ag}_2\text{SO}_4$  and  $2\text{Li}_2\text{SO}_4, 3\text{Na}_2\text{SO}_4$  form a continuous series of mixed crystals with each of their components.

A continuous transition point curve has been observed only in the case of the mixed crystals formed from sodium and silver sulphates. In most other cases (the system  $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$  is an exception) the mixed crystals are transformed into conglomerates.

The systems  $\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4$  furnish new types of transition point diagrams in that the double salts formed in these systems decompose when the temperature is lowered; thus the compound  $2\text{Li}_2\text{SO}_4, 3\text{Na}_2\text{SO}_4$  is capable of existence only between  $630^\circ$  and  $503^\circ$ , and the compound  $2\text{Li}_2\text{SO}_4, 3\text{Ag}_2\text{SO}_4$  only between  $572^\circ$  and  $420^\circ$ . It appears, further, that in these cases the transition point curve exhibits a discontinuity at a concentration corresponding with the composition of the double salt.

J. C. P.

**Ionic and Chromophoric Theory of Indicators.** ARTHUR HANTZSCH (*Ber.*, 1907, 40, 3017—3020).—A criticism of the views recently expressed by Rohland (this vol., ii, 519).

A. McK.

**Recent Investigations on Atomic Weights.** THEODORE W. RICHARDS (*Ber.*, 1907, 40, 2767—2779).—A lecture delivered to the German Chemical Society.

A. McK.

**A New Basis for Atomic Weights.** FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1907, 212—216).—It is suggested that the atomic weights should be based on the C.G.S. system by defining the molecular weight of a substance as the quantity of matter, expressed in grams, which in the state of a perfect gas is fixed by a pressure, volume, and absolute temperature such that  $PV/T = 10^n$ . If  $P$  is measured in dynes,  $V$  in cubic centimetres, energy in joules, and  $n = 1$ , the new atomic weights will equal the old atomic weights  $\times 1.2022$ . The atomic weight of oxygen will become 19.2, that of hydrogen, 1.21.

A system which greatly simplifies electrochemical calculations would be attained by fixing as the equivalent of an element that quantity which carries  $10^n$  coulombs. If  $n$  is made equal to 5, the conversion of the old system into the new would be effected by multiplying by 1.0359. Of the two systems, the first is preferable as being based more directly on chemical theory.

E. H.

**The Most Urgent Problem of Chemistry.** RAFFAELE NASINI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 847—853).—A reply to the criticisms of Wald (*Das nächste Problem der Chemie*, Ostwald's *Annalen der Naturphil.*, 6) on the author's views (*Abstr.*, 1905, ii, 514).

T. H. P.



**A New Laboratory Drying Apparatus.** PAUL DRAWE (*Chem. Zeit.*, 1907, 31, 655).—The apparatus consists of an outer horizontal copper cylinder, 50 cm.  $\times$  17 cm., through which passes lengthwise a copper tube, 60 cm.  $\times$  4 cm. The cylinder contains either water or toluene, and is fitted with a Soxhlet's double-sphere condenser; the vapour of the boiling liquid heats the tube, in which are placed boats containing the substance to be dried. In cases where the substance is liable to undergo oxidation, a stream of dry coal-gas is passed through the tube, then through a calcium chloride drying tower, and subsequently conveyed to the burner used for heating the apparatus.

W. H. G.

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## Inorganic Chemistry.

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**Loss of Nitre in the Chamber Process.** III. JOHN K. H. INGLIS (*J. Soc. Chem. Ind.*, 1907, 26, 668—670).—With the object of directly estimating any nitric acid that might be present in the flue gases, the method of analysis previously employed (*Abstr.*, 1906, ii, 226) has been further elaborated. From the results so obtained, the author concludes that a considerable portion of the nitre is lost as nitric peroxide and nitric oxide, the relative proportions of these two substances depending on the escape of sulphur dioxide. The loss of nitre as nitrous oxide is less than 10% of the total loss. There is also a possible reduction to nitrogen. W. H. G.

**Selenium.** WILLIAM ECHSNER DE CONINCK and RAYNAUD (*Bull. Acad. roy. Belg.*, 1907, 365).—When a moderately concentrated aqueous solution of selenious acid is treated with a solution of sulphur dioxide, saturated at the ordinary temperature, the selenium is precipitated. After exposure to diffused daylight, part of the latter gradually acquires a metallic appearance and is transformed into grey crystalline leaflets having a fine lustre; the remainder undergoes a slight agglomeration, but does not change colour and remains amorphous. The former change is visibly enhanced by sunlight. The authors consider that in this precipitation at least two varieties of selenium are formed. E. H.

**Action of Fluorine on Selenium in Glass Vessels.** PAUL LEBEAU (*Compt. rend.*, 1907, 144, 1347—1348).—In continuation of previous work (this vol., ii, 540) on Prideaux's supposed selenium hexafluoride (*Trans.*, 1906, 89, 316), and in reply to Ramsay (*Compt. rend.*, 1907, 144, 1196), it is suggested that Prideaux's compound may be a mixture of oxyfluorides, or of a fluoride with oxyfluoride, since on fractionation it can be separated into products of different density and composition. Ramsay's suggestion (*loc. cit.*) that the formation of selenium tetrafluoride, when selenium is treated with fluorine in copper vessels, is due to the reducing action of the copper is insufficient

as an explanation of this reaction, since the tetrafluoride is also formed when selenium is treated with fluorine in platinum vessels, and in the action of fluorine on selenium in presence of glass. T. A. H.

**Preparation of Selenic Acid from Selenious Acid.** R. TH. GLAUSER (*Chem. Zeit.*, 1907, 31, 630).—Selenic acid is readily prepared from selenious acid by the electrolysis of a strong solution of the latter in concentrated nitric acid at temperatures between 50–80°, with an anode current density of 4–5 amperes per sq. cm. for quantities of solution of roughly 100 c.c. and a small cathode current density. Under these conditions, it is possible to convert 1 gram of selenium dioxide completely into selenic acid in four to five ampere hours.

W. H. G.

**Application of the Law of Mass Action to the Combustion of Nitrogen in the High Tension Flame.** W. NÜRANEN and MAX LE BLANC (*Zeitsch. Elektrochem.*, 1907, 13, 297–305).—The flame is produced by the passage of an alternating current of 50 periods per second, transformed to 4000 or 6000 volts, between electrodes consisting of Nernst filaments. A mixture of oxygen and nitrogen is exposed to the flame in a glass globe until equilibrium is attained. The results show that the value of the expression  $[\text{NO}]^2/[\text{N}_2][\text{O}_2]$  is nearly constant when the percentage of oxygen in the mixture is increased from 3 to 87, provided the current is kept constant. This result is to be expected if the reaction  $\text{NO} = \text{N} + \text{O}$  is unimolecular in those parts of the flame where the temperature is too low for equilibrium to be reached.

Other experiments in which the gases from the flame are cooled rapidly, by means of a water-cooled quartz tube, show that larger yields of nitric oxide are obtainable in this way and that the law of mass action still holds good. T. E.

**Some Oxidising and Decolorising Properties of Graphite.** HENRI LOUIS DEJUST (*Compt. rend.*, 1907, 144, 1264–1265).—Graphite will decolorise solutions of litmus, red wine, or sulphoindigotic acid. By shaking 100 c.c. of a solution of litmus containing 0.98% extract at 100° with 5 grams of commercial graphite (containing 79% carbon) for thirty seconds, it is completely decolorised. The decolorising power is reduced by purification of the graphite. The acid, neutral, or alkaline condition of the liquid has very little effect on the activity of graphite, but a considerable influence on that of animal charcoal. The decolorising values of graphite and charcoal in terms of the thickness of the partially decolorised liquid having the same intensity of colour as unit thickness of the original solution being: graphite (containing 79% carbon), 6.8 in neutral solution; graphite (containing 93.1% carbon), 2 in neutral and alkaline solution, 2.2 in acid solution; animal charcoal, 1.8 in alkaline solution, complete decolorisation in neutral and acid solution. A solution of *p*-phenylenediamine in contact with graphite in air acquires a brown coloration (compare Cazeneuve, *Abstr.*, 1890, 690). The graphite will, however, decolorise in the absence of all air other than that occluded. E. H.

**Revision of the Atomic Weight of Potassium. II. The Analysis of Potassium Bromide.** THEODORE W. RICHARDS and EDWARD MUELLER (*Zeitsch. anorg. Chem.*, 1907, **53**, 423—445; *J. Amer. Chem. Soc.*, 1907, **29**, 639—656).—As it was found that potassium bromide could not readily be purified, pure potassium oxalate and pure bromine were prepared and the pure bromide then obtained by direct action of bromine on the oxalate.

In addition to the bromide prepared from the two samples of oxalate, a third supply was obtained by the action of potassium hydroxide (prepared by an electrolytic method) on ammonium bromide.

The precautions taken in precipitating, washing, and drying the silver salt were practically the same as those described in previous papers. Before being weighed out, the potassium bromide was fused on platinum in a current of nitrogen.

The mean of four determinations of the ratio  $\text{KBr} : \text{AgBr}$  gave for the atomic weight of potassium the value 39.1135, whilst twelve very concordant values for the ratio  $\text{KBr} : \text{Ag}$  gave as a mean,  $\text{K} = 39.1143$ . The corresponding ratios with the chloride (Richards and Staehler, *Abstr.*, 1906, ii, 848) gave for the atomic weight the values 39.1134 and 39.1145 respectively.

Combining the values obtained in all the series,  $\text{K} = 39.114$  ( $\text{O} = 16$ ), may be taken as the most probable value [ $\text{Ag} = 107.93$ ,  $\text{Cl} = 35.473$ ,  $\text{Br} = 79.953$ ].  
G. S.

**Preparation of Lithia.** ROBERT DE FORCRAND (*Compt. rend.*, 1907, **144**, 1321—1323).—The methods suggested by Troost (*Ann. chim. phys.*, 1857, [iii], **51**, 112) for the preparation of lithia, namely: (1) combustion of the metal, contained in an iron crucible, in a current of oxygen; (2) decomposition of the nitrate at a red heat in a silver crucible, and (3) ignition of a mixture of the carbonate with carbon in a platinum crucible, yield impure products.

Kahlbaum's lithium hydroxide contains 0.91% of impurities (ferric oxide and silicates), and on ignition at  $660^\circ$  in a platinum crucible in a current of dry hydrogen, is dehydrated in from seven to eight hours, or in one hour at  $780^\circ$ , yielding lithium oxide as a colourless, porous mass, which begins to volatilise at  $800^\circ$  to  $820^\circ$ . Hydrated lithium hydroxide,  $\text{LiOH} \cdot \text{H}_2\text{O}$  (*Abstr.*, 1906, ii, 445), is converted similarly into lithia when heated in a current of hydrogen at  $780^\circ$  during one hour.  
T. A. H.

**Ammonium Amalgam.** GEORGE MCPHAIL SMITH (*Ber.*, 1907, **40**, 2941—2947; *J. Amer. Chem. Soc.*, 1907, **29**, 844—855. Compare Le Blanc, *Abstr.*, 1890, 1204; Moissan, 1902, ii, 71; this vol., ii, 459; Rich and Travers, *Trans.*, 1906, **89**, 872).—The author considers Le Blanc's view that ammonium amalgam is a compound of ammonium and mercury to be correct. Moissan's experiments were repeated with the amalgams of sodium, potassium, lithium, barium, strontium, and calcium in ammonium hydroxide solution as well as ammonium chloride, and although the sodium amalgam, for example, swells twenty-fold in ammonium chloride solution, there is only a slight increase in volume in aqueous ammonia.

The conclusion is drawn that Moissan's experiments are irrelevant. Evidence is submitted that this amalgam is strictly analogous to those of the alkali or alkaline earth metals, and that the ammonia amalgam is a solution of  $Hgm \cdot NH_4$  in mercury where  $m$  is large (compare this vol., ii, 463).  
W. R.

**Action of Ozone on Metallic Silver and Mercury.** WILHELM MANCHOT and W. KAMPSCHULTE (*Ber.*, 1907, 40, 2891—2898).—The black stain produced by the action of ozone on silver is best shown when the metal is heated in a flame and then allowed to cool while the ozone impinges on it. Experiments at different temperatures show that the maximum effect is produced between  $220^\circ$  and  $240^\circ$ . At higher temperatures, the iridescent coloration is less marked, and at  $450^\circ$  no change is noticeable. Dry and moist ozone produce similar effects; the concentration of the ozone employed was 0.2 volume per cent. The silver surface must be specially purified, as otherwise darkening occurs at the ordinary temperature. The best method is to wash several times with benzene, polish with moist sand, and rub with a clean, dry cloth. It has been found that minute traces of numerous substances when present on the surface of the metal will cause a blackening at the ordinary temperature. Included in such substances are the oxides of most of the heavy metals, and finely-divided ruthenium, palladium, and platinum, in fact, substances which act as catalytic oxygen carriers.

When a sheet of silver, which has been blackened by ozone, is strongly heated, the colour disappears, but when exposed to ozone again at the ordinary temperature, is immediately blackened; this is probably due to minute particles of oxide which have not been decomposed at the high temperature. A plate which has been immersed in dilute nitric acid for several hours and then thoroughly washed and dried is also immediately blackened at the ordinary temperature, and it retains this property even after being heated to just below the melting point. A thorough rubbing with sand, however, destroys the activity. The increased activity of silver, due to the treatments already mentioned, gradually diminishes when the plate is kept.

The colorations produced at higher temperatures are more permanent than those obtained at the ordinary temperature.

In the case of mercury, brown vapours are noticeable at  $120^\circ$ , and these increase to a temperature of  $170^\circ$ , when the metallic surface assumes a blue colour. At temperatures above  $170^\circ$ , the effects are less marked, and at  $250^\circ$  no change in the appearance of the metal can be observed.  
J. J. S.

**Gaylussite and a Second Double Salt of Calcium and Sodium Carbonates.** O. BÜTSCHLI (*J. pr. Chem.*, 1907, [ii], 75, 556—560. Compare this vol., ii, 544).—In continuation of his investigation of the double carbonates of calcium, the author has studied the formation of gaylussite. This is formed by the action of an excess of a saturated solution of sodium carbonate on calcium chloride, or on either of the two calcium potassium carbonates described previously; it loses its water of crystallisation at  $105^\circ$ , becoming opaque. The gaylussite crystals are re-formed by the action

of saturated aqueous sodium carbonate on the effloresced substance. A second *calcium sodium carbonate*,  $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ , is obtained in rhombic or monoclinic crystals by the action of sodium hydroxide and carbonate on precipitated calcium carbonate. The hexagonal calcium potassium carbonate,  $2\text{CaCO}_3 \cdot 3\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$ , is formed by the action of saturated potassium carbonate solutions on either of the two calcium sodium carbonates.

Whilst the formation of calcium sodium carbonate takes place rapidly from amorphous calcium carbonate; arragonite crystals yield only a moderate amount, and calc spar almost none, of the double carbonate when in contact with sodium carbonate solution for thirty-six hours. These differences in behaviour of the various forms of calcium carbonate are applied to the determination of the nature of animal calcium carbonate deposits. G. Y.

**Phosphates of Magnesium and Iron.** FRANK K. CAMERON and JAMES M. BELL (*J. Physical Chem.*, 1907, 11, 363—368).—The composition of the acid solutions in equilibrium with the phosphates of magnesium and iron respectively at  $25^\circ$  has been determined by solubility measurements in the usual way.

In the case of magnesium, the solutions were prepared by adding dimagnesium phosphate,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ , to solutions of phosphoric acid of varying concentration and agitating continuously until equilibrium was attained. The stable solid in contact with the more dilute solutions is the dimagnesium phosphate just mentioned, whilst very concentrated solutions, containing over 700 grams of phosphoric acid ( $\text{P}_2\text{O}_5$ ) per litre, are in equilibrium with the compound  $\text{MgH}_4(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ . For solutions in contact with the former salt, the proportion of magnesia in solution increases regularly with increased concentration of phosphoric acid, whilst for those in equilibrium with the latter salt, the concentration of magnesia diminishes with increasing phosphoric acid concentration. Some evidence has been obtained that a magnesium phosphate more basic than the diphosphate exists at  $25^\circ$  in contact with very dilute solutions of phosphoric acid.

The action of water or of dilute phosphoric acid on ferric phosphate (compare Abstr., 1904, ii, 655) is similar to that on the phosphates of calcium and magnesium, the acid being removed more rapidly than the base so that a more basic precipitate results. In the former case, however, the composition of the solid phase varies continuously, indicating the formation of a solid solution. G. S.

**Electrolytic Precipitation of Zinc.** RALPH C. SNOWDON (*J. Physical Chem.*, 1907, 11, 369—381).—The metal was deposited both from acid and alkaline solutions of varying concentrations at  $20^\circ$ ,  $40^\circ$ , and  $70^\circ$ , a rapidly rotating zinc cathode between two zinc anodes being employed. Attention was specially directed to the conditions, including voltage (between the terminals) and current density, necessary for obtaining good deposits, and the results of numerous experiments are given in tabular form.

The results depend very largely on the speed at which the cathode is rotated, but the majority of the experiments had been made before

this fact was discovered. When the cathode is rotated very rapidly, good deposits can be obtained in acid and alkaline solutions even with a current density of 60 amp./dm<sup>2</sup>. The deposits from alkaline solutions are smoother than those obtained in the presence of acid; moreover, the voltage across the terminals in the former case is very low and the current efficiency high. An increase in concentration or in temperature causes an increase in the size of the crystals of the deposit, whilst an increase in the current density has the opposite effect.

The effect of reducing agents, such as resorcinol and formaldehyde, on the character of the deposit has also been investigated. G. S.

**Potential and Nature of Alloys.** NICOLAI A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 353—398. Compare *Trans.*, 1897, 71, 417; *Abstr.*, 1898, ii, 582; 1905, ii, 146; this vol., ii, 325).—The potential curves of the alloys, tin and bismuth, zinc and cadmium, confirm the results obtained by other methods, that these metals form no definite compounds and no solid solutions with one another.

The alloys formed by zinc with copper, silver and gold are very similar to one another. All the physical, chemical, and mechanical properties of these alloys indicate the existence of a whole series of definite compounds of the types  $Zn_6M$ ,  $Zn_4M$ ,  $Zn_2M$ ,  $ZnM$ ,  $ZnM_2$  (where  $M = Cu, Ag, Au$ ). The potential curve of zinc-copper indicates all these, with the possible exception of  $Zn_4Cu$ . Contrary to Shepherd (*Abstr.*, 1904, ii, 662), it is shown that Roberts-Austen's melting point curve does not indicate merely the existence of solid solutions between zinc and copper, but is in complete accordance with the existence of all these definite compounds. The potential curve of zinc-silver alloys indicates all these compounds with the exception of  $ZnAg$ . Petrenko's formulæ for these alloys (*Abstr.*, 1906, ii, 284) are probably incorrect. The potential curve of zinc-gold only indicates three compounds,  $Zn_6Au$ ,  $Zn_2Au$ ,  $ZnAu$ , and possibly the formation of solid solutions between gold and  $Zn_3Au$ ,  $Zn_6Au$  and  $Zn_2Au$ , and  $ZnAu$  and  $Au$ . Contrary to Vogel (*Abstr.*, 1906, ii, 287, 288), it is considered that such compounds as  $Zn_8Au$  and  $Zn_5Au_3$  do not exist.

The potential curve for cadmium-copper indicates: (1) the compound  $Cd_2Cu$ , which is very similar to  $Zn_2Cu$ , -Ag, -Au; (2) solid solutions of cadmium in  $Cd_2Cu$ , and (3) of  $Cd_2Cu$  in copper.

In all the systems investigated, the more electro-positive element forms solid solutions of considerable concentration. In general, the light metals of the second group give alloys with the heavy metals of the first and *vice versa*. The alloys formed by tin with copper, silver, and gold are very similar to one another and, contrary to Neville and Heycock (*Phil. Trans.*, 1897, A, 189, 40), the system tin-silver is shown to be completely analogous with the system tin-copper and not with that of lead-silver. The potential curves indicate the compounds  $SnCu_2$ ,  $SnCu_3$ ,  $SnAg_3$ , and possibly  $SnAg_5$  or  $Ag_6$ ,  $Sn_2Au$ ,  $SnAu$ . The three metals, tin, copper, and silver, form alloys together of very low melting point; the potential diagram indicates the possibility of a gradual transition from  $Cu_3Sn \rightarrow Cu_2AgSn \rightarrow CuAg_3Sn \rightarrow Ag_3Sn$ .

Z. K.

**Action of Nitric Acid on Certain Alloys.** CLEMENTE MONTMARTINI and ETTORE COLONNA (*Atti R. Accad. Sci. Torino*, 1907, 42, 551—564. Compare Abstr., 1892, 1278, 1279, 1402).—The authors have determined the amounts of ammonia evolved when the following zinc alloys are treated with nitric acid in large excess and in concentration varying from 0.25% to 60%, the temperature in all cases lying between 7° and 10°. Curves are given showing the amounts of ammonia evolved per 1 gram of alloy for the acids of different strength. Zinc-magnesium alloy containing 10.36% of magnesium; zinc-aluminium with 8.45% Al; zinc-cadmium containing 9.91% Cd; zinc-bismuth, 9.01% Bi; zinc-tin, 12.35% Sn; zinc-copper, 6.36% Cu; zinc-silver, 10.20% Ag.

For the zinc-silver and zinc-copper alloys, the production of ammonia is greatest for the most dilute acid. The zinc-tin alloy curve exhibits two maxima, one for very dilute and the other for about 40% acid. The other curves indicate a maximum production of ammonia for an acid of moderate concentration. In all cases the formation of ammonia tends to cease when very concentrated acid is used. With none of the alloys was hydrogen produced by the action of 27.5% nitric acid.

T. H. P.

**Reduction of Zinc Oxide.** F. O. DOELTZ and C. A. GRAUMANN (*Metallurgie*, 1907, 4, 290—293).—The reduction of zinc oxide by carbon in an atmosphere of nitrogen begins at 800° and increases rapidly with the temperature. The reduction by carbon monoxide commences at 600°, and also increases rapidly with rising temperature.

C. H. D.

**Melting Point of Lead Oxide.** F. O. DOELTZ and WL. MOSTOWITSCH (*Metallurgie*, 1907, 4, 289—290).—Pure lead oxide melts at 906°. The sintering observed at 850° when the powdered substance is slowly heated, is due to sublimation, and has also been noticed in the cases of zinc oxide, cadmium oxide, and lead sulphide.

C. H. D.

**Chemical Equilibrium of the Reaction between Lead Sulphide and its Oxidation Products.** II. RUDOLF SCHENCK and W. RASSBACH (*Ber.*, 1907, 40, 2947—2950. Compare this vol., ii, 546).—Doeltz and Mostowitsch's determination that lead oxide has m. p. 906° (preceding abstract) necessitates some modification of the authors' views. The fact that, on heating lead sulphide with oxide and metal, the equilibrium pressure of the sulphur dioxide obtained for any temperature between 700° and 850° is less than that found when a small excess of sulphur dioxide reacts with the solid product is explained as due to lead sulphate being formed in addition to the sulphide and oxide. The lead oxide is not, however, saturated with sulphate, but the sulphate solution saturated with oxide is in equilibrium with solid oxide. A diagram is given connecting all the possible reactions between lead, its oxide, sulphide and sulphate, and sulphur dioxide.

W. R.



**Alloys of Copper, Silver, and Lead.** K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1907, 4, 293—315).—A complete study of the binary and ternary alloys of copper, silver, and lead has been made. The freezing point curve of the copper-silver alloys is in agreement with that determined by Heycock and Neville (Abstr., 1897, ii, 245), but a determination of the solidus and of the eutectic times enables the diagram to be completed. Silver forms a solid solution containing up to 60% of copper at the ordinary temperature. The copper crystals are free from silver.

The freezing points found for the copper-lead alloys are in agreement with those found by Heycock and Neville (*loc. cit.*).

The freezing point surface of the ternary system is represented by a projection on a triangular diagram, and by a series of sections cut parallel with the sides of the triangle. The ternary eutectic contains 97.5% lead, 0.5% copper, and 2.0% silver, and melts at 302°. The three types of crystals observed are: copper containing some silver and possibly a little lead, silver containing both copper and lead, and practically pure lead. Within certain limits of composition, separation into two liquid layers takes place, but this tendency to separate is lessened by the presence of silver.

The paper is illustrated with thirty-four photo-micrographs.

C. H. D.

**Complex Carbonates.** THOMAS B. WOOD and HUMPHREY O. JONES (*Proc. Camb. Phil. Soc.*, 1907, 14, 171—176).—The copper potassium carbonate,  $K_2CO_3 \cdot CuCO_3$ , obtained by Reynolds (Trans., 1898, 73, 263) by adding copper acetate to a concentrated solution of potassium carbonate, is also obtained by shaking for several days a solution of 100 grams of potassium carbonate in 100 c.c. of water with a mixture of the basic copper carbonate,  $CuCO_3 \cdot Cu(OH)_2 \cdot 2H_2O$ , potassium carbonate, and hydrogen carbonate in the proportions required by the equation  $CuCO_3 \cdot Cu(OH)_2 \cdot 2H_2O + 2KHCO_3 + K_2CO_3 = 2CuCO_3 \cdot K_2CO_3 + 4H_2O$ . The double salt decomposes in contact with water, with the production of basic copper carbonate. A solution of potassium carbonate containing 85 grams to 100 c.c. of water dissolves the double carbonate, forming a deep blue solution, which, if not saturated with copper carbonate, does not change on boiling.

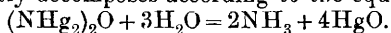
Solutions of basic copper carbonate give a precipitate of copper hydroxide on heating; the addition of potassium hydrogen carbonate prevents this decomposition. If potassium hydroxide is added to the hot solutions which are stable on boiling, a precipitate of copper hydroxide is at once obtained. From this it follows that the function of the hydrogen carbonate in the solutions of Soldaini (Abstr., 1877, i, 345) and Ost (Abstr., 1890, ii, 1031) is to ensure that the copper and potassium are combined with, or in equilibrium with,  $CO_3$  ions and not with hydroxyl ions. From its behaviour on electrolysis, the double salt probably has the formula suggested by Reynolds, and dissociates into the ions  $2K$  and  $Cu(CO_3)_2$ . The anion,  $Cu(CO_3)_2$ , dissociates partially into  $Cu$  and  $CO_3$  ions, since the copper is precipitated by ammonium sulphide and potassium ferrocyanide. From analytical results, it is probable that Gröger's salt (Abstr., 1901, ii, 240) is a

mixture; a solution of this salt in a strong solution of potassium carbonate deposits the double carbonate,  $K_2CO_3 \cdot CuCO_3 \cdot H_2O$ , described by Reynolds (*loc. cit.*); the formation of the salt  $K_2CO_3 \cdot CoCO_3 \cdot 4H_2O$ , obtained by this author, was not observed. The pink double cobalt potassium carbonate,  $K_2CO_3 \cdot CoCO_3 \cdot 4H_2O$ , prepared by Deville, is similar to the corresponding copper salt; its solution does not give any precipitate on boiling, but becomes blue, returning to the original pink colour when cool. From its behaviour on electrolysis, it is probable that there is present the complex ion  $Co(CO_3)_2$ , which is pink and negatively charged.

W. H. G.

[Millon's Base.] H. GAUDECHON (*Compt. rend.*, 1907, 144, 1268—1270).—When recently precipitated yellow mercuric oxide, which either has not been dried, or has been dried in a vacuum at  $15^\circ$ , is added to ammonia, the compound,  $(NHg_2)_2O \cdot nH_2O$ , is formed immediately. Gerresheim's tetrahydrate is obtained under these conditions as an amorphous, yellow powder. The only hydrate stable in dry air at  $10$ — $15^\circ$  is  $(NHg_2)_2O \cdot H_2O$ . The tetrahydrate is stable at  $0$ — $20^\circ$  in an atmosphere saturated with water, but free from carbon dioxide, but in dry air containing ammonia it loses  $3H_2O$ , forming the brown, amorphous monohydrate, which reabsorbs water from a moist atmosphere, passing back into the yellow tetrahydrate. By heating the latter at  $100^\circ$  in an atmosphere containing ammonia, but free from carbon dioxide, Weyl's anhydrous base,  $(NHg_2)_2O$ , is obtained in a brown, amorphous condition. This absorbs  $4H_2O$  when kept in air saturated with water, and re-acquires a yellow colour. The anhydrous base can also be prepared by treating mercuric oxide at  $100^\circ$  with gaseous ammonia, but is then formed in a condition in which it does not absorb water.

When the finely-ground base, free from carbonate, is boiled with water, it completely decomposes according to the equation:



The decomposition is slow, and the reaction is shown to be a balanced one. The mercuric oxide separates, not in the known yellow or red form, but as transparent, brown needles.

E. H.

**Solubility of Alumina in Aluminium Sulphide and of Magnesia in Magnesium Sulphide.** MARCEL HOUDARD (*Compt. rend.*, 1907, 144, 1349—1351).—By heating alumina in five times its weight of aluminium sulphide in the electric furnace, the crucible being suitably insulated to allow of slow cooling, a mass is obtained, which, on treatment with hydrochloric acid, leaves a residue of alumina crystallising in rhombohedra, which act on polarised light. Attempts to produce coloured alumina crystals by means of chromium, under these conditions, were unsuccessful.

By the same method, using magnesia and magnesium sulphide, cubical crystals of magnesia were obtained, having  $D^0$  3.579—3.582 (compare Ditte, *Compt. rend.*, 1871, 73, 111, 191, and Moissan, *Abstr.*, 1894, ii, 281). The crystallised magnesia dissolves slowly in warm hydrochloric or nitric acid, and rapidly in warm sulphuric acid. The crystals are without action on polarised light.

T. A. H.

**Absolute Atomic Weight of Manganese.** GUSTAVE D. HINRICHS (*Compt. rend.*, 1907, 144, 1343—1344).—Using the data afforded by Baxter and Hines' revision of the atomic weight of manganese (this vol., ii, 28) and applying the method of calculation suggested previously (*Abstr.*, 1893, ii, 317), the author finds that the value 55 should be accepted for the atomic weight of manganese in place of the value 54·951 to 54·959, adopted by Baxter and Hines. The value deduced from the first series of determinations made by these authors is shown to be more trustworthy than those obtained from the second, third, and fourth series of determinations.

T. A. H.

**Alloys of Nickel and Tin.** EMILE VIGOUROUX (*Compt. rend.*, 1907, 144, 1351—1353. Compare this vol., ii, 354).—Alloys of nickel and tin containing respectively 9·01, 22·74, 35·05, and 37·50% of the latter metal were prepared. All of these were magnetic, and, on treatment with nitric acid, the greater part of the nickel passed into solution, leaving a crystalline residue mixed, in the case of the alloys richer in tin, with some metastannic acid, which could be removed by treatment with a solution of potassium hydroxide. The crystalline residue has the composition represented by the formula  $\text{Ni}_3\text{Sn}$ , is bright brown in colour, non-magnetic, has  $D^{20}_D$  8·98 (calculated, 8·17), and is soluble in molten nickel. At a red heat, it is attacked by oxygen and also, with incandescence, by chlorine; hydrochloric acid attacks it at the atmospheric temperature, and dissolves it completely on warming. Sulphuric acid or *aqua regia* effects solution more rapidly. Dilute nitric acid has little action even on warming, but the concentrated acid produces some metastannic acid.

T. A. H.

**Chromic Chloride. II.** NIELS BJERRUM (*Zeitsch. physikal. Chem.*, 1907, 59, 581—604. Compare this vol., ii, 554).—In order to interpret the behaviour of concentrated chromium chloride solutions, it is necessary to assume that they contain a third substance in addition to the blue chromium chloride and the green chromium chloride (dichlorochromium chloride). This substance has been prepared. It is a green, crystalline, very deliquescent compound with the formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . One of the three chlorine atoms is present in the form of a complex, so that the substance may be regarded as a monochlorochromium chloride (see *loc. cit.*). It can be separated from the other chromium chlorides by virtue of its solubility in a mixture of equal volumes of ether and fuming hydrochloric acid. When kept, it is gradually converted into the dichlorochromium chloride.

Solutions, which were left until a state of equilibrium was reached, have been examined, and the proportions of the three chromium chlorides have been determined. The position of equilibrium is affected by changes of concentration and temperature in harmony with theory, and the effect of adding various salts and hydrochloric acid is in qualitative agreement with the law of mass action.

J. C. P.

**Dehydration Products of Dichlorochromium Chloride.** NIELS BJERRUM (*Ber.*, 1907, 40, 2915—2917. Compare this vol., ii, 554, and *Olie*, this vol., ii, 177).—The green hydrate of chromic

chloride,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , which loses  $2\text{H}_2\text{O}$  over sulphuric acid in a vacuum, suffers a further loss when kept over phosphoric oxide under 1 mm. pressure; after four and a half months it is converted into a red substance,  $\text{CrCl}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , which forms a yellowish-green solution in water, changing to the violet-blue colour of the solution of the green chromium chloride. The electrical conductivity at  $25^\circ$  is less than that of the latter salt, but increases rapidly after a few minutes.

By heating the green hexahydrate very slowly to  $155^\circ$  in a current of hydrogen chloride,  $5\frac{1}{2}\text{H}_2\text{O}$  are expelled; the residue consists of a red powder. C. S.

#### Dichlorochromium Bromide and Dibromochromium Chloride.

NIELS BJERRUM (*Ber.*, 1907, 40, 2917—2922).—*Dibromotetra-aquochromium chloride*,  $[\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ , is precipitated when a cold solution of dibromotetra-aquochromium bromide in dilute hydrochloric acid is saturated with hydrogen chloride. Its constitution is deduced from its method of formation, its colour, which resembles that of the dibromo-bromide, and from the ease with which the halogen in the metallic complex is brought into the ionised state by solution in water or nitric acid. The last-mentioned property is of the same order as in the case of the dibromo-bromide, and is much greater than the similar tendency in the case of the dichloro-chloride. *Dichlorotetra-aquochromium bromide*,  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Br}$ , prepared in a similar manner, is an unstable, green, crystalline powder; titration by silver nitrate shows that only one halogen atom is in the ionised state in solution.

Hexahydrated chromium bromide quickly loses  $2\text{H}_2\text{O}$  over sulphuric acid in a vacuum; further loss occurs very slowly and the salt acquires a superficial brown colour.

The nature of the halogen in the metallic complex does not affect the colour of the salt, but influences the solubility. Thus the dibromo-chloride is insoluble in concentrated hydrochloric acid, whereas the dichloro-chloride is soluble. C. S.

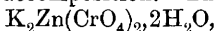
#### Chlorochromium Sulphate, $(\text{CrCl}_3 \cdot 5\text{H}_2\text{O})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ .

RUDOLF F. WEINLAND and THEODOR SCHUMANN (*Ber.*, 1907, 40, 3091—3095. Compare Weinland and Krebs, *Abstr.*, 1906, ii, 233).—A chlorochromium sulphate,  $\text{CrClSO}_4 \cdot 8\text{H}_2\text{O}$ , is formed when green hydrated chromium chloride is dissolved in its own weight of water, the solution kept at the ordinary temperature for twenty-four hours, and then mixed with fairly concentrated sulphuric acid. It separates in the form of pale green, crystalline plates. In dilute nitric acid solution, the chlorine is not immediately precipitated by silver nitrate, whereas the  $\text{SO}_4$  group is precipitated by barium chloride. When a 20% solution of the salt is saturated at low temperatures with hydrogen chloride, crystals of neither of the two hydrated chromium chlorides separate. It is not certain whether this compound is identical with the green chlorosulphate crystallising in needles which has been described previously (*loc. cit.*). A *benzenesulphonate*,  $\text{CrCl}(\text{SO}_3\text{Ph})_2 \cdot 8\text{H}_2\text{O}$ , and a *phenolsulphonate*,  $\text{CrCl}(\text{SO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2 \cdot 8\text{H}_2\text{O}$ , may be obtained by using the corresponding acids in place of sulphuric acid.

J. J. S.

**Normal Double Chromates of Potassium.** MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1907, 54, 185—195. Compare Abstr., 1905, ii, 393; 1906, ii, 451).—The compounds in question were prepared by mixing 50 c.c. of a nearly saturated potassium chromate solution with 10 c.c. of a strong solution of the appropriate salt, the mixture was shaken for some time, kept until the precipitate showed no further change, and the latter then separated and dried.

*Potassium barium chromate*,  $K_2Ba(CrO_4)_2$ , occurs in small, pale yellow granules; the corresponding *strontium* salt in light yellow, polygonal crystals; both are decomposed by water. The *calcium* and *magnesium* double salts,  $K_2Ca(CrO_4)_2 \cdot 2H_2O$ , thin, light yellow needles, and  $K_2Mg(CrO_4)_2 \cdot 2H_2O$ , light yellow, prismatic crystals, are both soluble in water without decomposition. The *zinc* compound,



occurs in large, light yellow, prismatic crystals, always mixed with a certain proportion of basic chromate. The *cadmium* salt,  $K_2Cd(CrO_4)_2 \cdot 2H_2O$ , forms transparent, light yellow, granular crystals, decomposed by water.

Unsuccessful attempts were made to prepare a double silver potassium chromate. The small, red granules obtained by the general method appear to be mixed crystals of the two chromates. *Potassium mercurous chromate*,  $K_2Hg_2(CrO_4)_2$ , was obtained as brownish-yellow leaflets; it is slowly decomposed by water with precipitation of basic mercurous chromate. *Potassium lead chromate*,  $K_2Pb(CrO_4)_2$ , was obtained as a yellow, amorphous precipitate by interaction of lead acetate and potassium chromate, whilst by interaction of the latter salt and lead nitrate, only mixtures of the double salt just mentioned and basic lead nitrate could be isolated.

The action of potassium chromate on solutions of ferrous, ferric, cupric, mercuric, and aluminium chlorides, and of mercuric and bismuth nitrates was also investigated, but no definite double salts could be isolated.

G. S.

**Preparation and Properties of the Fluorides of Sexavalent Molybdenum.** OTTO RUFF and FRITZ EISNER (*Ber.*, 1907, 40, 2926—2935. Compare Abstr., 1905, ii, 255; this vol., ii, 268).—*Molybdenum hexafluoride*,  $MoF_6$ , is best obtained by the action of fluorine on finely-divided molybdenum at 60—70°, the product being collected in a glass receiver at -70°; it is purified by redistillation. It forms white crystals, has m. p. 17° and b. p. 35°, reacts with water to form blue molybdenum oxide, is absorbed by alkali or ammonium hydroxides, and yields double salts with alkali fluorides. It does not react with chlorine, sulphur dioxide, or air, and yields a brown powder by the action of gaseous ammonia. It reacts with arsenic trichloride, antimony pentachloride, phosphorus trichloride, or oxychloride, and is reduced and turned blue by organic substances. Metals and metalloids, with the exception of gold and platinum, react with the hexafluoride to form variously coloured products.

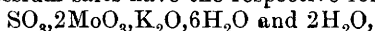
*Molybdenum oxytetrafluoride*,  $MoOF_4$ , is obtained by the action of three times the calculated amount of anhydrous hydrogen fluoride on molybdenum oxytetrachloride in a platinum vessel cooled in a freezing

mixture. After removing the by-products at  $100^{\circ}$ , the oxyfluoride is distilled at  $230^{\circ}$ . It is a white, very hygroscopic solid, which turns blue and decomposes in the air. It has m. p.  $97-98^{\circ}$ , b. p.  $180^{\circ}$ , and D 3.001 at the ordinary temperature. Molybdenum trioxide remains after the evaporation of the colourless aqueous solution.

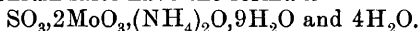
*Molybdenum dioxydifluoride*,  $\text{MoO}_2\text{F}_2$ , obtained from the dioxydichloride in a similar manner to the oxytetrafluoride, is a white, hygroscopic, crystalline substance, which sublimes at  $265-270^{\circ}$ , and has D 3.494 at the ordinary temperature. It gives a blue coloration with a small quantity of water, but dissolves in an excess to a colourless solution. C. S.

**Compounds of Molybdates with Sulphates.** RUDOLF F. WEINLAND and HUGO KÜHL (*Zeitsch. anorg. Chem.*, 1907, 54, 259—264).—When 5 to 8 mols. of sulphuric acid are added to 1 mol. of ammonium or potassium molybdate and the mixture evaporated over sulphuric acid, well crystallised double salts of the respective formulæ  $3\text{SO}_3, 2\text{MoO}_3, (\text{NH}_4)_2\text{O}, 10\text{H}_2\text{O}$  and  $3\text{SO}_3, 2\text{MoO}_3, \text{K}_2\text{O}, 6\text{H}_2\text{O}$  separate.

Compounds of a different type are obtained by dissolving molybdenum oxysulphate,  $\text{MoO}_2\text{SO}_4$ , in concentrated solutions of the alkali sulphates. Two potassium salts have the respective formulæ



whilst the ammonium salts have the formulæ



All these compounds crystallise in slender, lustrous needles, and are decomposed by water with precipitation of molybdic acid.

G. S.

**Amount of Tin in Pure Stannic Chloride Solutions of Known Density.** PAUL HEERMANN (*Chem. Zeit.*, 1907, 31, 680).—The percentage of tin present in solutions of stannic chloride of known density at  $17.5^{\circ}$  has been determined accurately and the results recorded in a table, the densities being given in degrees Beaume.

W. H. G.

**Compounds of Stannic Sulphate with Metallic Sulphates.** RUDOLF F. WEINLAND and HUGO KÜHL (*Zeitsch. anorg. Chem.*, 1907, 54, 244—252).—The double salts in question, with the exception of those containing the sulphates of the rare earths, were obtained by mixing solutions of stannic acid and the respective metallic sulphates in strong sulphuric acid and concentrating. The double salts with the rare earths were prepared by long-continued heating of the sulphates with a solution of  $\alpha$ -stannic acid in sulphuric acid. The compounds are all decomposed by water with precipitation of stannic acid. They may be regarded as derivatives of the stannic acids,  $\text{H}_2\text{SnO}_8$  or  $\text{H}_4\text{SnO}_4$ , in which part or the whole of the oxygen is replaced by the  $\text{SO}_4$  group.

The rubidium salt,  $\text{Rb}_2\text{Sn}(\text{SO}_4)_3$ , crystallises in six-sided leaflets; the potassium and silver salts,  $\text{K}_2\text{Sn}(\text{SO}_4)_3$  and  $\text{Ag}_2\text{Sn}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , in slender needles. The calcium salt,  $\text{CaSn}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , and the corre-

sponding barium, strontium, and lead salts have been described already (Abstr., 1906, ii, 762).

The compound,  $\text{CeHSn}(\text{SO}_4)_4$ , forms a colourless, microcrystalline powder;  $\text{LaHSn}(\text{SO}_4)_4$  crystallises in small, six-sided plates;  $\text{Y}_2\text{Sn}(\text{SO}_4)_6$ , as a microcrystalline powder;  $\text{ThSn}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , in slender needles; and  $\text{Bi}(\text{OH})\text{Sn}(\text{SO}_4)_3$ , in rhombic leaflets. G. S.

**Compounds of Titanic Sulphate with Sulphates of the Alkaline Earths.** RUDOLF F. WEINLAND and HUGO KÜHL (*Zeitsch. anorg. Chem.*, 1907, 54, 253—255).—The compounds,  $\text{Ti}(\text{SO}_4)_2 \cdot \text{CaSO}_4$ ;  $\text{Ti}(\text{SO}_4)_2 \cdot \text{SrSO}_4$ , and  $3\text{Ti}(\text{SO}_4)_2 \cdot 2\text{BaSO}_4$ , were prepared by mixing solutions of titanium dioxide in concentrated sulphuric acid with solutions of the appropriate sulphates in the same solvent and concentrating. The calcium and strontium salts crystallise in small, well-formed, colourless, lustrous cubes; the barium salt in slender needles. All the salts are decomposed by water with precipitation of titanic acid. They may be derived from complex titanic acids in which part of the oxygen is replaced by  $\text{SO}_4$ . G. S.

**Zirconium Carbide from Natural Zirconia.** EDGAR WEDEKIND (*Chem. Zeit.*, 1907, 31, 654—655. Compare Moissan and Lengfield, Abstr., 1896, ii, 428).—Zirconium carbide may be prepared from natural zirconia by heating a mixture of the very finely-powdered mineral with pure charcoal for some time in an electric furnace with a current of 600 amperes. The partially fused metallic mass so obtained is zirconium carbide with about 1% of impurity. When heated to a red heat in a stream of nitrogen, it is converted into zirconium nitride and not into cyanide or cyanamide; the product obtained, when fused with potassium hydroxide, readily evolves ammonia. Zirconium carbide in compact masses is an excellent conductor of electricity. W. H. G.

**Zirconium Sulphates.** OTTO HAUSER (*Zeitsch. anorg. Chem.*, 1907, 54, 196—212. Compare Abstr., 1905, ii, 531).—A new acid sulphate of zirconium has been obtained and the behaviour of zirconium sulphate solutions under different conditions has been investigated further.

The solubility of zirconium sulphate in sulphuric acid and water diminishes with increased concentration of acid up to a point beyond which it begins to increase, attains a maximum at 61%  $\text{SO}_3$ , and then slowly decreases. From solutions containing 61—64% of the trioxide, an acid sulphate,  $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , separates in four to twelve days on keeping the solution at  $40^\circ$ . From solutions containing more than 70%  $\text{SO}_3$ , crystals of the corresponding monohydrate separate, but the transition point of the tri- to the mono-hydrate has not been established. The solubility at  $22^\circ$  is much the same as at  $40^\circ$ , so that the acid sulphate can be obtained in a similar way at the lower temperature.

The compound,  $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , occurs in well-formed prisms of  $D^{19} 2.02$ ; it is very hygroscopic and rapidly deliquesces in the air with formation of the tetrahydrate,  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . The mono-

hydrate,  $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , has  $D^{20}_D$  2.05 and is even more hygroscopic than the trihydrate.

When very concentrated solutions of zirconium sulphate are kept at the boiling point, the temperature gradually falls and a basic salt of the formula  $2\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 5\text{H}_2\text{O}$  separates in a crystalline form. From more dilute solutions, no separation of crystals takes place. The basic salt just mentioned has  $D^{19}_D$  2.834, is slightly soluble in water, the solution having a faintly acid reaction, and readily soluble in acids.

The observation of Berzelius and others that zirconium hydroxide is soluble in zirconium sulphate solutions has been further investigated, and it is suggested, in agreement with Ruer (*Abstr.*, 1905, ii, 863), that the hydroxide is converted by the sulphate to the hydrosol form. Ruer's view that the solution thus obtained contains zirconosulphuric acid is criticised.

G. S.

**Compounds of Hypovanadic Acid with Some Oxygen Acids.** GUSTAVE GAIN (*Compt. rend.*, 1907, 144, 1271—1273).—By dissolving hydrated hypovanadic acid,  $\text{V}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , in a dilute solution of selenic acid, a fine blue solution is obtained, which, after fifteen days' evaporation in a vacuum, deposits a bright blue, deliquescent, micro-crystalline powder having the composition  $\text{V}_2\text{O}_4 \cdot 3.5\text{SeO}_3 \cdot 7\text{H}_2\text{O}$ . When excess of selenic acid is used, another blue salt, more deliquescent than the preceding, is obtained, having the composition  $\text{V}_2\text{O}_4 \cdot 5\text{SeO}_3 \cdot 10\text{H}_2\text{O}$ . These differ from the corresponding sulphates only in the proportion of water. Similar reactions with phosphoric acid give two salts, both forming blue needles having the composition  $\text{V}_2\text{O}_4 \cdot 2\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$  and  $\text{V}_2\text{O}_4 \cdot 3\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$  respectively. Arsenic acid gives a fine blue, crystalline substance which rapidly turns green in air; it has the composition  $\text{V}_2\text{O}_4 \cdot 3\text{As}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ .

E. H.

**Compounds of Antimony Sulphate with Sulphates of the Alkaline Earths and with Silver Sulphate.** HUGO KÜHL (*Zeitsch. anorg. Chem.*, 1907, 54, 256—258. Compare preceding abstracts).—The double salts were obtained from solutions of antimony sulphate and excess of the alkaline earth or silver sulphate in strong sulphuric acid, on concentrating. The alkaline earth sulphates have the formula  $\text{Sb}_2(\text{SO}_4)_3 \cdot \text{MSO}_4 \cdot 6\text{H}_2\text{O}$ , crystallise in slender needles, and are decomposed by water with precipitation of basic antimony sulphate. The water of crystallisation is completely driven off on prolonged heating at 110—120°. The silver salt,  $\text{Ag}_2\text{Sb}_2(\text{SO}_4)_4$ , forms colourless, cubic, doubly refracting crystals.

G. S.



## Mineralogical Chemistry.

**Minerals from Sardinia. Hæmatite from Padria.** FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 884—889).—A sample of lamellar hæmatite from Padria exhibits the few simple forms and combinations usual with volcanic hæmatite, its peculiar structure being due to twinning (compare Strüver, *Mem. R. Accad. Lincei*, 1889, [v], 16, 153). T. H. P.

**A New Mineral from the High Temperature Fumaroles of the Recent Eruption of Vesuvius.** ALFRED LACROIX (*Compt. rend.*, 1907, 144, 1397—1401).—After the denudation of the surface accumulations formed by the eruption of April, 1906, on the cone of Vesuvius, a buried lava flow was found to be still incandescent in October, 1906, and in the fumaroles on this were found scoriaceous crusts of white, yellow, and green salts, consisting of alkali chlorides and sulphates. By the action of sulphur dioxide and air on the chlorides, these have been transformed progressively into sulphates, and in places the crusts consist mainly of apthitalite,  $K_3Na(SO_4)_2$ . A study of these crusts in thin sections by petrographical methods led to the detection of the new mineral. The apthitalite is distinguished in the sections by its low birefringence and positive uniaxial character; enclosed in it are vast numbers of minute, hexagonal scales of a uniaxial mineral with strong negative birefringence, and arranged in parallel position with respect to the host. On dissolving the apthitalite in the least possible quantity of water, the new mineral was isolated as minute spangles; this material gave on analysis by F. Pisani after deducting 22.59% insoluble (consisting largely of hæmatite together with an undetermined mineral) and 2.46% NaCl:

SO <sub>3</sub> .	PbO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
29.4	54.8	12.3	3.5

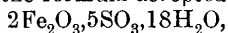
This agrees approximately with the formula  $PbSO_4 \cdot (K, Na)_2SO_4$ , and for the new mineral the name *palmierite* is proposed. The mineral is decomposed by boiling water with separation of minute crystals of anglesite. It was prepared artificially, as hexagonal plates with the same optical characters as the natural crystals, by fusing lead sulphate with an excess of alkali sulphates; the sodium chloride deducted from the above analysis is therefore not an essential constituent. Palmierite is a double sulphate, similar to glauberite, vanthoffite, and langbeinite.

The presence of crystallised anglesite ( $PbSO_4$ ) recorded by F. Zambonini amongst the products of the recent Vesuvian eruption was explained by him as due to the action of sulphuric acid on lead chloride. The existence of the new mineral, palmierite, however, suggests the following series of reactions: (1) the lead was carried as volatile chloride with alkali chlorides; (2) transformation of the chlorides to sulphates, with the production of apthitalite and palmierite; (3) solu-

tion of the apthitalite in water; (4) decomposition of the palmierite by water with the production of crystallised anglesite.

A microscopical examination of the deliquescent crusts formed by the acid fumaroles of April, 1906 (this vol., ii, 33), showed the presence of rhombohedral crystals with the same optical characters (strong negative birefringence) as the artificial salt,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , thus confirming A. Scacchi's determination of chloralluminite as a Vesuvian mineral. L. J. S.

**Janosite.** ZOLTÁN TOBORFFY (*Zeitsch. Kryst. Min.*, 1907, 43, 369—378. Compare *Ann. Rep.*, 2, 279; 3, 321).—An examination of copiapite from Chile shows that the characters of the minute scales, as determined under the microscope, agree with those of janosite and with the determinations of E. Bertrand (1881) and A. Des Cloizeaux (1881) for copiapite from Chile; in all these, the plates are orthorhombic with a prism-angle of  $102^\circ$  and a perfect basal cleavage; the acute negative bisectrix of the optic axes is perpendicular to the cleavage and the optic axial plane is parallel to the brachypinacoid. All the published analyses of copiapite (including misy and janosite) and of coquimbite are tabulated and compared. Owing to the presence of various impurities and of free sulphuric acid, these analyses show considerable variations; the formula accepted for copiapite is



and for coquimbite,  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$ . It is concluded that janosite is identical with copiapite, since the crystallographic and optical characters are the same, and the chemical composition given for janosite lies between the limits of variation shown by copiapite. Further, it is held that copiapite is orthorhombic and not monoclinic as stated by G. Linck (1888) and E. Weinschenk (1906). L. J. S.

**Composition of Molybdenite from Arizona.** F. N. GUILD (*Amer. J. Sci.*, 1907, [iv], 23, 455—456).—The mineral analysed occurs with molybdenite and limonite in milky quartz at the Santa Rita Mountains, Arizona. In some of the cavities, the bright yellow, silky tufts of acicular crystals are free from limonite:

	$\text{MoO}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{H}_2\text{O}$ .	Insoluble (quartz).	Total.
I.	57.38	20.88	16.83	4.86	99.95
II.	59.79	21.18	16.61	2.66	100.24

These results correspond with the formula  $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ , agreeing with that recently proposed by W. T. Schaller (this vol., ii, 480) except in the amount of the water. L. J. S.

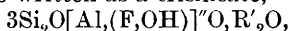
**Minerals from Lyon Mountain, Clinton Co., New York.** HERBERT P. WHITLOCK (*Bull. N.Y. State Museum, Geological Papers*, No. 107, 1907, 55—96).—A description with full crystallographic details is given of the various secondary minerals, calcite, hornblende, apatite, orthoclase, titanite, &c., which as fine, large crystals encrust cavities in the magnetite deposits of the Chateaugay mines. That part of the paper which deals with the calcite crystals is translated in *Zeitsch. Kryst. Min.*, 1907, 43, 321—330. L. J. S.

**Irvingite, a New Variety of Lithia-Mica.** SAMUEL WEIDMAN (*Amer. J. Sci.*, 1907, [iv], 23, 451—454).—A nearly colourless mica occurring with marignacite, &c. (this vol., ii, 482), in pegmatite veins in the quartz-syenite and nepheline-syenite near Wausau, Wisconsin, gave on analysis by V. Lenher :

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	K <sub>2</sub> O.
57.22	0.14	18.38	0.32	0.53	0.09	0.20	9.12
Na <sub>2</sub> O.	Li <sub>2</sub> O.	F.	H <sub>2</sub> O (at 110°).	H <sub>2</sub> O (ignition).	Total (less 0 for F.).		
5.14	4.46	4.58	0.42	1.24	99.91.		

The mineral differs from cryophyllite, zinnwaldite, and lepidolite in its higher content of silica and soda, and from polyolithionite in containing more alumina and less fluorine and in the different proportions of the alkalis. The name *irvingite* is therefore proposed.

The formula may be written as a trisilicate,



or, according to F. W. Clarke's theory of the mica group, as  $\text{R}'_2\text{AlX}(\text{F},\text{OH})$ , where X represents  $\text{Si}_3\text{O}_8$  and  $\text{SiO}_4$  in the ratio 4 : 1.

L. J. S.

**A Crystallised Product of the Weathering of Augite.** W. P. SMIRNOFF (*Zeitsch. Kryst. Min.*, 1907, 43, 338—346).—The pseudomorphs after augite, occurring in decomposed basalt at Mt. Hradischt, near Bilin in Bohemia, consist of an earthy mass of cimolite in which is embedded a birefringent, crystallised substance to which Breithaupt in 1838 gave the name anauxite. The latter was separated by means of a heavy liquid and gave analysis I. This differs considerably from the previous analysis (presumably on less pure material) made by von Hauer in 1854 ; on the other hand, it agrees closely with an analysis by K. D. Glinka of an alteration-product of augite from Tschakwa in the Caucasus ; analysis I corresponds with the formula  $\text{H}_4\text{Al}_4\text{Si}_5\text{O}_{18}, 2\text{H}_2\text{O}$ . A hot solution of magnesium chloride under a pressure of about 20 atmospheres had little effect on the mineral :

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	50.75	33.34	2.45	0.32	0.27	12.64	99.77	2.524
II.	56.75	28.43	3.17	0.54	0.34	10.67	99.90	—

The earthy portion (cimolite) of these pseudomorphs gave analysis II, corresponding with  $\text{H}_2\text{Al}_2\text{Si}_3\text{O}_{10}, \text{H}_2\text{O}$  ; this material represents the final stage of the alteration of the augite.

L. J. S.

## Physiological Chemistry.

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**Influence of Increased Barometric Pressure on Man. III. The Possibility of Oxygen Bubbles being Set Free in the Body.** LEONARD E. HILL and MARION GREENWOOD (*Proc. Roy. Soc.*, 1907, *B*, 79, 284—287).—Oxygen has never been regarded as a factor in the production of decompression symptoms, as the avidity of the tissues for this gas is so great. On subjecting animals, however, to decompression after exposure to high oxygen pressures, oxygen was found to be a large component of the gas liberated. Oxygen inhalations during rapid decompression in man has little or no advantage; the only safe method is slow decompression at a uniform rate. W. D. H.

**Physical Properties of Horse-Serum.** JOHN MELLANBY (*J. Physiol.*, 1907, 35, 473—499).—After freezing and thawing a column of serum, the concentration of the solids in different layers, except those near the top, varies in a continuous manner. The concentration is directly proportional to its distance from the top, but the ratio between the different solids is the same as in the original serum. When a constant current is passed through serum, the solids travel from cathode to anode, the main mass having the same velocity of transport, but a small amount of protein has a higher velocity; the water is intimately associated with the substances dissolved in it. Ninety % of the total protein forms molecular complexes with a portion of the inorganic salts; the remaining 10% is free in solution. The amount of salt existing in combination with the protein is a function of the temperature and degree of dilution of the serum. The main bulk of the protein present has the same coagulation temperature. Two proteins may be prepared from serum which are nearly colourless; these are globulin (prepared by dilution and neutralisation) and crystalline albumin; they comprise about 10% of the total protein. The pigment is associated with the remaining 90%. W. D. H.

**Blood-Jecorin and the Physico-chemical Behaviour of Sugar in the Blood.** PAUL MAYER (*Biochem. Zeitsch.*, 1907, 4, 545—553, Compare Abstr., 1906, i, 915).—Jecorin, or jecorin-like substances, were separated in small quantities from the blood of various animals; these substances differ in their reactions in different animals, and differ also from liver-jecorin; they contain sulphur and sodium in addition to a lecithin complex. The liver-jecorin in dogs yields 18.5% to 20.9% of sugar; the blood-jecorin yields with different diets, 4.48% to 8.2%; the quantity of sulphur and phosphorus shows also wide differences. The amount of sugar in the blood-jecorin shows no relationship to the amount in the food. W. D. H.

**Hæmolytic Power of Alcohols.** HERMANN FÜHNER (*Bull. Soc. chim. Belg.*, 1907, 21, 221—224. Compare Abstr., 1906, ii, 687; this vol., ii, 485).—The author replies to the criticisms of Vandeveld

(*Bull. Soc. chim. Belg.*, 21, 32). Measurements were made of the limiting hæmolytic values for *n*-propyl and *n*-butyl alcohols, both alone and when dissolved in ethyl alcohol, the results being as follows:

Alcohol.	Mol. wt.	Alcohols alone.			Alcohols dissolved.		
		Concentration in		Quotient	Concentration in		Quotient
		Per cent. by weight.	Mols. per litre.		Per cent. by weight.	Mols. per litre.	
Ethyl.....	46	18.0	3.91	} 2.8	18.0	3.91	} 2.8
<i>n</i> -Propyl .....	60	8.2	1.36		8.4	1.40	
<i>n</i> -Butyl.....	74	3.1	0.42	} 3.0	3.5	0.47	} 2.9

The ox-blood employed, obtained in Würzburg, is more resistant than that obtained in Vienna, with which the limiting hæmolytic value for ethyl alcohol was found to lie between 14.50% and 16.25% by weight.

The numbers given above do not correspond with those obtained by Vandeveldé (*loc. cit.*), who found that the toxicity of *n*-propyl alcohol for plant cells is approximately doubled by dissolving in ethyl alcohol. Vandeveldé's results hence cannot be applied to hæmolysis.

T. H. P.

**Quantitative Estimations by Hæmolysis.** ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1907, 21, 225—229. Compare preceding abstract).—The author replies to the criticisms of Fühner (*loc. cit.*) and gives the following limiting doses having a toxic action on blood corpuscles (I), together with the values obtained by the plasmolytic method (II):

	I.	II.
<i>n</i> -Propyl alcohol } alone .....	45	44
<i>iso</i> Propyl alcohol } .....	58	64
<i>n</i> -Propyl alcohol } dissolved in ethyl alcohol ...	19	23
<i>iso</i> Propyl alcohol } .....	47	37

Hence, both by the hæmolytic method and by the plasmolytic method, alcohols in solution yield coefficients different from those exhibited by the alcohols alone.

The limiting hæmolytic value of ethyl alcohol towards ox-blood obtained in Ghent is 15.4888% by weight and presents no such variations as those observed by Fühner, using ox-blood from Vienna (see preceding abstract). These variations may be explained by the fact that Fühner uses volumes of liquid measured in drops, whilst the author employs volumes carefully measured to 0.1 c.c.

Further, the author finds no such variations in the case of human blood, and, on the basis of this observation, is enabled to draw a clear distinction between foetal and maternal blood. T. H. P.

**Sham Feeding in Men.** HELENE KAZNELSON (*Pflüger's Archiv*, 1907, 118, 327—352).—Stimuli of the taste and smell organs excite the flow of gastric juice. Purely mechanical stimuli are ineffective. The latent period is about five minutes. The juice contains a fat-splitting ferment; its freezing point is approximately that of human blood; its acidity in the adult is relatively constant; the quantity secreted varies greatly. The main conclusions confirm those of Pawloff on animals. W. D. H.

**The Action of Sodium Chloride and Sodium Hydrogen Carbonate on the Secretion of Gastric Juice.** HENRYKA ROZENBLAT (*Biochem. Zeitsch.*, 1907, 4, 500—541).—The experiments were made on dogs with a Pawloff fistula. Sodium chloride was found to stimulate the formation of gastric juice and raise its acidity. Sodium hydrogen carbonate acts in the contrary way. W. D. H.

**The Part taken by Elementary Nitrogen in Animal Metabolism.** CARL OPPENHEIMER (*Biochem. Zeitsch.*, 1907, 4, 328—470. Compare Abstr., 1906, ii, 869).—A very complete historical and experimental study of the question. The conclusion reached is that elementary nitrogen takes no part in animal metabolism. W. D. H.

**Metabolism during Starvation.** I. E. PROVAN CATHCART (*J. Physiol.*, 1907, 35, 500—510).—The subject of the observations was a professional fasting man. Every care was taken to render the experiment genuine. The loss of weight was irregular, being most rapid during the first four days; on one day no loss occurred, which is difficult to account for, but has been noticed in previous cases. There was diminution in most of the body measurements, but no great loss of muscular power at the end of the fortnight's fast. Particulars are given of pulse, blood pressure, and respiration. The body temperature was slightly subnormal, and the man complained of cold, although living in an overheated atmosphere. Before the fast, the urine agreed with urines observed by Folin on a similar diet (purine-free); the amount and specific gravity were less during the fast, but irregularities are noted. During the fast, the total intake of water was 16,055 c.c., and the output of the kidneys, 12,855 c.c., leaving 3200 c.c. for excretion by skin and lungs. On the first day of the fast, the total nitrogen fell from 16.3 to 10.5 grams; the next day it rose to 14.4, and then steadily fell to 8.4 grams, until on the tenth day it rose slightly and then fell to a still lower level. At the end of the fast, a low nitrogen diet (starch and cream) was given, and the nitrogen fell rapidly still more (less than 3 grams). The next day the man refused the starch and cream diet and resumed the egg and milk diet; the output of nitrogen immediately increased fourfold, and steadily rose to the level it had before the fast. Particulars are given in full relating

to urea (the variations in which generally resemble those in total nitrogen), ammonia, uric acid (which after an initial fall remained very constant), total purine, creatinine, and creatine. The total purine excretion was very irregular; the creatinine fell throughout the experiment; creatine was also excreted, especially at first. The undetermined nitrogen was at first very variable, but fell towards the end of the fortnight.

W. D. H.

**Protein Metabolism in Inanition.** CHARLES G. L. WOLF (*Proc. Amer. physiol. Soc.*, 1907, xiv; *Amer. J. Physiol.*, 19).—Dogs were fed for eight days on a starch and fat diet developing 80 Cal. per kilo. A large quantity of casein was then given, and the metabolism followed during four days of inanition. In a second series, 160 Cal. were given at the end of the 80 Cal. period; this was done in an attempt to change the distribution of nitrogen and sulphur as a consequence of the high caloric value of the diet. The total nitrogen excretion was reduced to a level not previously observed in dogs. The ammonia-nitrogen was increased by the starch and fat diet. The oxidised sulphur was markedly lowered both absolutely and relatively; the relative excretion rose at once when protein was given. The absolute creatinine excretion was unchanged throughout. The undetermined nitrogen and neutral sulphur were increased by giving protein, but decreased relatively to the total nitrogen and sulphur outputs respectively. No constant relation was found between the elimination of ethereal sulphates and indican.

W. D. H.

**Glycogen Metabolism in the Rabbit's Liver. II.** IVAR BANG, MALTE LJUNGDAHL, and VERNER BOHM (*Beitr. Chem. Physiol. Path.*, 1907, 10, 1—34. Compare this vol., ii, 487).—The present experiments relate to the influence of the nervous system on glycogen metabolism. The effect of a blow on the neck is to cause an increased secretion of the liver diastase; the glycogen diminishes in the liver, and glycosuria ensues. The liver enzyme is independent of the blood-diastase. Bernard's puncture-diabetes is similarly produced; the primary stimulation is, however, followed by inhibition, and it is believed that, physiologically, sugar production is a balanced action between the stimulation and inhibition. The suggestion is made that the centres for sugar production and inhibition are distinct. Puncture-diabetes occurs whether the liver contains glycogen or not. Stimulation of the central end of the vagus causes glycaemia and glycosuria, whether the liver contains much or little glycogen; the effluent path is the sympathetic, and this form of diabetes is regarded as a muscle-diabetes, whereas stimulation of the central nervous system causes a liver-diabetes.

W. D. H.

**Purine Metabolism of the Embryo.** LAFAYETTE B. MENDEL (*Proc. Amer. physiol. Soc.*, 1907, xvii—xviii; *Amer. J. Physiol.*, 19).—The liver of the embryo pig resembles that of the adult in containing adenase, but no guanase. The latter enzyme, however, is present in extracts of other parts. The view that the two enzymes are specific is thus corroborated. No extracts were capable of forming

uric acid from free purines, even after prolonged digestion for five days in the presence of oxygen; xantho-oxydase was therefore absent. The liver extracts of adult, or even of very young, pigs contained xantho-oxydase. The uricolytic enzyme was not identified in any embryonic extracts under conditions where it is readily demonstrable in adult organs.

W. D. H.

**Prolonged Protein Feeding.** DAVID FORSYTH (*Proc. physiol. Soc.*, 1907, xl—xli; *J. Physiol.*, 35).—Domestic fowls kept on a meat diet for periods up to two years remained healthy; *post mortem*, no changes in the viscera were found. An ample supply of lime was given, and it was found the changes in the long bones described by Chalmers Watson were not due to excessive protein, but to lack of lime. The changes described by Watson in the thyroid are regarded as inconclusive; in only one of his cases was there undoubted hypertrophy of the thyroid; this may have been a case of sporadic goitre, which is found in birds independently of protein diet. Many graminivorous birds have larger thyroids than those which are carnivorous.

W. D. H.

**The Lowering of the Freezing Point of Pancreatic Juice.** LUDWIG PINCUSOHN (*Biochem. Zeitsch.*, 1907, 4, 484—487).—The lowering of the freezing point of dog's pancreatic juice is approximately the same as that of the blood. It is the same whether the animal is fasting or fed. The small differences noted are attributed to experimental errors.

W. D. H.

**The Ferment Law of Trypsin.** OTTO FAUBEL (*Beitr. chem. Physiol. Path.*, 1907, 10, 35—52).—The introduction of a large quantity of oil into the stomach causes a back flow of pancreatic juice into that organ, and so enables it to be obtained even in the human subject. The amount of trypsin in it varies in different people. The Schütz-Borissoff law of square roots does not hold for trypsin, but the amount of digestion is directly proportional to the amount of trypsin. Volhard's method of estimating trypsin was employed.

W. D. H.

**Chemistry of Digestion in Animals. IX. Bacteria of the Digestive Tract in the Dog.** L. M. HOROWITZ (*Zeitsch. physiol. Chem.*, 1907, 52, 95—106. Compare this vol., ii, 367).—The number of bacteria in the small intestine increases towards its lower end; they increase markedly during digestion. Some multiply more specially in certain regions, or when certain foods are given, for instance, *Bacterium acidi lactici* on a milk diet, and *B. Proteus vulgaris* on protein diet. Some micro-organisms, especially in the lower part of the small intestine, resolve proteins, and the majority act on carbohydrates, especially on lactose; none of those investigated act exclusively on fats. The bacteria in the food are rapidly destroyed; the gastric juice is powerfully bactericidal, but bile, pancreatic and intestinal juices form good nutrient media for bacteria; the protein cleavage products also favour bacterial growth.

W. D. H.



**Production of "Shock" by Loss of Carbon Dioxide.** YANDELL HENDERSON (*Proc. Amer. physiol. Soc.*, 1907, xiv—xv; *Amer. J. Physiol.*, 19).—Pain produces hyperpnœa; the carbon dioxide content of arterial blood and tissues is thus reduced. This lowers the tonus of peripheral vessels, induces tachycardia, shallow respiration, failure of reflexes, and the mental condition characteristic of "shock." The liability to shock which attaches to the exposure of the abdominal viscera is explained by the exhalation of carbon dioxide from the exposed organs. Rapid recovery can be effected by restoring the carbon dioxide, either by increasing the dead space of the respiratory tract or by the intravenous injection of saline solution saturated with the gas.

W. D. H.

**Action of Cyanides on the Heart.** A. J. CARLSON (*Amer. J. Physiol.*, 1907, 19, 223—232).—The cyanides have a primary, stimulating, and a secondary depressing action on the heart of *Limulus*. The heart-muscle is less sensitive in this direction than the heart-ganglion, and that is less sensitive than the mammalian central nervous system. Prevention of tissue respiration is not the only action of cyanides.

W. D. H.

**The Oxidising Power of Various Sugars and the Oxidising Power of Different Tissues.** HUGH MCGUIGAN. **The Oxidising Power of Cupric Acetate Solutions.** ALBERT P. MATHEWS and HUGH MCGUIGAN (*Amer. J. Physiol.*, 1907, 19, 175—198, 199—222).—The addition of acetic acid to cupric acetate solutions checks the oxidation of sugars; the more cupric acetate in solution, the greater is the amount of acid necessary to check oxidation. The amounts of acid necessary to check oxidation to a given point are given for different concentrations of cupric acetate. The sugars are oxidised *in vitro* with different speeds, which correspond with their ease of oxidation in the body; most acid is required for lævulose, then follow galactose, dextrose, maltose, and lactose in the order named. Equal quantities of various dried and powdered tissues require different quantities of acid to retard the catalysis of hydrogen peroxide to a certain point; the kidney requires most, then follow in order liver, spleen, pancreas, and muscle. In such powders, particles with a pressure of at least 0.125 volt of positive electricity exist in greatest numbers in the kidney, and in the other tissues in the order named. It is probable that the body may be able to utilise lævulose and galactose and yet is unable to utilise dextrose. The mechanism of oxidation in the cell is thus probably the same as that of cupric acetate; "protoplasm hydrate and oxide" taking the place of the copper.

In the second paper, the differences between the various solutions used are stated to be due to differences in speed of oxidation, and not of potential. Such reagents as Barfoed's can thus only be used for the differentiation of sugars within certain time limits. Even sucrose will reduce Fehling's solution if sufficiently concentrated and sufficient time is allowed to elapse; no inversion apparently precedes the reduction. The addition of acid reduces the velocity of the reaction by reducing the dissociation of the sugar molecules and the concentration of the oxygen ions

W. D. H.

**The Behaviour of Creatine in Autolysis.** RUDOLF GOTTLIEB and R. STANGASSINGER (*Zeitsch. physiol. Chem.*, 1907, 52, 1—43).—At the beginning of autolysis in the expressed juice of muscle and other organs, creatine is formed. Later, the creatine is in part changed into creatinine by the action of an enzyme. Later still, both creatine and creatinine are destroyed by ferments, termed creatase and creatinase respectively. The curves representing these changes are complex, and differ in different organs. Similar ferment actions can be detected also in the urine.

W. D. H.

**Perfusion Experiments on Excised Kidneys. VII. Solutions of Electrolytes.** TORALD SOLLMANN. **VIII. Effect on Histological Appearance of the Kidney.** W. W. WILLIAMS (*Amer. J. Physiol.*, 1907, 19, 233—251, 252—257).—A series of electrolytes were used. Solutions of the same freezing point as a 1% solution of sodium chloride are not always isotonic towards kidney cells, and some of the changes observed on perfusing such solutions are osmotic, but in most cases chemical and “vital” factors come in also. The results throw but little light on the comparative diuretic effect of salts in animals. As regards the size of the cells, the histological examination sometimes agreed with changes in weight, but in many cases the microscope failed to reveal any alteration. Histology does not really throw any light on the changes observed.

W. D. H.

**Potassium Salts in Nerve-Fibres.** JOHN S. MACDONALD and F. F. FINCH (*Proc. physiol. Soc.*, 1907, xxxviii—xxxix; *J. Physiol.*, 35).—Frog's nerve-fibres placed in Macallum's reagent show the potassium reaction at the cut ends and at the nodes of Ranvier also. After immersion in 0.6% solution of sodium chloride, the precipitate extends over greater distances, and these portions are distended as by a greatly increased internal pressure. The addition of chloroform to the saline solution tends to limit this extension, and of ammonia to the entire disappearance of the precipitate. Modifications of the strength of this and other saline solutions produce changes corresponding with the influence of these modifications on the injury current. The passage of an electrical current through a nerve leads to a heavy precipitation in the nodes of the cathodic region only.

W. D. H.

**Choline in Cerebro-spinal Fluid.** OTTO ROSENHEIM (*J. Physiol.*, 1907, 35, 465—472. Compare Abstr., 1906, ii, 133).—The statement that in cases of acute degenerative disease of the nervous system the cerebro-spinal fluid and blood contain choline, originally made by Halliburton and Mott, is confirmed by the use of the new tests previously described. Other bases are also present, but were not identified; the idea that they might be betaine, neurine, dimethyl-hydroxyethylamine (from kephalin), or sphingosine (from phrenosin) was not established. Another feature of these diseases is the rise in the amount of potassium salts present; this is intelligible when it is remembered that potassium salts have recently been shown to be important constituents of nervous material. Choline is also dis-

coverable in extracts of many organs and tissues where lecithin is present. In some cases, the breakdown of lecithin must be attributed to ferment action.

W. D. H.

**Formation of Protamine in the Salmon.** FRANZ WEISS (*Zeitsch. physiol. Chem.*, 1907, 52, 107—120).—A salmon weighing 9 kilos. contains in its testes about 27 grams of protamine, containing 22·8 grams of arginine. Its muscle protein yields 5·67% of arginine, so that at breeding time, 402 grams of muscle-protein must be decomposed to yield the necessary amount of arginine. A female salmon of the same weight loses about 600 grams of its muscle at the corresponding period, or about half as much again as the male. From actual observations on the male, it is calculated that about 38% of its muscle is utilised in the formation of the generative organs.

W. D. H.

**The Sugar from Frog-Spawn.** WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1907, 4, 407—411).—The authors have obtained galactose by hydrolysing the jelly-like envelope of frog-spawn with dilute hydrochloric acid.

A. J. W.

**Further Observations on the Pupæ of Calliphora.** ERNST WEINLAND (*Zeitsch. Biol.*, 1907, 49, 351—372, 421—465, 466—485, 486—493. Compare Abstr., 1906, ii, 560).—By means of experiments with light petroleum, it is shown that in presence of oxygen there is in the pupæ a decomposition of fat, as a rule. The carbon dioxide liberated is not equal to that which would be formed by complete combustion of the fat. Lecithin is also decomposed. Little or no hydrogen is liberated, thus contrasting with what occurs in the absence of oxygen. Another process which occurs is the formation of sugar; this is independent of the decomposition of the fat, and the origin of the sugar is probably protein; this is succeeded by the formation of chitin from sugar. Ferments are considered to be responsible for the changes. Liberation of ammonia is not due to bacterial action, or to the tryptic ferment present in the intestinal secretion, but to further splitting in the tissues.

W. D. H.

**The True Mean Percentage of Urea in Normal Human Urine.** FRITZ LIPPICH (*Zeitsch. physiol. Chem.*, 1907, 52, 219—224).—Polemical. The incorrectness of W. O. Moor's views on the subject (Abstr., 1903, ii, 343; 1904, ii, 192, 274; 1906, ii, 693) is maintained.

W. D. H.

**Organic Bases in Horses' Urine.** W. ACHELIS and FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1907, 52, 91—94).—The detection of methylguanidine in horses' urine rendered necessary the further examination of this fluid for other bases. There are several present, and the present communication deals mainly with the method of separating them; at present, the only one identified is 4-methylpyridine.

W. D. H.

**Chloroform Apnœa.** BERTRAM COLLINGWOOD and H. L. F. BUSWELL (*Proc. physiol. Soc.*, 1907, xxxiv; *J. Physiol.*, 35).—A low percentage of chloroform quickly produces apnœa of a pronounced character if administered by rapid artificial respiration. This is not due to diminution of carbon dioxide in the blood, for it can be produced by chloroform mixed with expired air; expired air by itself does not cause apnœa. The apnœa occurs after cutting both vagi in cats. There are several indications that chloroform diminishes the excitability of the respiratory centre to the carbon dioxide stimulus.

W. D. H.

**Protein Metabolism in Cystinuria.** CHARLES G. L. WOLF and PHILIP A. SHAFFER (*Proc. Amer. physiol. Soc.*, 1907, xiii—xiv; *Amer. J. Physiol.*, 19).—The cystinuric patient observed could oxidise the sulphur of hair-cystine to sulphuric acid like a normal person. This confirms Alsberg and Folin's statement. The same is true for cysteine or cystine prepared from the urine. The cystin excreted is evidently not absorbed as such, but in the form of a larger molecule. Increase of protein food increases the cystine excreted, but isolated cystine is merely excreted as sulphate. Cystine injected subcutaneously is excreted as "neutral sulphur" (probably as cystine). Cysteine similarly injected leads to an increase of sulphur in the urine; the increase being equally divided between inorganic sulphates and neutral sulphur. In addition to cystine derived from protein food (exogenous metabolism), part of the cystine excreted is independent of the food.

W. D. H.

**Pancreatic Diabetes.** EDUARD PFLÜGER (*Pflüger's Archiv*, 1907, 118, 265—266, 267—321).—In frogs, extirpation of the pancreas leads to fatal diabetes; this is not prevented by transplantation of the pancreas from another animal. Extirpation of the duodenum, or complete separation of the duodenum from the pancreas, leads to the same result. The two latter operations do not affect the nutrition of the pancreas.

So far as experiments on dogs have been at present performed, the results are confirmatory. Extirpation of the duodenum in these animals produces glycosuria, although the pancreas remains untouched. The condition is attributed to nervous disturbance, and the internal secretion theory of pancreatic diabetes is condemned.

W. D. H.

**The Course of Acidosis in Diabetes.** ED. ALLARD (*Arch. exp. Path. Pharm.*, 1907, 57, 1—26).—This paper does not deal with the source of acetone,  $\beta$ -hydroxybutyric acid, &c., but with the amounts secreted. Systematic observations on the course of the excretion are stated to be wanting. In the present research, the urine was examined at intervals of three hours in a number of cases over long periods, and the results are given in tables and curves. One noteworthy general result is the increase of these substances after fasting. Observations are also given relating to the proportion of ammonia to total nitrogen in the urine; this does not diminish in the same proportion as the total nitrogen during fasting.

W. D. H.

**The Action of Various Chemical Substances on Sugar Excretion and Acidosis.** JULIUS BAER and LÉON BLUM (*Beitr. chem. Physiol. Path.*, 1907, 10, 80—104).—In dogs made diabetic by phloridzin, the administration of acetic acid increases the excretion of substances of the acetone group, but not of sugar or nitrogen. Glycollic acid, glycine, and propionic acid have a similar action. Lactic acid, glutamic acid, and alanine have no such effect. Glutaric acid markedly lessens the excretion both of the sugar and the substances of the acetone group. Malonic, succinic, and pyrotartaric acids have no such effect. The mechanism of the action of these various substances is discussed at length. Sugar formation is believed to be due to substances other than carbohydrates, and the fall in acidosis when glutaric acid is given, to be due to the burning up of the precursors of the sugar. W. D. H.

**The Glycogen in Organs, and Acidosis in Phloridzin Diabetes.** ARTUR MARUM (*Beitr. chem. Physiol. Path.*, 1907, 10, 105—110).—If animals in a state of inanition are given large doses of phloridzin, they secrete sugar and exhibit acidosis in a marked degree. In a short time their organs are free from glycogen, and a marked reaction for acetone in the urine is a good index of the disappearance of the glycogen. W. D. H.

**Action of Sulphuretted Waters on Mercurial Treatment.** ALBERT DESMOULIÈRES and A. CHATIN (*Compt. rend.*, 1907, 144, 1177—1180).—Patients taking sulphuretted waters can tolerate much larger doses of mercurial salts in treatment for syphilis than others can. This is not due to the formation of an insoluble sulphur compound of mercury, but to an increase in the power of the serum of the blood to hold albuminates of mercury in solution, and therefore mercury does not accumulate in the tissues. W. D. H.

**A Case of Sulph-hæmoglobinæmia [Thiohæmoglobinæmia].** ALFRED E. RUSSELL (*Trans. Path. Soc. London*, 1907, 58, 177—183).—This is a description of a rare condition in a young woman who suffered from attacks of circulatory and respiratory failure. Cyanosis was a marked feature, and the remarkable observation was made that the blood exhibited the spectrum of thiohæmoglobin. W. D. H.

**[Physiological] Action of Oxycaffeine and other Methyl Derivatives of Uric Acid.** EMIL STARKENSTEIN (*Arch. exp. Path. Pharm.*, 1907, 57, 27—47).—In rabbits, uric acid acts as a diuretic, and in large doses is harmful to the kidneys; 3- and 7-methyluric acids stimulate the central nervous system and produce anuria, later polyuria, and then death. 1:3-Dimethyluric acid is harmless, and only causes slight diuresis; 1:3:7-trimethyluric acid (oxycaffeine) is also harmless and a good diuretic; it is possible it may prove of therapeutic value. There is no parallelism between the diuretic action of the members of the purine group and their action on nerve and muscle. W. D. H.

**Fate of Phenylurea and of Oxanilic Acid in the Organism of the Dog.** SERGEI SALASKIN and KATHARINA KOWALEVSKY (*Biochem. Zeitsch.*, 1907, 4, 210—214. Compare Abstr., 1904, ii, 674).—When diphenylurea is administered to dogs, none is found in the urine, and the amount of combined sulphuric acid is small. Considerable amounts of the diphenylurea are, however, found in the faeces.

When phenylurea is administered, aniline can be detected in the urine, and the amount of combined sulphuric acid is considerable. This is mainly in the form of *p*-aminophenyl sulphate, as, after hydrolysis with hydrochloric acid, *p*-aminophenyl can be detected.

Oxanilic acid appears to pass through the system unchanged. The behaviour of phenylurea and oxanilic acid is comparable with that of acetamide and glycine.

J. J. S.

**Action of Parathyroid Extract.** S. P. BEEBE (*Proc. Amer. physiol. Soc.*, 1907, xiii; *Amer. J. Physiol.*, 19).—The tetany produced in dogs by removal of the parathyroid is completely inhibited by the hypodermic injection of the nucleo-protein of ox parathyroid. The symptoms are in abeyance for three days after a single injection, but, so far, the animals have not been saved from ultimate death by a continuance of the treatment. After an alkaline solution of the protein has been boiled, it fails to act. The active principle is not destroyed by peptic or tryptic digestion for forty-eight hours.

W. D. H.

**Solution Tension and Toxicity in Lipolysis.** RAYMOND H. POND (*Amer. J. Physiol.*, 1907, 19, 258—283).—The toxicity of the salts tested does not under the conditions described vary inversely with their decomposition tension.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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Co-operation of Micro-organisms in the Utilisation of the Potassium of Leucite by Higher Plants. SANTE DE GRAZIA and G. CAMIOLA (*Chem. Zentr.*, 1907, i, 1451; from *Staz. sper. agrar. ital.*, 1906, 39, 829—840).—Solutions containing micro-organisms dissolved far more potassium than when micro-organisms were absent. Probably the potassium is first taken up by micro-organisms and then, being in a more readily assimilable form, by the higher plants.

N. H. J. M.

“Internal Antisepsis.” HEINRICH BECHHOLD (*Zeitsch. physiol. Chem.*, 1907, 52, 177—180).—Some recently introduced antiseptics kill bacteria in cultures when they are added in very small amounts

(1:500,000). Such small amounts have no deleterious effects, but it is found that on administration *in vivo* their bactericidal action is lessened. In the present research, tetrachloro-2:2'-diphenol was found to pass through a filter of colloid material readily, the loss being 22%. But when it was dissolved in serum and filtered, there was a loss in the filtrate of 87.5%. The proteins of the serum doubtless either adsorb it physically or enter into chemical union with it. A 1% solution in serum is therefore equivalent only to a 1 per 1000 solution in water.

W. D. H.

**Influence of Bacteria on the Changes of Nitric Acid in Soils.** JULIUS STOKLASA, JOHAN JELINECK, and ADOLF ERNEST (*Bied. Zentr.*, 1907, **36**, 370—371; from *Zeitsch. landw. Versuchswes. Oesterr.*, 1906, 844).—The organic matter present in Bohemian sugar-beet soils was found to be unsuitable as a source of carbon for the respiration processes of denitrifying bacteria; nitrates are therefore not appreciably reduced to nitrogen. It is, however, very possible that nitrites are formed when the soil is abundantly aerated.

N. H. J. M.

**Lactic Acid Fermentation in Milk.** MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 17—35).—Temperature and oxygen pressure determine the nature of the auto-fermentation of milk. At temperatures much below 40°, the fermentation due to *Bacillus coli*, &c., after lasting some hours, is replaced by a butyric fermentation, which, after some time, is succeeded by a lactic acid fermentation. In good milk, even at 40°, this temperature being that at which the development of gas-producing bacteria takes place most readily, no gas is evolved, and this fact forms the basis of a dairy test of the purity of milk.

In milk, three forms of lactic acid fermentation, determined by temperature, are to be distinguished. At a very low temperature, the slimy lactic acid fermentation, where the smaller cell walls of the organism account for the slime observed, takes place. At a middle temperature, the common lactic acid fermentation caused by *Lactococcus* predominates, and at a higher temperature is found the lactic acid fermentation of *Lactobacillus*.

Methods of isolating these organisms are given, and also their morphological characteristics and fermentation reactions. Some of the methods of diagnosis are of much interest; for instance, the presence or absence of catalase, indicated by flooding a culture plate with dilute hydrogen peroxide and seeing which colonies give rise to bubble formation, and the occurrence of emulsin as judged by the hydrolysis of indican and esculin. Mannitol may be discovered, if present, as a reduction product of lævulose by evaporating to dryness a drop of the medium on a slide and examining the crystals formed microscopically.

The active lactic acid ferments are very variable. They occur in the intestinal flora and play there an inferior part. Hereditarily constant variation is recognised when cultivation takes place at too high, or too low, oxygen pressure, or at a temperature above the optimum.

G. S. W.



**Fermentation of Glucosides by Bacteria of the Typhoid-Coli group, and the Acquisition of New Fermenting Powers by the Bacillus Dysenteriae and Other Micro-organisms.** F. W. TWORT (*Proc. Roy. Soc.*, 1907, B, 79, 329—336).—A large number of glucosides are fermented by many members of the typhoid-coli group of bacteria. Variations occur even within sub-groups. The sugar-fermenting powers of an organism may be changed by cultivating it for generations in a medium containing a sugar which at first it is unable to ferment. By such means, a pathogenic can be converted into a non-pathogenic member of the group, and so it may become unrecognisable when growing outside the body in soil, water, &c. This may account for the difficulty often experienced in isolating *B. typhosus* from these situations. It is further suggested that the reverse change may occur, and an organism become pathogenic when it again finds a suitable medium, such as the alimentary canal. W. D. H.

**Nitrification in Egyptian Soil.** RAOUL ROCHE (*Bull. Assoc. chim. Sucr. Dist.*, 1907, 24, 1699—1701).—The soils nitrify readily when suitable amounts of moisture (15—25%) are present; with a greater amount of water, denitrification rapidly takes place.

N. H. J. M.

**Beyerinck and Gosling's Sarcina.** JOHAN F. A. POOL (*Pharm. Weekblad*, 1907, 44, 664—672. Compare Beyerinck, *Abstr.*, 1906, ii, 696).—The author has applied the method of Beyerinck and Winogradsky for obtaining a pure culture of sarcina, and records results showing the influence of the experimental conditions on the purity of the culture. A. J. W.

**Stimulating Action Exercised by Mixtures of Colloidal Solutions on Germination.** H. MICHEELS and P. DE HEEN (*Bull. Acad. roy. Belg.*, 1907, 119—121).—The germination of wheat is favoured by solutions of colloidal magnesium or colloidal tin, or both together. The mean weight of the seedling is increased from 0.125 gram in distilled water to 0.151 gram in a colloidal solution of magnesium, the mean length of the first leaf from 50 to 70 mm., and the mean length of the roots from 8 to 50 mm. The stimulating effect of colloidal tin is less than that of colloidal magnesium, but the greatest effect is produced by a mixture of equal volumes of each colloidal solution. In the latter case, the number of seedlings is 96%, the mean weight of the seedling, 0.182 gram, the mean length of the first leaf, 105 mm., and the mean length of the root, 95 mm. The action of solutions containing colloidal tin and colloidal magnesium in the ratios 4:1 and 1:4, although less than that of the mixture of equal parts, is greater than that of either solution alone. E. H.

**Relation of Magnesium Oxide to Calcium Oxide in the Leaves of Different Native Plants at One or Several Periods of Growth.** JOSEF SEISSL (*Chem. Zentr.*, 1907, i, 1441; from *Zeitsch. landw. Versuchswes. Oesterr.*, 10, 88—101).—The requirement for

lime is essentially greater than that for magnesia, and the relation  $MgO : CaO$  widens with the advance of the vegetative period.

N. H. J. M.

**The Milk Curdling Ferment of the Juice of the Fig (*Ficus Carica*).** A. BRIOT (*Compt. rend.*, 1907, 144, 1164—1166).—The existence of the power to curdle milk which fig-juice has, has long been known. It is shown that fresh milk contains an anti-substance which tends to inhibit this action. The anti-ferment is destroyed by heat, and so boiled milk is more readily curdled by fig-juice than is fresh milk.

W. D. H.

**Formation of Proteins in the Lower Fungi.** OSCAR LOEW (*Ber.*, 1907, 40, 2871).—Attention is drawn by the author to the fact that he had, several years ago (*Abstr.*, 1880, 816), arrived at the same conclusions as Ehrlich (this vol., ii, 383).

W. H. G.

**A Constituent of the Wood of *Morinda Citrifolia*.** OTTO A. OESTERLE (*Arch. Pharm.*, 1907, 245, 287—290).—By extracting the powdered wood with alcohol, evaporating, extracting the residue with chloroform, evaporating, extracting this residue with benzene, and concentrating, crystals were obtained; after purification, attended with much difficulty, these melted at  $216^{\circ}$ , and had the composition  $C_{16}H_{12}O_5$ , and reactions of a *trihydroxymethylanthraquinone monomethyl ether*; the *diacetyl* derivative melts at  $184$ — $185^{\circ}$ . Possibly the substance is identical with the emodin methyl ether isolated by Perkin and Hummel from the bark of *Ventilago madraspatana* (*Trans.*, 1894, 65, 940).

C. F. B.

**Constituents of Rush-pith (Tōshin).** KINTARO OSHIMA (*J. Sapporo Agric. Coll.*, 1906, 2, 87—96).—The composition of rush-pith was found to be as follows: water, 7.15; protein, 1.73; fat, 6.55; crude fibre, 33.16; *N*-free extract, 47.02; pentosan, 35.02; methyl-pentosan, 2.82; and ash, 4.39 per cent. The pentosan consists of xylan and araban, the former predominating.

N. H. J. M.

**Presence of Sucrase and Sucrose in Different Organs of the Vine and in Some Fruits.** V. MARTINAND (*Compt. rend.*, 1907, 144, 1376—1378).—Sucrase occurs in all parts of the vine, in cherries, currants, and pomegranates, but not in apples, oranges, and lemons, and very little in pears.

Sucrose was found in the vine leaves, in the pulp of the grapes, and, in very small quantity, in the roots. It was not detected in grape-juice, or in the woody parts. It occurs in apples, oranges, and lemons.

The conclusion is drawn that the hydrolysis of sucrose is effected in the organs of vines by sucrase, and that a sufficient quantity occurs in the must from acid fruits to invert all the sucrose which may be added, without the intervention of the acids or of the sucrase secreted by yeast.

N. H. J. M.

**Action of Soil Moisture and Nitrogen Manure on the Amounts of Starch and Nitrogen in Barley.** DENSCH (*J. Landw.*, 1907, 55, 173—178).—Moderate variations in the amount of moisture in soils have no practical effect on the amounts of starch and the relation to each other of the different proteins. As regards nitrogenous manures, moderate variations in the amounts applied have no marked effect on the proteids of the barley, but have a distinct effect on the amount of starch, the best results being obtained when the manure is applied in such quantity that it is completely utilised by the plant.

N. H. J. M.

**Action of Potassium Manure on Barley.** ALEXANDER CSERHÁTI (*Chem. Zentr.*, 1907, i, 1451; from *Oester.-ung. Zeitsch. Zucker-Ind. Landw.*, 35, 676—702).—Potassium manures acted chiefly in increasing the mealiness of barley, and were also, to a less extent, beneficial as regards absolute weight, uniformity of grain, and amount of protein.

N. H. J. M.

**Action of Very Large Amounts of Ammonium Sulphate in Presence of Organic Matters and Calcium Carbonate.** ALBERT STUTZER (*J. Landw.*, 1907, 55, 81—91).—The results of pot experiments with Japanese buckwheat showed that higher yields were obtained with sodium nitrate than with ammonium sulphate, and that the addition of calcium carbonate (1%) diminished the yield without, however, increasing the percentage of calcium in the ash. Addition of straw considerably reduced the yield, especially when no calcium carbonate was present; peat and starch did not greatly affect the yield. With very large amounts of ammonium sulphate, addition of straw is beneficial.

The buckwheat was followed by mustard in the same pots. In the case of mustard, calcium carbonate proved to be beneficial, the yields being generally more than double the yields obtained without calcium carbonate. The effects of different forms of organic matter were variable, the results being generally lower, in presence of calcium carbonate, with than without organic matter, whilst in absence of calcium carbonate the organic substances increased the yields when 0.5 and 1 gram of nitrogen were added, and diminished the yields when a greater amount of nitrogen (1.5 grams) was present.

N. H. J. M.

**Nutritive Value of Non-Proteins in Hay.** MAX MÜLLER (*J. Landw.*, 1907, 55, 123—141).—The material was prepared by boiling hay with water and distilling off the water of the filtrate in a vacuum. The dried residue was digested with absolute alcohol for ten days, the residue stirred with 90% alcohol, left for two days, filtered, and distilled. The residue, which dissolved readily in water, contained 1.84% of nitrogen.

The results of feeding experiments with a dog showed that the mixture of amides, prepared as described, is utilised in the production of flesh; amide nitrogen in foods should therefore be reckoned as protein.

N. H. J. M.

**Action of Nitrite and Inoculating Soil on Soja Beans.** ALBERT STUTZER (*J. Landw.*, 1907, 55, 78—80).—It was shown previously that red clover and some non-leguminous plants are greatly injured by nitrites. Experiments made with soja beans grown in soil deficient in nitrogen showed that application of nitrite had no injurious effect and enabled the plants to grow luxuriantly. The plants, as is usually the case with soja beans grown in German soils, were free from root-nodules.

Inoculation experiments with soil sent from Japan were not very successful the first year, probably owing to the partial drying of the soil on the way. The next year, however, very luxuriant plants, with numerous nodules, were obtained, indicating that the bacteria remained uninjured during the winter in East Prussia.

N. H. J. M.

**Morphological Effect of Manures on Potatoes.** P. VAGELER (*J. Landw.*, 1907, 55, 193—214).—Phosphoric acid acts chiefly on the fundamental tissues, whilst nitrogen increases the productive tissues. Potassium promotes the productive tissues especially, and seems to have a beneficial effect on the other tissues as well.

N. H. J. M.

**Vegetation Experiments and Critical Studies on the Relation of the Activity of Sodium Nitrate and Ammonium Sulphate.** H. SÜCHTING (*J. Landw.*, 1907, 55, 1—46).—The absolute amount of water used by potatoes manured with sodium nitrate is less than when ammonium sulphate is employed, and is considerably greater when potassium manure is employed than without potassium. The relative amount of water is, however, less with than without the potassium.

As regards the yield of potatoes, ammonium sulphate had a greater effect than sodium nitrate. The amount of nitrogen taken up was the same when calcium nitrate was employed as with ammonium sulphate.

The sodium of the manure remaining in the soil diminished the assimilation of nitrogen and potassium, probably, in part, owing to its alkalinity. Unlike mangolds, barley, and other plants, potatoes are not directly benefited by sodium.

N. H. J. M.

**Action of Calcium Nitrate.** ALBERT STUTZER (*J. Landw.*, 1907, 55, 69—77).—Experiments in which potatoes were manured with different amounts of calcium and sodium nitrates respectively showed in each case that the calcium salt produced the greater yields of tubers and of starch. In the case of mangolds, sodium nitrate gave the highest yields when the amount of nitrogen applied was 26 kilos. per hectare; with 65 kilos. of nitrogen, the yields were practically the same with both manures, and with 130 kilos., calcium nitrate gave a further increase, whilst sodium nitrate reduced the yield.

N. H. J. M.

**Field Experiments on Calcium Cyanamide with Sugar-Beet.** FRIEDRICH STROHMER (*Chem. Zentr.*, 1907, i, 1451; from *Oester.-ung. Zeitsch. Zucker-Ind. Landw.*, 35, 663—675).—The manure "Stick-

stoffkalk" differs from "Kalkstickstoff" only in the manner of its preparation; calcium chloride being added to the carbide before heating (F. E. Polzeniusz, D.R.-P., 163320). Results of manurial experiments showed that the manure is suitable for sugar-beet.

N. H. J. M.

**Experiment on Late Pulling of Mangolds.** JOHN A. VOELCKER (*J. Roy. Agric. Soc. Engl.*, 1906, 67, 307—308).—Analysis of mangolds pulled on October 10th and on November 12th, 1906, showed that the weight of the crop increased considerably, and that the increase was not merely due to water.

The percentage amounts of different constituents and the amounts in lb. per acre were as follows:

	Per cent.				lb. per acre.			
	Dry matter.	N.	Non-nitrogenous.	Ash.	Dry matter.	N.	Non-nitrogenous.	Ash.
Oct. 10 .....	10.68	0.16	8.83	0.85	4357	65	3603	347
Nov. 12 .....	10.56	0.17	8.55	0.95	5766	93	4669	519

The weights of the crop at the two dates were 40,800 and 54,600 lb. per acre.

N. H. J. M.

**Changes in a Light Sandy Soil when Sterilised.** ALFRED KOCH and G. LÜKEN (*J. Landw.*, 1907, 55, 161—172).—The soil, which contained 0.0164% of nitrogen, was sterilised by heating for two hours under a pressure of 2 atmospheres. Experiments with oats showed that the yields of grain and straw were considerably increased by sterilisation. Analysis of the soil before and after sterilisation showed that the nitrogen soluble in hydrogen chloride (D 1.026) was doubled, and that the organic matter and nitrogen soluble in cold water were increased to a still greater extent by the heating.

During the early period of growth the plants did not thrive in the sterilised soils, the first leaves becoming white. Subsequently the plants recovered, and finally produced more grain and straw than the others. It was found that by sowing the seed at a later and warmer period the injurious effects can be avoided altogether. The nature of the poisonous substance was not ascertained. It was, however, found that calcium carbonate was not beneficial, and it is therefore improbable the injury was due to the production of acids.

N. H. J. M.

**Relation between the Properties of the Soil and Assimilation by Plants.** JOSEF KÖNIG, E. COPPENRATH, and J. HASENBÄUMER (*Landw. Versuchs-Stat.*, 1907, 66, 401—461).—The experiments were made with six soils having widely different physical properties and containing very different amounts of nutritive substance. The latter were determined in extracts obtained by means of strong sulphuric acid, hydrofluoric acid, 10% hydrochloric acid, dilute organic acids, ammonium citrate, 6% ammonia, and water under 5 atmospheres' pressure. In addition, determinations of hygroscopicity and catalytic power were made.

Experiments in pots and in large boxes were made, in which oats,

rye, peas, and potatoes were grown in the six soils. The dry matter, nitrogen, and ash constituents were determined in the different portions of the plants.

The nutritive substances dissolved from the soil by water under pressure corresponded more nearly with the amounts assimilated than the amounts dissolved by chemical solvents. A relation was found to exist in five out of the six soils between the catalytic power and the amount of humus.

Assimilation by plants depended on the amount of moisture and on the depth of the soil, as well as on the amount of readily soluble plant-food present. The amount of produce increased with the percentage of water up to 60% of the total water-holding capacity, and with the depth of the soil up to 30 cm. N. H. J. M.

**Solubility of Certain Salts Present in Alkali Soils.** FRANK K. CAMERON, JAMES M. BELL, and W. O. ROBINSON (*J. Physical Chem.*, 1907, 11, 396—420).—The conditions which may exist in systems containing the salts commonly found in the soils of arid regions have been established by solubility determinations and investigation of the solid phases under equilibrium conditions at 25°. The method employed was to commence with simple systems and proceed to more complex systems by the successive addition of other components. The results are given in tabular form and are also represented diagrammatically.

The nine systems investigated are as follows: (1) chlorides of calcium and sodium with water; (2) sodium chloride and sulphate with water (compare Meyerhoffer and Saunders, *Abstr.*, 1899, ii, 410); (3) sodium chloride and sulphate, calcium sulphate and water; (4) sodium chloride, calcium carbonate and water; (5) sodium chloride, calcium carbonate, carbon dioxide and water; (6) sodium sulphate, calcium carbonate and water; (7) sodium sulphate, sodium chloride, calcium carbonate and water; (8) sodium sulphate and chloride, calcium sulphate and carbonate and water; (9) as (8), except that the water was saturated with carbon dioxide.

From the results, it is shown that solid calcium chloride cannot be a normal component of alkali soils. Further, under certain conditions, a double sulphate of calcium and sodium can be obtained from system (3); at low temperatures, the salt has the formula  $2\text{CaSO}_4 \cdot 3\text{Na}_2\text{SO}_4$ , and at higher temperatures it corresponds in composition with the mineral glauberite. G. S.

**Humic Acids.** A. J. VAN SCHERMBECK (*J. pr. Chem.*, 1907, [ii], 75, 517—525).—The work of Malkomesius and Albert (*Abstr.*, 1905, i, 119) is criticised; these authors' supposed pure humic acid contained phenols, and the nitro-derivative, picric acid.

Experiments are quoted to show that the so-called humic acids, which are precipitated on addition of mineral acids to alkaline extracts of soils, are absorption complexes formed from precipitated colloids and resins; the most varied electrolytes are absorbed by these in amounts depending on their specific dissociation constants. The acidity of a soil dangerous to roots may be determined by titration of an aqueous extract. If amelioration of the soil is desired, the boil-

ing concentrated alcoholic extract is distilled, after addition of water, until the alcohol is expelled completely; one half of the resulting aqueous solution is titrated whilst hot, the other after being cooled and filtered, the difference giving the acidity of the resins. The soil is treated with 47.5 m.g. of commercial ammonium carbonate for each c.c. of *N*-acid equivalency of the resins, and the total acids are neutralised with the calculated amount of calcium carbonate.

G. Y.

**Analyses of Soils and Slimes of the Nile.** HENRI PELLET and RAOUL ROCHE (*Bull. Assoc. chim. Sucr. Dist.*, 1907, 24, 1691—1698).—Analyses of thirty samples of sugar-cane soil from Nag-Hamadi. The average amounts of the chief constituents are as follows:  $P_2O_5$ , 0.175;  $K_2O$ , 0.228; N, 0.072%. The amount of magnesium is high, varying from 1% to 3%.

N. H. J. M.

**Swedish Soils.** MATS WEIBULL (*J. Landw.*, 1907, 55, 215—231).—Mechanical and chemical analyses of several Moraine soils are given (for full results see *K. Landtbr. Akad. Handl. och Tidskr. Stockholm.*, 1907, 107). In the classification of these soils, determination of the aluminium dissolved by strong sulphuric acid was found to be most useful.

The potassium requirements of the soils could generally be ascertained from the amount of potassium dissolved by hot strong hydrochloric acid, in conjunction with the aluminium determination.

The phosphoric acid soluble in hot 18% hydrochloric acid gave useful indications only when the amount present was very small.

N. H. J. M.

**Use of Manganese Compounds as Fertilisers.** W. VAN DAM (*Chem. Weekblad*, 1907, 4, 391—397).—When seeds are soaked in manganese sulphate solution, or the salt used as a fertiliser, the yield is increased, and the plants have a darker green colour than otherwise. The author considers that the darker colour is due to the direct or indirect influence of the manganese salt on the formation of chlorophyll. The higher the percentage of chlorophyll, the greater the yield of organic material.

A. J. W.

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### Analytical Chemistry.

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The Testing of Measuring Vessels Intended for Use in Volumetric Analysis. W. SCHLOESSER (*Zeitsch. anal. Chem.*, 1907, **46**, 392—414).—An account of methods in use by the K. Normal Eichungs Kommission.

A New Apparatus for Rapid Electrolytic Estimations. FRANCIS C. FRARY (*Zeitsch. Elektrochem.*, 1907, **13**, 308—309).—In



order to avoid the use of a motor and rotating electrodes, the author causes the electrolyte itself to rotate by placing it in a magnetic field. In one form of apparatus a beaker is placed within a solenoid and the electrodes are concentric cylinders standing in the beaker. The current, used for the electrolysis, passes through the solenoid. In this case the magnetic lines of force are vertical, whilst the current in the electrolyte flows horizontally. Another, somewhat more complicated, form of apparatus is described in which this arrangement is reversed; this allows of the use of a mercury cathode lying on the bottom of the glass vessel containing the electrolyte. T. E.

**Volumetric Estimation of Hydrogen in Inorganic and Organic Substances.** ALEXANDER P. LIDOFF (*Zeitsch. anal. Chem.*, 1907, 46, 357—370).—The method proposed previously (Abstr., 1906, ii, 201) for the analysis of gaseous hydrocarbons may be employed for estimating hydrogen in many other substances, both mineral and organic. From 0.25 to 0.5 gram of the substance is mixed with about 1 gram of powdered magnesium, which has been ignited previously in a current of hydrogen, and the mixture is introduced into a thick-walled test-tube made out of combustion tubing. This tube should be 130 mm. long and 9 mm. in diameter, and a layer of magnesium powder is placed above the mixture so as to fill the tube to a height of about 80 mm. After connecting the open end of the tube with a gas measuring burette, the layer of magnesium is heated to redness, and the heat is then gradually extended to the lower part of the tube containing the mixture. The usual precautions are taken in adjusting the zero of the burette and in reading off the volume of the hydrogen. The method gives trustworthy results with ammonium chloride, sodium hydrogen carbonate, alum, ammonium thiocyanate, sucrose, starch, tartaric acid, iodoform, and many other substances, but in the case of fatty acids, theine, acetamide, and *o*-toluidine, the figures obtained are from 1% to 2% too low. W. P. S.

**Micro-chemical Detection of Sulphur, Selenium, and Tellurium in Copper.** F. WILLY HINRICHSSEN and A. BAUER (*Metallurgie*, 1907, 4, 315—317).—The reaction described by Heyn and Bauer (Abstr., 1906, ii, 230) depends on the fact that cuprous sulphide and selenide are dissolved by potassium cyanide, the copper passing into the state of a complex ion, the free sulphide or selenide ions being detected by the addition of a cadmium salt. The object of adding alcohol is to render the cadmium sulphide less soluble.

The reddish-violet coloration given by copper telluride on treatment with potassium cyanide is due to the formation of a polytelluride. The addition of a cadmium salt is not necessary in the detection of tellurium. C. H. D.

**Oxidations by Means of Electrolysis in Quantitative Analyses.** ORESTE GASPARINI (*Chem. Zeit.*, 1907, 31, 641).—The author states that the action of nitric acid on substances containing sulphur and phosphorus, &c., is much more energetic when the acid is being electrolysed. The apparatus used varies with the nature of

the substance operated on. For details, the original article and illustrations should be consulted.

L. DE K.

**New Method for the Estimation of Ammonia.** A. RONCHÈSE (*J. Pharm. Chim.*, 1907, [vi], 25, 611—617).—The method proposed is based on the fact that when formaldehyde is added to an ammonium salt, combination takes place between the aldehyde and the ammonia, and the acid of the salt is set free; the acidity may then be titrated. The neutral solution of the ammonium salt is diluted to about 100 c.c. with water free from carbon dioxide, a little phenolphthalein is added, and then an excess of formaldehyde, the quantity of the latter necessary being at least 20 c.c. of a neutral 20% solution for each 0.017 gram of ammonia present. The solution is now titrated with *N*/10-sodium hydroxide solution until a faint pink coloration is obtained. If the solution containing the ammonium salt is acid, it must be neutralised before carrying out the estimation. As ammonium salts interfere with the sensitiveness of phenolphthalein, it is better to neutralise an aliquot portion of the solution, using another indicator, and then to add the required amount of alkali to the portion taken for the estimation. Hexamethylenetetramine does not affect phenolphthalein. The method may be applied to the estimation of ammonia in urine, as the results obtained are not influenced by the presence of urea.

W. P. S.

**Volumetric Estimation of Nitrogen in Nitrates.** JOHANNES G. C. VRIENS (*Zeitsch. anal. Chem.*, 1907, 46, 414—420).—The nitrate is heated with sulphuric acid and a ferrous salt; the amount of ferrous salt oxidised being a measure of the nitric acid present. A weighed portion of the nitrate to be examined is dissolved in water and diluted to 1 litre. Ten c.c. of this solution are placed in a flask, 10 c.c. of concentrated sulphuric acid and a known volume of ferrous ammonium sulphate solution are added, and the mixture is boiled with continual shaking for two minutes. One c.c. of 0.1% potassium ferricyanide solution is then added; if the coloration produced is blue, too much of the iron solution has been used; if brown, too little. Separate portions of the nitrate solution are then treated as described above with increasing (or decreasing) quantities of the iron solution until with one test a blue coloration is obtained on adding the indicator, whilst the next successive test, containing 0.1 c.c. more of the iron solution, gives a brown coloration. As the brown coloration is not permanent, the colour should be observed within thirty seconds after adding the indicator, subsequent changes in colour being ignored. The ferrous ammonium sulphate solution should contain 25 grams of the salt per litre, a little sulphuric acid being also added, and the solution must be standardised from time to time on pure potassium nitrate. The presence of considerable quantities of potassium sulphate, ammonium sulphate, and sodium oxalate has no influence on the results obtained by the method.

W. P. S.

**Estimation of Nitrates by Busch's Method.** R. ADAN (*Bull. Soc. chim. Belg.*, 1907, 21, 229—233).—Busch's method (Abstr.,

1905, ii, 282; 1906, i, 118) for the estimation of nitrates in water gives results agreeing well with those obtained by the colorimetric methods, even when the water contains considerable proportions of mineral matter, organic colouring matter, &c. If nitrites are present, however, the results yielded are high by an amount which does not correspond with the content of nitrite. T. H. P.

**Action of Iodine on Phosphorus Sesquisulphide; Detection of the Latter in Matches.** LUDWIG WOLTER (*Chem. Zeit.*, 1907, 31, 640).—About 200 to 300 match tops are extracted with carbon disulphide, the filtrate is mixed with a 10% solution of iodine in carbon disulphide, and cooled to 0°. If phosphorus sesquisulphide is present, characteristic crystals of di-iodophosphorus sesquisulphide are obtained, which consist of beautiful, silky, shining, rhombic leaflets melting at 119.5°. Alcohol decomposes it with separation of sulphur; when boiled with water, it evolves hydrogen sulphide. It is soluble in boiling ether, but separates again on cooling. Benzene, light petroleum, chloroform, and glacial acetic acid dissolve it but sparingly, but it is soluble in xylene and toluene. L. DE K.

**Estimation of Phosphoric Acid as Phosphomolybdic Acid.** GUNNER JÖRGENSEN (*Zeitsch. anal. Chem.*, 1907, 46, 370—392).—The precipitate obtained by the addition of molybdic acid solution to a phosphoric acid solution may be ignited to constant weight, if the heat applied is not too high. It is recommended that the ignition be carried out over an Argand burner, the precipitate being stirred constantly until the combustion of the filter paper is complete. The excess of molybdic acid solution added should not be excessive, and the precipitate must not be collected on a filter until after the lapse of about twenty-four hours, the mixture being placed aside at the ordinary temperature for this period of time. The precipitate thus obtained has, after ignition, the formula  $P_2O_5 \cdot 24MoO_3$ . If too large an excess of molybdic acid solution is used, or if the temperature is too high, the proportion of molybdic acid in the precipitate is increased, but it is lowered as the concentration of the nitric acid in the solution is increased, as well as by the addition of hydrochloric acid. On the contrary, concentration of the ammonium nitrate has little influence on the composition of the precipitate. W. P. S.

**Detection of Calcium.** HENRI BAUBIGNY (*Compt. rend.*, 1907, 144, 1342).—Flanders' proposal (Abstr., 1906, ii, 901) to use potassium ferrocyanide in presence of excess of ammonium chloride as a method of detecting calcium in presence of barium or strontium is not new, having been suggested by the author (Abstr., 1895, ii, 461), who, however, showed that it was first necessary to remove the barium. T. A. H.

**Simple Method for the Estimation of Calcium in Organic Materials.** HANS ARON (*Biochem. Zeitsch.*, 1907, 4, 268—270).—The organic matter is destroyed by Neumann's method of using a mixture of equal parts of nitric and sulphuric acids. Not more than 10 or, at

most, 15 grams of material should be used in one experiment. If the percentage of calcium is very small, the solution obtained from two or more experiments may be united. Water is added to the cold mixture, the nitric acid removed by boiling, and the calcium completely precipitated as sulphate by the addition of 4 to 5 volumes of alcohol. The mixture is warmed on the water-bath to render the precipitate granular, kept for six to twelve hours, then filtered through a Gooch crucible, washed with 80—90% alcohol, dried at 105°, and weighed. J. J. S.

**Application of Micro-chemical Analysis to the Reaction of Alkaline Earths with Heavy Metals the Oxides of which are Soluble in Ammonia. Mixed Calcium Salts.** M. EMMANUEL Pozzi-Escot (*Ann. Chim. anal.*, 1907, 12, 237—239).—Fifty c.c. of the solution containing about 1 mg. of the metal are mixed with 1—2 c.c. of ammonia and 15—20 c.c. of lime-water. The liquid is filtered and boiled, and a drop is then placed on an object glass. After a minute or two, the film of calcium carbonate is destroyed by means of a platinum wire and the drop is then examined under the microscope.

Zinc yields very small crystals in stars or rosettes having, more or less, the form of lozenges, sometimes lenticular, seemingly rhombs; the field also contains many small crystals, difficult to observe amongst the mass of calcium carbonate. Cadmium yields crystals somewhat resembling thallium uranyl carbonate. They form colourless, flattened, and acute rhombs. Cobalt yields extremely delicate, lozenge-like crystals, but the reaction is not very distinct. Copper yields small crystals, formed of very small, oblique prisms grouped in confused masses. Nickel behaves like copper, but the crystals are more voluminous and distinct. For the microscopical appearances of these calcium compounds, the illustrations in the original article should be consulted. L. DE K.

**Colorimetric Estimation of Lead in Drinking Water.** M. R. MOFFATT and H. S. SPIRO (*Chem. Zeit.*, 1907, 31, 639).—One hundred c.c. of the sample are introduced into a cylindrical glass and 0.5—1 c.c. of hæmatin solution (0.5 gram per litre) is added, and the blue coloration, if any, compared with that given by other samples containing a known amount of lead. One part of lead in two million parts of water may be recognised.

Copper, zinc, and iron should be absent.

L. DE K.

**Titration of Lead without Indicators.** G. BIANCHI (*Boll. Chim. Farm.*, 1907, 46, 385—389).—A standard solution of potassium dichromate containing 7.117 grams of the salt per litre (1 c.c. = 0.01 gram lead) is added to the neutral solution of lead until no further turbidity is produced on adding another drop of the solution; the end-point is very sharply defined, owing to the colour of the precipitate, and the results obtained are of a high degree of accuracy. The titration is carried out in presence of an excess of sodium acetate. Using metallic lead, the metal is dissolved in a slight excess of nitric acid, the excess neutralised with ammonia, and sodium acetate then added. For the apparatus used in the titration, see Tarugi and Bianchi (*Abstr.*, 1906, ii, 627). W. A. D.

**Estimation of Small Amounts of Manganese in Natural Silicates.** PHILIP HOLLAND (*Chem. News*, 1907, 95, [2489], 2—3).—The manganous sulphide, obtained in due course, is ignited, then dissolved in hydrochloric acid, and boiled to expel free chlorine. Excess of sodium hydroxide is added and the liquid well shaken in contact with air. The manganese precipitate is thus converted into manganic hydroxide, which is then titrated as usual with potassium iodide and very dilute, standardised sodium thiosulphate. L. DE K.

**Electrolytic Deposition of Nickel from Ammonium Oxalate Solution.** ARTHUR FISCHER (*Zeitsch. Elektrochem.*, 1907, 13, 361—362. Compare Thiel and Windelschmidt, this vol., ii, 601).—Comparative estimations of nickel by electrolytic deposition according to the methods described by Fresenius and Bergmann, by Oettel, and also by the oxalate method, have shown that the first method gives the smallest values and the third the largest. Although the oxalate solution does not appear to yield very accurate results, yet the author recommends it for the separation of nickel from chromium and aluminium.

The periodic phenomena, which are observed in the electrolysis of oxalate solutions of nickel with a platinum anode, do not occur when a nickel anode is used. H. M. D.

**Estimation of Chromium in Alloys.** ARCHIBALD ALLISON (*Chem. News*, 1907, 95, [2484], 1—2).—The following process is recommended. One gram of the powdered sample is fused in a nickel crucible with 8 grams of sodium peroxide. The mass is extracted with 500 c.c. of hot water and boiled for ten minutes to expel hydrogen peroxide. The filtrate is acidified with sulphuric acid and the chromic acid formed titrated as usual with ferrous ammonium sulphate and potassium dichromate.

It is not strictly necessary to subject the undissolved matter to a second fusion with sodium peroxide. The alkaline liquid should be filtered through asbestos and not through paper, as this exerts a reducing action. This may, however, be remedied by boiling the acid solution with a little potassium permanganate and removing the excess by boiling with hydrochloric acid. L. DE K.

**Delicate Test for Titanium.** EDMUND KNECHT (*Chem. Zeit.*, 1907, 31, 639).—The mixture of titanic and silicic acids obtained in the course of analysis is heated in a test-tube with dilute hydrochloric acid (1 : 1) and a piece of zinc foil. Meanwhile a solution is prepared by dissolving 0.5 gram of Rochelle salts in hot water and colouring this slightly with indigotin solution. The acid solution is now added, and should titanium be present the blue colour disappears, but reappears on shaking. Instead of indigotin, an aqueous solution of methylene-blue may be used, which is still more sensitive. L. DE K.

**Estimation of Small Amounts of Antimony by the Marsh-Berzelius Method.** CHARLES ROBERT SANGER and JAMES ANDREW GIBSON (*J. Soc. Chem. Ind.*, 1907, 26, 585—589).—It is shown that

practically all the antimony added to the reduction flask of the apparatus is evolved as hydride if the amount taken is small, that is, not more than 0.1 mg. of antimonious oxide, and if the capillary portion of the mirror-tube is heated to a temperature of about 500° through a space of 3 mm. A convenient form of apparatus is described; the antimony solution is placed in a reduction flask, already containing about 5 grams of zinc and 20 c.c. of dilute hydrochloric acid, and, during the estimation, a current of hydrogen free from hydrogen sulphide is passed through the flask from a separate hydrogen generator. The mirrors obtained are compared with those yielded by known amounts of antimony, as in the arsenic test.

W. P. S.

**Estimation of Antimony in Hard Lead.** H. BECKMANN (*Zeitsch. angew. Chem.*, 1907, 20, 997—998).—The sample is, if necessary, fused with a definite proportion of pure lead so as to reduce the amount of antimony to at most 12%. The antimony is then estimated by observing the solidifying point with a suitable thermometer. An empirical table is then consulted.

L. DE K.

**Separation and Estimation of Bismuth and Mercury by the Sodium Phosphate Method.** ARTHUR STÄHLER (*Chem. Zeit.*, 1907, 31, 615—616).—The solution is mixed in a 500 c.c. Jena beaker with 3 c.c. of 10% orthophosphoric acid, diluted to 200 c.c. with boiling water, and a boiling 10% solution of trisodium phosphate is added until the liquid is only faintly acid. After a few minutes, the bismuth phosphate is collected on a Gooch crucible and washed with 200 c.c. of boiling water containing 1 gram of ammonium nitrate and four drops of nitric acid. The first filtrate is tested for bismuth by adding sodium phosphate to neutral reaction, and then acidifying with a few drops of phosphoric acid.

The bismuth phosphate is then ignited and weighed. The filtrate and washings are mixed with ammonium chloride and excess of ammonia and the mercury is recovered as sulphide by heating the solution to boiling and passing a current of hydrogen sulphide. The precipitate is collected on a Gooch crucible, washed with boiling water, then with alcohol and ether, dried at 105°, and weighed.

L. DE K.

**Rapid Estimation of Alcohol and Ethyl Ether in their Mixtures.** JULIUS FLEISCHER and HEINRICH FRANK (*Chem. Zeit.*, 1907, 31, 665).—The sp. gr. of the mixture is determined; 10 c.c. are then shaken in a graduated measure with 5 c.c. of benzene and 5 c.c. of water. The increase in the volume of benzene represents the ether; the increase in the water volume represents the alcohol plus any water contained in the mixture. The alcohol may then be calculated from the equation  $\delta = (10d - a \cdot 0.729)/(10 - a)$ , in which  $\delta$  = the sp. gr. of the aqueous alcohol,  $d$  the sp. gr. of the mixture,  $a$  the volume of the ether in c.c., and 0.729 the sp. gr. of ethyl ether. The usual alcohol tables are then consulted.

L. DE K.

**Estimation of Tartaric Acid in Argol and Wine Lees.** P. CARLES (*J. Pharm. Chim.*, 1907, [vi], 25, 617—619).—In carrying out the estimation of tartaric acid by the method already described

(Abstr., 1898, ii, 465, 545 ; 1906, ii, 710), if the mixed tartrate contains much calcium tartrate it is necessary to add the hydrochloric acid solution of the sample to the prescribed quantity of potassium carbonate, in order to prevent the precipitation of calcium tartrate before it is decomposed by the alkali. W. P. S.

**Criterion of the Purity of Salicylic Acid.** OTTORINO CARLETTI (*Boll. Chim. Farm.*, 1907, 46, 421).—The presence of traces of phenol in salicylic acid may be detected as follows : 0.25 gram of the acid is pounded in a mortar with 5 c.c. of distilled water and the mixture poured into a test-tube. Two drops of a 2% alcoholic solution of furfuraldehyde are then added and, after the liquid has been gently shaken, 2—3 c.c. of concentrated sulphuric acid are carefully poured to the bottom of the tube. The presence of as little as 0.00005 gram of phenol causes the formation, between the alcoholic liquid and the sulphuric acid, of a yellow ring, above which a dark blue ring appears with a rapidity depending on the amount of phenol present. The test may also be used to detect phenoxides in salts of salicylic acid. T. H. P.

**Identification of Aldehydes by the Spectroscope and their Differentiation from Ketones.** P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1907, 217—231).—When a 4% solution of defibrinated blood to which yellow ammonium sulphide has been added is treated with a very small quantity of a simple fatty or aromatic aldehyde, it gradually becomes brown and acquires a characteristic absorption spectrum. The latter at first contains the two bands,  $\alpha$  (maximum absorption at  $\lambda=580$ ) and  $\beta$  (maximum absorption at  $\lambda=540$ ), characteristic of oxyhæmoglobin. These gradually become less intense, and a third band, feeble and diffuse at first, appears between the other two and gradually increases in intensity. Then the  $\beta$ -band seems to be displaced towards the right and soon afterwards the  $\alpha$ -band disappears. The resulting spectrum, consisting of an intense well-defined band (mean  $\lambda=560$ ) and a wide diffuse band (mean  $\lambda=520$ ), is characteristic of hæmochromogen. If the solution of blood has been previously reduced by ammonium polysulphide, only Stokes' band is visible at first, of which the central portion gradually concentrates, forming the intense band, whilst the diffuse band forms on the right. The position of the bands is independent of the nature of the aldehyde, but their width and intensity varies with the quantity of aldehyde present. When a ketone is used instead of an aldehyde, merely the spectrum (containing Stokes' band only) of hæmoglobin is observed. Aqueous solutions of the lower, and alcoholic solutions of all, aldehydes rapidly lose their activity, probably owing to combination with the solvent. Up to a certain point, the activity increases with the molecular weight of the aldehyde. Polymerised aldehydes are inactive. Complex fatty aldehydes containing hydroxyl in the  $\beta$ -position are active, but the aldohexoses and aldopentoses are inactive. Since *p*-hydroxybenzaldehyde, protocatechuic aldehyde, and vanillin are inactive, whilst salicylaldehyde, *p*-anisaldehyde, and dimethylprotocatechuic aldehyde are active, the inactivity of the former cannot be due to the mere presence of the hydroxyl group, but is probably the result of polymerisation.

The reaction is very sensitive and, its intensity and time of appearance being proportional to the amount of aldehyde present, has been used with accurate results for the estimation of citral in essential oil of lemons.

E. H.

**Estimation of Chloral Hydrate.** P. A. W. SELF (*Pharm. J.*, 1907, [iv], 25, 4—7).—The following method, based on the reduction of the chloral hydrate by zinc dust, is stated to be trustworthy. A weighed quantity of about 0.3 gram of chloral hydrate is boiled with 60 c.c. of water and 2 grams of pure zinc dust for twenty minutes in a reflux apparatus. The condenser is then washed with a little water, and the solution is treated, while still hot, with 10 c.c. of acetic acid. After the lapse of about two minutes, the solution is filtered through a small plug of cotton-wool, and the chlorine in the filtrate is estimated either gravimetrically or volumetrically with silver nitrate.

Aluminium powder may be used in place of the zinc dust, but acetic acid must be added at the beginning of the operation in order to hasten the action of the reducing agent. The method proposed by Wallis (*Abstr.*, 1906, ii, 255) is capable of giving correct results, but is considered to be long and tedious. If other substances, which may react with sodium hydroxide, be absent, the Pharmacopœia process may be modified so as to yield trustworthy results, the modification being the estimation of, and allowance for, the sodium chloride formed by the action of the sodium hydroxide on the chloroform.

W. P. S.

**Estimation of Pentoses and Pentosans and its Practical Applications.** R. ADAN (*Bull. Soc. chim. Belg.*, 1907, 21, 211—221).—The estimation of pentoses or pentosans by distilling with hydrochloric acid and weighing the furfuraldehyde formed as phenylhydrazone or phloroglucide, gives good results, but is slow. A quicker method consists in estimating the phenylhydrazine used for the precipitation, and that present in the filtrate from the precipitate by measuring the volume of nitrogen evolved in its reaction with copper sulphate:  $\text{NHPh}\cdot\text{NH}_2 + 2\text{CuSO}_4 = \text{H}_2\text{SO}_4 + \text{C}_6\text{H}_6 + \text{Cu}_2\text{SO}_4 + \text{N}_2$ ; this reaction does not, however, proceed quantitatively in presence of hydrochloric acid, which causes the formation of secondary products such as *p*-chlorophenylhydrazine and a diazo-compound.

The results of a number of analyses show that the average contents of pentosans in cocoa beans freed from the husks, and in the husks, are 1.53 and 9.96 (7.57—10.53) respectively. The presence of husks in cocoa powder may hence be detected by estimating the content of pentosans.

T. H. P.

**Estimation of Dextrose in Urine.** H. L. VISSER (*Pharm. Weekblad*, 1907, 44, 820—823).—The author reviews the methods of estimating dextrose in urine and considers that the best results are obtained by fermentation and determination of the rotation of the fermented liquid.

A. J. W.



**A Colour Reaction with Mixtures of Carbohydrates and Proteins.** W. GRIMMER (*Milchw. Zentr.*, 1907, 3, 296—299).—If lactose is heated in a dilute sodium hydroxide solution, a yellow coloration is obtained at a temperature of 30°, and, shortly before the boiling temperature is reached, the coloration changes to bright red. The presence of casein in the solution hastens the appearance of the red coloration, the influence being noticed particularly if the mixture is left in the cold. For instance, with lactose alone the coloration appears after one hundred and twenty hours, but in seventy-two hours with the addition of 0.5 per cent. of casein. Dextrin also gives a similar coloration, but lævulose and galactose yield a brown coloration in the presence of a protein. Of the proteins examined, serum-albumin appears to be the most active in promoting the coloration; then come ovalbumin, peptone, and, lastly, casein. W. P. S.

**Detection and Estimation of Emetine.** BERNARDINO PERONI (*Boll. Chim. Farm.*, 1907, 46, 273—282).—On adding a few drops of a solution of potassium permanganate in concentrated sulphuric acid to the residue obtained on evaporating a solution of emetine, a violet coloration is obtained (sensitiveness 1 part in 10,000). On dissolving a trace of emetine in a solution of iodic acid in sulphuric acid, reddish-brown streaks appear, and, on shaking, the whole of the solution takes the same colour. On adding a trace of emetine to sulphuric acid containing a little sodium peroxide, a yellowish-green coloration appears. *s*-Diphenylcarbazine gives with emetine a rose coloration with a violet margin (characteristic; sensitiveness 1 in 100,000). Silver nitrate in sulphuric acid gives with emetine a dark green coloration which becomes intense brown, and, finally, orange-red; tungstic acid in sulphuric acid gives a dark green coloration, changing to blue. Selenious acid in concentrated sulphuric acid produces a distinct green coloration which, on adding a drop of water, becomes pale violet and then rose-coloured.

To detect emetine in ipecacuanha, 0.5 gram of the latter is mixed into a paste with about half its weight of slaked lime and a little water, and, after drying on a water-bath, the mixture is extracted with five or six times its volume of chloroform; the alkaloid is then removed from the chloroform by shaking with dilute acid, and the acid solution subjected to the tests for emetine.

The methods now in use for estimating emetine do not give satisfactory results, but the following process is stated to be trustworthy: 10 grams of ipecacuanha is intimately mixed with 10 c.c. of water and 8 grams of slaked lime, and, after evaporating the water, the dry powder is extracted with chloroform; the alkaloid is extracted with a known volume of *N*/10 hydrochloric acid, and the amount of acid left uncombined determined by titration with *N*/10 sodium hydroxide.

W. A. D.

**Alkaloid Reactions [Pilocarpine].** C. REICHARD. (*Pharm. Centr.-h.*, 1907, 48, 417—424).—This alkaloid is characterised by the liquid state of the pure base, the hygroscopic properties of the hydro-

chloride, and the insolubility of the nitrate in cold absolute alcohol. The author has tried the action of a large number of tests, of which the following are of special importance.

Sulphuric acid gives a splendid blue colour. Ammonium molybdate is not reduced in the cold. If a little of the hydrochloride and a minute crystal of potassium ferrocyanide is moistened with a drop of water, an intense yellow coloration is noticed, and on spontaneous evaporation a yellow residue is obtained which turns bluish-white when a drop of hydrochloric acid is added. If the solution is now evaporated to dryness and moistened with a drop of sulphuric acid, a splendid sky-blue coloration is obtained. If potassium ferricyanide is used and the mixture evaporated with a drop of hydrochloric acid, a residue is obtained with a beautiful bluish-green in the centre. When moistened with sulphuric acid this turns dark green. L. DE K.

**Estimation of Extractive and Protein Phosphorus.** WALDEMAR KOCH (*J. Biol. Chem.*, 1907, 3, 159—164).—Animal tissues contain phosphorus in protein, in lecithin and kephalin, and, lastly, in extractives. The latter is estimated in the filtrate after the precipitation of the lipoids by acid chloroform. After extraction with alcohol, ether, and water, the phosphorus present is combined as nuclein, phosphoprotein, and tricalcium phosphate. The latter is considered to be absent except in pathological conditions. Illustrative analyses based on these considerations are given. W. D. H.

**Formaldehyde Colour Test for Proteins.** SALOMON F. ACREE (*Amer. Chem. J.*, 1907, 37, 604—619. Compare Rosenheim, *Abstr.*, 1906, ii, 508).—If about 0.01 gram of a protein is mixed with 0.1 c.c. of formaldehyde solution (0.02%) and about 0.5 c.c. of concentrated sulphuric acid is added, a violet zone appears between the sulphuric acid and the solution. This test has been applied to a large number of substances; the results are recorded and show that the test is characteristic of proteins, but not of any other class of substances. It is preferable to the biuret reaction, since it enables complex proteins to be distinguished from such compounds as polypeptides, uric acid derivatives, and pyrimidines. Rosenheim's views with regard to the mechanism of the reaction are discussed.

It has been found that vanillin also yields a violet coloration with proteins. E. G.

**Modification of the Tannin-Salt Method for Separating Proteoses and Peptones.** FRANK C. COOK and T. C. TRESCOT (*J. Amer. Chem. Soc.*, 1907, 29, 605—606).—A slight modification of the process proposed by Bigelow and Cook (*ibid.*, 28, 1485) so as to prevent foaming of the liquid and possible loss.

Fifty c.c. of the tannin-salt filtrate are evaporated to dryness in a Kjeldahl flask with addition of a few drops of sulphuric acid, the flask being placed in a steam-bath and connected with a vacuum. Thirty c.c. of sulphuric acid are then added and the liquid boiled as usual. Addition of potassium sulphate is unnecessary, as there is already a large amount of sodium sulphate present. L. DE K.

**Guaiacum Test for Oxyhæmoglobin.** A. BOLLAND (*Bull. Acad. Sci. Cracow*, 1907, 196—203. Compare Schär, *Abstr.*, 1899, ii, 195; Vitali, *ibid.*, 1904, ii, 104; Petit and Mayer, *ibid.*, 1905, i, 655; and Willcock, *Proc. Chem. Soc.*, 1904, 20, 197).—The author finds that solutions of iron salts in solvents such as acetic acid, chloral hydrate solution or ammonia solution, which are generally employed in extracting blood from blood-stains, give a blue colour with alcoholic solution of guaiaconic acid in presence of ozonised turpentine oil. The intensity of the colour produced is greatest with 0·000,002 to 0·000,006 gram of iron in a dilution of 1 in 2,500,000, and with larger quantities of iron in solution the intensity of the colour produced diminishes. The production of the blue colour with iron compounds is inhibited by citric acid, which has, however, no effect on the production of the blue colour obtained when guaiaconic acid and ozonised turpentine oil are added to solutions of oxyhæmoglobin, and consequently blood can be detected in presence of iron by the application of this test in presence of citric acid. T. A. H.

**Behaviour of Blood and Hæmatoporphyrin towards Guaiaconic Acid and Aloin.** GEORGE A. BUCKMASTER (*Proc. physiol. Soc.*, 1907, xxxv—xxxvii; *J. Physiol.*, 35).—Properly carried out with boiled solutions, the guaiacum test is regarded as a delicate reaction for blood. It is given by the corpuscles, not by the plasma. The material in the corpuscles responsible for the reaction is hæmoglobin, and the element in hæmoglobin necessary is iron. Iron-free derivatives of hæmoglobin (such as bilirubin, hæmatoidin, or hæmatoporphyrin) do not give it. If iron is again united with the hæmatoporphyrin, the reaction returns.

Aloin behaves exactly like guaiaconic acid in the reaction. The oxidation product (aloin-red) is a mixture of acids, chiefly aloetic acid. Aloin is a less sensitive reagent, but the colour formed is more stable. Two % of hydrocyanic acid does not interfere with these reactions. Suggestions as to how the iron acts are put forward. W. D. H.

**Volhard's Method of Estimating Pepsin.** SIEGMUND KÜTTNER (*Zeitsch. physiol. Chem.*, 1907, 52, 63—90).—The principle of Volhard's method is to digest a solution of casein hydrochloride and estimate the digestive power by the amount of hydrochloric acid liberated. Several subsequent workers have used the method with certain modifications, and have found that the results fit in well, in the early stages of the digestive process, with the Schütz-Borissoff law of square roots. In the present research, this is not confirmed; the departures from this law, as well as from that of direct proportionality, are extremely wide. W. D. H.

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## General and Physical Chemistry.

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**Chemical Constitution and Rotatory Power.** MARIO BETTI (*Gazzetta*, 1907, 37, i, 62—68).—In order to throw light on the relations existing between chemical constitution and rotatory power, the author has prepared and measured the rotations of a number of aromatic aldehydic derivatives of *d*-aminobenzyl- $\beta$ -naphthol (Abstr., 1906, i, 950). This compound has a high rotatory power,  $[\alpha]_D + 58.9^\circ$ , and a simple constitution, the molecule containing only one asymmetric carbon atom which is united with four groups with the respective masses, 1, 16, 77, and 143.

The following derivatives of *d*-aminobenzyl- $\beta$ -naphthol were prepared by heating an alcoholic solution of the base with slightly more than one molecular proportion of the aldehyde. The compounds have the structure  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHPh}\cdot\text{N}\cdot\text{CHR}$ . The rotations were measured in benzene solution.

*Benzaldehyde* compound, shining white needles, m. p.  $158^\circ$ ,  $[\alpha]_D + 110.72^\circ$ ; the *r*-compound has m. p.  $150^\circ$ . *Cuminaldehyde* compound, slender, silky needles, m. p.  $155\text{--}156^\circ$ ,  $[\alpha]_D + 196.97^\circ$ . The *salicylaldehyde* compound crystallises from alcohol in massive, lemon-yellow needles, m. p.  $164^\circ$ ;  $[\alpha]_D - 15.65^\circ$ ; the *r*-compound has m. p.  $174^\circ$ . The *p*-hydroxybenzaldehyde compound forms tufts of minute, white needles, m. p.  $181\text{--}182^\circ$ ;  $[\alpha]_D + 297.31^\circ$ . *Methylsalicylaldehyde* compound, shining, white needles, m. p.  $152^\circ$ ;  $[\alpha]_D + 243.60^\circ$ . *Anisaldehyde* compound, shining, white needles, m. p.  $137\text{--}139^\circ$ ;  $[\alpha]_D + 314.48^\circ$ .  $\beta$ -Hydroxynaphthaldehyde compound, minute, yellow, highly refractive crystals, m. p.  $218^\circ$ ;  $[\alpha]_D - 232.34^\circ$ .  $\beta$ -Methoxynaphthaldehyde compound, straw-yellow, crystalline crusts, m. p.  $145^\circ$ ;  $[\alpha]_D + 133.42^\circ$ . The *protocatechualdehyde* compound, obtained in a slightly impure state, forms straw-yellow needles, m. p.  $149^\circ$ ;  $[\alpha]_D + 159.57^\circ$ . *Vanillin* compound, shining, white needles;  $[\alpha]_D + 318.55^\circ$ . *Piperonaldehyde* compound, silky, white crystals, m. p.  $187^\circ$ ;  $[\alpha]_D + 259.57^\circ$ .

The above rotations are by no means in accord with the values calculated by the method proposed by Guye (Abstr., 1892, 399; compare also Piutti, Abstr., 1895, ii, 1). Thus the derivatives of salicylaldehyde and *p*-hydroxybenzaldehyde, although they contain substituents of equal masses, have very widely differing rotations. Also, the entrance of the methyl group into the molecule is not sufficient to explain the very large value of the rotation of the methylsalicylaldehyde compound compared with that of the salicylaldehyde derivative. The influence of free hydroxyl in the ortho-position on the magnitude and sign of the rotation is seen on comparing the rotations of the hydroxy- and methoxy-naphthaldehyde compounds. On the other hand, free hydroxyl in the meta- or para-position does not appear to exert any marked influence on the rotatory power, as may be seen from the values for the *p*-hydroxybenzaldehyde and anisaldehyde derivatives and those for the protocatechualdehyde, vanillin, and piperonaldehyde compounds. It is evident that the

chemical character of the substituents is of great influence on the rotatory power, and that the group  $\cdot\text{N}:\text{C}\cdot$ , like the ethylene linking, conditions a great increase in the rotation of an optically active compound.

T. H. P.

**Valency of the Dissolved Salt Molecule Deduced from the Dispersive Properties of the Solution and from the Theory of Electrons.** C. CHÉNEVEAU (*Compt. rend.*, 1907, 145, 176—178).—Assuming that the atom of a transparent substance is constituted by a positively charged centre, the mass of which is of the same order of magnitude as that of the atom, around which gravitate electrons and negatively charged corpuscles having a mass equal to about  $\frac{1}{1000}$  of that of the atom of hydrogen, it may be supposed that light is propagated in the substance by the vibration of a certain number of negative corpuscles as well as of the positive charge. Drude (*Ann. Physik.*, 1904, 14, 677) has shown that, if the vibrations peculiar to the positive centres explain the presence of absorption bands in the infra-red, it is the vibrations of the electrons which take part in the formation of absorption bands in the ultra-violet. From the law of dispersion of a substance, this author deduced the lower limit of the number of electrons capable of acting in the dispersion of light by the substance.

Starting from these considerations and from the specific refractions (Lorentz formula) of a dissolved salt (compare Abstr., 1904, ii, 641) for two different wave-lengths, the author calculates the inferior limit of the number of electrons influencing the dispersion of the dissolved salt molecule. The value found is always of the order of magnitude of the number expressing the total valency of the molecule or double the number expressing the valency uniting the two ions in an ionisable molecule. Hence it seems probable that the atoms in a molecule do not always act individually in the phenomena of refraction and dispersion of light, but often in groups, which may have optical effects varying widely according to the nature of the elements combined and to the method of combination. This may explain why the molecular refraction or dispersion of a compound, calculated from those of its elements, often differs widely from the observed value.

T. H. P.

**Radioactivity of Some Swiss Mineral Springs.** JOSEPH VON SURY (*Chem. Zentr.*, 1907, i, 1282—1283; from *Mitt. naturforsch. Ges. Freiburg (Schweiz)*, *Chemie*, ii, 1906, 1—78).—The radioactivity of one-third to two-thirds of a litre of water from various Swiss mineral springs has been examined by Mache and Meyer's method. In order to remove the "water fall" electricity, the air containing the emanation was made to traverse a brass tube containing filings; the tube was connected to earth. The data have been calculated in electrostatic units and corrected for induced activity, normal dispersion in the air, and for residual emanation contained in the water and the apparatus.

The waters of the strong Baden springs produced distinct images on the photographic plate after two days' exposure, and gave  $2.1 \times 10^{-3}$  electrostatic units per litre of gas. Different samples of water from

the same fissure, which had the same chemical composition, gave values varying from  $0.28$  to  $0.54 \times 10^{-3}$ . The radium emanations were practically pure, but in two cases there was a slight indication of the presence of thorium. The absorption coefficient was  $0.32$  at the ordinary temperature,  $0.27$  at  $37.1^\circ$ , and  $0.12$  at  $46.9^\circ$ . The velocity of decay was measured in 10 litres of gas, the half value being attained in 3.79 days. The curves for the decrease of induced activity resembled Rutherford's curves for radium. The composition of the gas was practically the same as that given by Treadwell:  $69\%$  N,  $31\%$   $\text{CO}_2$ ,  $0.05\%$   $\text{H}_2\text{S}$ . A precipitate of sulphates from the warm springs and the potassium carbonate formed by absorbing the carbon dioxide in potassium hydroxide were only faintly active. Barium could not be detected in the water or the sediment, and the latter is not active or only slightly so. The radioactive substance appears to be derived from the deep strata. The gas contains  $1.20\%$  by volume of argon, which is 208 times more active than the original gas; helium could not be detected.

The Lorenz spring of Leukerbad gave a saturation current,  $0.26 \times 10^{-3}$ , a period of 3.68 days for decay to half value, and of 12 mins. for the half constant of the induced activity. The emanation of the sediment decreased rapidly, and the mud appeared to contain radium. The gas of the Tarasp spring is very faintly active, the activity being possibly due to radium and thorium; it gave  $0.59 \times 10^{-3}$  and constant of half decay 2.70 days.

Since activity has been supposed to vary with the quantity of hydrogen sulphide, some of the springs of the Prealpes romandes were examined, but the activity was found to be insignificant. A spring at the foot of the Braulère gave  $0.22 \times 10^{-3}$ ; water from Ragaz,  $0.33 \times 10^{-3}$ ; from Bad Alvaneu,  $1.12 \times 10^{-3}$ , and from Andeer, near Thusis,  $0.51 \times 10^{-3}$ ; the half decay constants for the activity and induced activity in the two latter cases were 3.62 and 3.50 days and 22.5 and 17 minutes respectively.

The St. Placidus spring at Disentis, which springs from diorite containing pyrites, gave a saturation current  $11.36 \times 10^{-3}$  when the water was a day old. The water contains an active salt, since the activity can be restored to water which was no longer active. The gas gave a saturation current  $= 45.4 \times 10^{-3}$ , and a period of half decay  $= 3.42$  days. The decrease of the induced radioactivity of the water or gas is practically identical with that of radium. The gas contains  $97\%$  of nitrogen. The sediment is not strongly active. The activity can be increased in the same way as that of radium.

E. W. W.

**Radioactivity of Vesuvian Cotunnite.** FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 975—978).—Cotunnite formed during the eruption of Vesuvius in April, 1906, and also that formed in the fumaroles of the crater in 1872, have a radioactivity of about 1.1 compared with that of crystallised uranyl nitrate as 1. This mineral is hence enormously more radioactive than the other Italian volcanic products examined, and the latter probably owe their slight activity to the presence of small proportions of cotunnite. The

galena formed during the Vesuvian eruption of April, 1906 (compare Abstr., 1906, ii, 766), is also strongly radioactive. T. H. P.

**Radium  $E_1$  and Radium  $E_2$ .** STEFAN MEYER and EGON VON SCHWEIDLER (*Physikal. Zeitsch.*, 1907, 8, 457. Compare Schmidt, this vol., ii, 520).—The peculiarities of the decay of the radiation of radium  $E$  cannot be explained by an admixture of radium  $D$ . The difference observed by Rutherford (Abstr., 1905, ii, 644) between the transformation periods deduced from the recovery curve and the decay curve of radium  $E$  is also best explained by the assumption of two successive products, radium  $E_1$  and radium  $E_2$ . C. H. D.

**Rays from Thorium Products.** OTTO HAHN (*Ber.*, 1907, 40, 3304—3308).—The existence of mesothorium as an intermediate product of thorium is confirmed (compare this vol., ii, 359), and it has been further ascertained that there exists another active product of complex nature in the active precipitate, thorium  $B$  and thorium  $C$ , which emit  $\alpha$ ,  $\beta$ , and  $\gamma$ -rays. By three indirect methods: (1) comparison of the activity of thorium preparations of different ages as to their  $\alpha$ -rays and emanations; (2) examination of thorium preparations free from thorium  $X$ , and (3) examination of radiothorium free from thorium  $X$ , the conclusion is drawn that thorium itself has a typical  $\alpha$ -radiation.

There have now been recognised eight degradation products of thorium: mesothorium ( $\beta$ -rays), radiothorium ( $\alpha$ -rays), thorium  $X$  ( $\alpha$ -rays), emanation ( $\alpha$ -rays), thorium  $A$  (slow  $\beta$ -rays, which may be  $\delta$ -rays and are scarcely more penetrating than  $\alpha$ -rays), thorium  $B$  and thorium  $C$  ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays). W. R.

**Ionisation by Spraying.** MAURICE DE BROGLIE (*Compt. rend.*, 1907, 145, 172—173).—The intensity of the ionisation produced by spraying varies considerably with the diameter of the orifice, being small when the latter is capillary or large and having a maximum value for an orifice of intermediate size. On varying the pressure of spraying through a narrow tube open to the air, the current indicated by the electrometer varies at first slowly and afterwards proportionally with the difference of pressure. On gradually adding different salts, such as sodium, potassium, or barium chloride, potassium iodide, &c., and tracing curves with the concentrations of salt as abscissæ and the currents obtained as ordinates, it is found that: (1) for positive charges, the ionisation, which is very slight at first and is possibly zero for pure water, increases rapidly to a flattened maximum for concentrations of about  $M/1000$  and then diminishes to an apparently constant value. (2) For negative charges, the ionisation starts from a value sensibly greater than with (1), passes through a sharper maximum at about  $M/2000$ , cuts curve (1) at a slight angle at about  $M/106$ , and then continues to fall slowly. In the initial rising portion of each curve, the sensitiveness to slight variations of concentration is very great. Dilute solutions of hydrochloric, sulphuric, or acetic acid, or of potassium or sodium hydroxide,

exhibit behaviour similar to that of salt solutions. On adding alcohol to the water, the ionisation increases regularly until about 30% of alcohol is present and then remains constant until 100% of alcohol is reached. The action of radium or X-rays on the gases issuing from the sprayer produces the following effects. (1) The ionised gases from salt solutions have their conductivity reduced to  $1/6$ — $1/10$  of its original value. (2) The almost non-conducting gases, from sprayers containing benzene, toluene, or turpentine, become conductors; they hence contain neutral primitive centres, chargeable by radium. The presence in the sprayed gases of neutral centres, such as exist in flame gases de-electrified by a condenser, increases appreciably the ionisation produced by spraying, but this effect is not so sensitive to variations of concentration as in ordinary air. T. H. P.

**The Electrolytic Dissociation of Fused Salts.** RICHARD LORENZ (*Ber.*, 1907, 40, 3308—3311).—A reply to Arrdt (this vol., ii, 598), who found  $\lambda\eta = k$ , where  $\eta$  is the viscosity and  $\lambda$  the equivalent conductivity, and concluded that fused univalent salts are completely dissociated. The author deduces from the Kohlrausch-Arrhenius law that  $\lambda\eta = \alpha K$ , where  $\alpha$  is the degree of dissociation, and therefore the expression  $\lambda\eta = k$  does not enable the degree of dissociation, complete or otherwise, to be ascertained. Further experimental results are given (compare this vol., ii, 430, 438) which show that the degree of dissociation does not appreciably alter with the temperature. W. R.

**Discharge of the Anion of Acetic Acid.** GERHARD PREUNER (*Zeitsch. physikal. Chem.*, 1907, 59, 670—681).—The mixture of gases evolved during the electrolysis of a solution containing acetic acid and potassium acetate has been analysed. When the anode is of bright platinum, it is found that there is a considerable range of potential above 1.7 volts, over which no discharge of acetate ions takes place. When, however, the anode *P.D.* reaches a value of about 2.5 volts, the amount of carbon dioxide and ethane in the evolved gas begins to rise rapidly, and increases as the anode *P.D.* is raised. This point of discontinuity at 2.5 volts is indicated also on the current-*P.D.* curve. This value is about 0.4 volt higher than the *P.D.* recorded by Bose (*Abstr.*, 1899, ii, 348).

When the anode is platinised, the gas evolved, even at about 2.5 volts *P.D.*, contains only small quantities of carbon dioxide and ethane. It is suggested that this is due to the predominating secondary production of oxygen from the action of the discharged acetate ions on water. J. C. P.

**Decomposition Potential of Acetic Acid and Propionic Acid.** GERHARD PREUNER and ERNEST B. LUDLAM (*Zeitsch. physikal. Chem.*, 1907, 59, 682—690).—The decomposition potential of acetic acid in a solution which is  $N/2$  with regard to acetic acid and  $N/2$  with regard to potassium acetate is found to be 2.54 volts, both by analysis of the evolved gas (see preceding abstract) and by a study of the current-*P.D.* curves. The corresponding value for propionic acid in a solution which is  $N/2$  with regard to the free acid and also with regard to the potassium salt lies at 2.58 volts. The decomposition potentials found



by Bose (Abstr., 1899, ii, 468), namely, 2.05 volts for acetic acid and 2.07 volts for propionic acid, could not be detected.

The points of discontinuity in the current-*P.D.* curves are most clearly indicated when the logarithm of the current strength is plotted against the *P.D.* This supports the view (already probable on theoretical grounds) that the relation between the current strength and the potential is a logarithmic one.

When the anode is platinised and the current density is high, the oxidation of acetic acid is probably effected by the formation of oxides of platinum.  
J. C. P.

**Attainment of High Temperatures in Laboratory Experiments.** CAMILLE CHABRIE (*Compt. rend.*, 1907, 145, 188—189).—The author has investigated various means of obtaining high temperatures in the laboratory without using the electric furnace. The best results are obtained by placing the substance to be heated in a crucible of magnesia, which is surrounded, in an ordinary clay crucible, with a mixture of ferric oxide and aluminium. This mixture is then ignited by means of barium peroxide and magnesium wire. In this way, a temperature higher than the melting point of platinum is reached. The magnesia crucible may be replaced by a tube of the same substance traversing the outer crucible by means of two apertures. Porcelain tubes do not resist the high temperature attained.  
T. H. P.

**The Variation of the Melting Point of Eutectic Mixtures.** CARL BENEDICKS and RAGNAR ARPI (*Metallurgie*, 1907, 4, 416—419).—A mechanical mixture of two substances in the eutectic proportion will only melt at the true eutectic temperature when the particles of the two components are sufficiently small. The melting point is higher the coarser the particles of the mixture. The greatest influence is exerted by the size of grain of that component which occurs in the smaller proportion. Experiments with mixtures of lead and tin confirm this conclusion.

The melting point of grey cast iron, in which the graphite is comparatively coarse and scattered, is considerably higher than the freezing point. White cast iron, however, in which the ferrite and cementite are intimately mixed, shows identical freezing and melting points.  
C. H. D.

[Application of Thermal Analysis to Ternary Systems.] ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1907, 59, 697—702).—Remarks bearing on the recent paper by Sahmen and von Vegesack (this vol., ii, 532).  
J. C. P.

**Direct Determination of Heats of Reaction.** LAWRENCE J. HENDERSON and CHARLES T. RYDER (*Proc. Amer. Soc. Biol. Chemists*, 1907, xvii—xviii, *J. Biol. Chem.*, 3).—A thermometric method is described for determining the heat of slowly occurring reactions; the mixture was kept in a thermostat which showed variations of not more than two-hundredths of a degree. In tryptic digestion, the heat of the

reaction is small, but positive, unless the observed change of temperature is due to secondary reactions. Further studies of biochemical reactions are promised. W. D. H.

**Mercuric Iodide. Calorimetry and Cryoscopy.** JOSEPH GUINCHANT (*Compt. rend.*, 1907, 145, 68—70. Compare Abstr., 1904, ii, 538).—By direct calorimetric measurement, the value  $L = 9.79$  Cal. is obtained for the latent heat of fusion of mercuric iodide at  $250^\circ$ , the values 0.0406, 0.0446, and 0.0554 for the specific heats of red, yellow, and fused mercuric iodides respectively, and the value 1.53 Cal. for the heat of transformation of 1 kilogram of the yellow into the red iodide at  $130^\circ$ . The last four data agree with the values obtained by Regnault and by Schwarz.

By substitution of the above value of  $L$  in the equation  $K = 0.0198T^2/L$ , the value 550 is obtained for the cryoscopic constant  $K$ . From the depression of the freezing point of mercuric iodide, produced by dissolving other iodides in it, the following experimental values of  $K$  are obtained: with lead iodide, 565, silver iodide, 530, potassium iodide, 535, and mercurous iodide, 540. When mercuric oxide, mercuric chloride, and mercurous chloride are substituted for these iodide, the values 850, 970, and 1070 respectively are obtained for  $K$ , indicating that these salts show similar anomalies to solutions in water. The author concludes that for substances giving a normal depression of the freezing point, Raoult's constant  $K$  agrees with van't Hoff's theoretical value, but that Raoult's second empirical law  $K/M' = 0.50$  is not applicable to solvents of which the freezing temperatures differ largely ( $\text{Sb}_2\text{S}_3$ , Al, Pb,  $\text{HgI}_2$ ). E. H.

**Thermochemical Data Relating to [Millon's] Base and its Hydrates.** H. GAUDECHON (*Compt. rend.*, 1907, 144, 1419—1422. Compare this vol., ii, 621).—The ammonio-mercuric base is not attacked by cold potassium hydroxide of any strength, but at  $100^\circ$  it is decomposed into ammonia and the brown, crystallised mercuric oxide previously described. An instantaneous solvent being necessary for calorimetric estimations, potassium cyanide solution is used. The author shows that this reacts with the base according to the equation  $(\text{NHg}_2)_2\text{O} + 7\text{H}_2\text{O} + 8\text{KCN} = 4\text{Hg}(\text{CN})_2 + 2\text{NH}_3 + 8\text{KOH}$ . The heat of formation of the anhydrous base has been determined by three systems of different cycles, giving the values  $-75.4$  Cal.,  $-75.3$  Cal., and  $-76.7$  Cal. respectively. The difference of the latter from the two former results is due to some uncertainty in the final result of one of the reactions of the third cycle, and by substituting a heat of reaction obtained indirectly the third result is reduced to  $-75.7$  Cal. The mean value for the heat of formation of  $(\text{NHg}_2)_2\text{O}$  (solid) from nitrogen (gas), mercury (liquid), and oxygen (gas) is  $-75.5$  Cal. The heat of formation of  $(\text{NHg}_2)_2\text{O}, \text{H}_2\text{O}$  from the anhydrous base and water (solid) is  $+1.6$  Cal., or  $+3.0$  Cal. from water (liquid); of  $(\text{NHg}_2)_2\text{O}, 4\text{H}_2\text{O}$  from the monohydrate and water (solid),  $+4.0$  Cal., or from water (liquid),  $+8.2$  Cal.; of the pentahydrate from the tetrahydrate and water (solid),  $+1.0$  Cal., or from water (liquid),  $+2.4$  Cal.,

and of  $(\text{NHg}_2)_2\text{O} \cdot 9 \cdot 5\text{H}_2\text{O}$  from the pentahydrate and water (solid),  
-5.1 Cal. E. H.

**Scale of Molecular Weights of Gases.** DANIEL BERTHELOT (*Compt. rend.*, 1907, 145, 180—183).—The author discusses the determination of the molecular weights of gases from their densities (compare this vol., ii, 154). Guye (this vol., ii, 437, and previous papers) assumes that the molecular weight of a gas can be calculated, knowing its compressibility and density alone, by means of the formula  $M = V_0 d(1 - A)$ . But this is an illusion, since  $V_0$  has not an a priori value, but is defined by the expression:  $V_0 = M/d(1 - A) = M'/d'(1 - A') = \&c.$ , its actual value being obtained by substituting in this expression the observed magnitudes of the various terms for a particular gas, generally oxygen. Guye has also adopted for  $V_0$  the value 22.412, obtained from the molecular weights of a number of gases, and has employed this value of  $V_0$  to calculate the molecular weights of the same gases. T. H. P.

**Endosmosis between Two Liquids of the Same Chemical Composition, but at Different Temperatures.** G. LIPPMANN (*Compt. rend.*, 1907, 145, 104—105).—The author finds that endosmosis takes place, not only between liquids of different chemical composition, but also between two masses of the same liquid, provided these are at different temperatures. In experiments with cold and hot water, separated by a permeable membrane of goldbeater's skin, collodion, or gelatin in a special form of apparatus, which is described, a transference of the cold towards the hot liquid was observed.

G. Y.

**Thermo-endosmosis of Gases.** G. LIPPMANN (*Compt. rend.*, 1907, 145, 105—106).—Endosmosis has been observed between two volumes of air at different temperatures, separated by a permeable membrane of goldbeater's skin or paper. A water manometer connected with the vessel containing the cold air showed a fall of 40 mm. pressure. The transference of the cold towards the hot air takes place more rapidly than the similar transference in the case of water.

G. Y.

**Diffusion of Salts in Solution. II.** J. C. GRAHAM (*Zeitsch. physikal. Chem.*, 1907, 59, 691—696).—A continuation of earlier work (Abstr., 1905, ii, 147). When the diffusion constant for the chloride of a metal is taken as the unit, the diffusion constants for the other salts of the same metal are as follows: hydroxide, 1.26; nitrate, 1.018; sulphate, 0.565; iodide, 0.945; acetate, 0.773; sulphite, 0.582; carbonate, 0.633, and hydrogen sulphate, 0.795. These numbers are mean values, obtained from the relative values for the chlorides, hydroxides, &c., of different metals. Similarly, when the diffusion constant of a salt of potassium is taken as the unit, the mean diffusion constants for the same salt of various other metals are as follows: sodium, 0.775; lithium, 0.726; ammonium, 1.02; zinc, 0.542; manganese, 0.552; magnesium, 0.531, and ferrous iron, 0.521.

The author shows from his results that the diffusion velocity of a salt is proportional to the product of the velocities of anion and cation. It will be observed from the foregoing numbers that lithium salts diffuse more slowly than the corresponding sodium salts, and these again more slowly than the corresponding potassium salts. This may be connected with hydration in solution, and it is noteworthy that when the anions and cations are arranged according to their diffusion velocities the order is very similar to that obtained when they are arranged according to their mobilities under the action of an electric potential.

J. C. P.

**Solubility. II.** EUGENE C. BINGHAM (*Amer. Chem. J.*, 1907, 38, 91—118. Compare this vol., ii, 536).—In the earlier paper, a discussion was given of the conditions in which liquids are immiscible and of the change of temperature which will render such liquids miscible. It was found that substances of small molecular volume are often immiscible with those of large molecular volume.

The present paper deals with the cause of this phenomenon, and from theoretical considerations it is suggested that miscibility is dependent primarily on the attractions between the particles, and evidence is adduced to prove that molecular attractions are inversely proportional to molecular volumes.

It is shown that there is an intimate connexion between the critical solution temperature (Masson, *Abstr.*, 1891, 791) and the ordinary critical temperature, and it is demonstrated that a solution of a liquid in a liquid passes imperceptibly into that of a gas in a liquid and of a gas in a gas.

The following explanation is given of the critical solution temperature. On raising the temperature of the liquid, expansion takes place, the attraction between the molecules is diminished, and a large number of the particles of each liquid are able to pass into solution in the other liquid. The dissolved particles ultimately become so crowded together that they are no longer independent of each other, that is, the osmotic pressures no longer obey the gas laws. When the forces tending to bring the liquids into solution become equal to the sum of the cohesive forces between the particles of each liquid, the surface separating the two liquids vanishes, and all parts of the mixture become identical, the temperature at which this takes place being the critical solution temperature.

A consideration of the behaviour of aniline when added to water illustrates the fact that below the critical solution temperature only mutual partial solubilities exist, which, however, gradually increase until the critical solution temperature is reached, whilst above this temperature the liquids are completely miscible.

The lower critical solution temperature (Guthrie, *Abstr.*, 1885, 337, 339) is regarded as due to the introduction of some new attractive force, probably chemical, between the molecules. The only case hitherto recorded of a mixture yielding both an upper and a lower critical solution temperature is that of nicotine and water (Hudson, *Abstr.*, 1904, i, 446).

It is shown that the critical pressure is a measure of the molecular

attraction at the critical temperature, and a number of data are quoted which indicate that the product of the molecular volume and the critical pressure is a constant.

The connexion between solubility and molecular volume is emphasised by reference to a list of solubilities given by Rothmund (Abstr., 1898, ii, 503), in which the order of the molecular volumes agrees almost entirely with that of the solubilities. Rothmund (*loc. cit.*) has pointed out a relation between the order of the solubilities and that of the dielectric constants of the substances. This relation is in harmony with the theory now put forward, since dielectric constants are also connected with the molecular volumes.

E. G.

**The Spontaneous Crystallisation of Binary Mixtures. Experiments on Salol and Betol.** HENRY A. MIERS and Miss FLORENCE ISAAC (*Proc. Roy. Soc.*, 1907, 79, A, 322—351).—For a complete study of the crystallisation of binary mixtures, the consideration of the freezing point curve is insufficient, and needs to be supplemented by a study of the "supersolubility curve" (*Trans.*, 1906, 89, 430). The two branches of the supersolubility curve are approximately parallel with those of the freezing point curve, and intersect at a "hypertectic" point lying below the eutectic point. The conditions of such crystallisations have been studied experimentally in mixtures of salol (phenyl salicylate) and betol ( $\beta$ -naphthyl salicylate). In a mixture of 90% salol and 10% betol, it is possible to observe four freezing points, none of which coincide with the eutectic temperature, namely, the separation of crystals of salol by inoculation at 38°, a labile shower of salol at 28°, crystallisation of betol by inoculation when supercooled to 17.5°, and a labile shower of betol at 10.5°. The experiments were made by observing the temperatures at which crystals appeared, and also by the method of change in the refractive index (*loc. cit.*). The hypertectic point lies at 15° and about 74% of salol.

In most experiments with alloys and other mixtures, agitation and inoculation have been employed. But in the solidification of natural rocks, the conditions are not, in general, favourable to solidification as a eutectic, and the frequent absence of the eutectic structure in rocks is thus accounted for. The mixture which, under normal conditions, may be expected to yield a eutectic structure is that of which the composition corresponds with the hypertectic point.

The sudden change in the velocity of crystallisation of salol and betol, observed by Tammann (Abstr., 1899, ii, 548), occurs almost exactly at the temperatures of spontaneous crystallisation.

C. H. D.

**Kinetics of Reactions in Non-aqueous Solutions.** CARL TUBANDT [and, in part, K. MOHS] (*Annalen*, 1907, 354, 259—324. Compare Abstr., 1905, ii, 424; Vorländer, Abstr., 1903, i, 230).—A study of the influence of the solvent on the velocity of the inversion of *l*-menthone by bases and acids. The method employed is that previously described, but as most of the solvents studied are insoluble

in water the titrations have been performed in alcoholic solution with  $N/20$  sodium methoxide.

The following values have been obtained for  $k + k'$  in the equation :  $k + k' = 1/t.ln.\xi/\xi - x$ , with the alcohols named as solvents and the sodium alkyloxides as the catalysts ;  $c$  is the concentration of the catalyst.

At  $20^\circ$ ,  $c = 0.02N$ : methyl alcohol, 0.00317; ethyl alcohol, 0.00826; *n*-propyl alcohol, 0.0107; *n*-butyl alcohol, 0.0130; *isobutyl* alcohol, 0.0147; *isoamyl* alcohol, 0.0159; *n*-heptyl alcohol, 0.0165; *n*-octyl alcohol, 0.0191; *isopropyl* alcohol, 0.0171; *sec.*-butyl alcohol, 0.0336; *sec.*-octyl alcohol, 0.0572; *tert.*-butyl alcohol, 0.0712; allyl alcohol, 0.0020; benzyl alcohol, 0.0012. At  $25^\circ$ ,  $c = 0.01N$ : *n*-butyl, 0.0092; *isobutyl*, 0.0105; *sec.*-butyl, 0.0244; *tert.*-butyl alcohol, 0.0504.

With alcohols of a homologous series, the velocity of inversion increases with the molecular weight; with isomeric alcohols, the velocity of the reaction is greatest in the tertiary and least in the primary, the values obtained with the propyl alcohols being in the proportion: primary, 1:secondary 1.6; with the butyl alcohols: primary, 1:secondary, 2.65:tertiary, 5.48, and with the octyl alcohols: primary, 1:secondary, 3, whilst the velocity is smaller in an unsaturated than in the corresponding saturated alcohol. These results show that the velocity of inversion of menthone by sodium alkyloxides increases as the dielectric constant of the solvent diminishes (compare Menschutkin, Abstr., 1890, 1366).

The following values for  $(k + k').10^4$  were obtained with sodium alkyloxides as catalysts and mixtures of the alcohols and indifferent liquids as solvents; the percentages quoted are those of the indifferent liquid in the mixture.

At  $20^\circ$ ,  $c = 0.02N$ : methyl alcohol-benzene: 33.3%, 23; 50%, 23; 75%, 25; 90%, 54; 95%, 101; 97%, 170. Ethyl alcohol-benzene: 10%, 76; 20%, 64; 33.3%, 58; 50%, 61; 66.6%, 69; 80%, 95; 90%, 172; 95%, 266. *iso*Butyl alcohol-benzene: 25%, 133; 50%, 148; 75%, 214; 90%, 426. Ethyl alcohol-carbon tetrachloride: 33.3%, 68; 96%, 310. Ethyl alcohol-ether: 10%, 84; 25%, 89; 50%, 113; 75%, 230; 88%, 462.

The curves representing the values obtained with mixtures of alcohols and benzene fall at first as the percentage of benzene increases, reach a minimum with less than 50% of benzene present, and then rise with increasing rapidity. The curve representing the values obtained with mixtures of ethyl alcohol and ether rises with increasing percentages of ether without first falling to a minimum. The inversion of *l*-menthone cannot depend on the presence of ions, since it is entirely different in nature from such an action as that of methyl iodide on sodium methoxide or ethoxide, the velocity constants for which in alcohol-benzene mixtures, when calculated with the aid of the equation for bimolecular reactions, diminish steadily as the percentage of benzene increases.

The following values were obtained for  $k + k'$  with sodium alkyloxides as catalysts in mixtures of alcohols and water at  $20^\circ$ , with  $c = 0.02N$ ; the percentages are the proportion of water.

Methyl alcohol: 5%, 0.00325; 10%, 0.00333; 20%, 0.00369; 30%, 0.00380. Ethyl alcohol: 5%, 0.00726; 10%, 0.00621; 20%, 0.00504;

30%, 0.00407; 40%, 0.00330. Propyl alcohol: 20%, 0.0038; 40%, 0.0019. Allyl alcohol: 30%, 0.00180.

The addition of water to the various alcohols influences the velocity of the inversion in different directions. The curves for aqueous ethyl and propyl alcohols falls rapidly, but that for allyl alcohol only slightly with the increase in the amount of water present, whilst that for methyl alcohol rises, probably to a maximum with about 10% of water present. A relation between the velocity of the inversion and the conductivity of the aqueous alcohol cannot be assumed; the increase of the velocity on addition of water to the methyl alcohol solution is observed also with higher concentrations of the catalyst: with  $c = 0.2N$ , in absolute methyl alcohol,  $k + k' = 0.0333$ ; in 75% methyl alcohol, 0.0370.

The inversion of menthone, by means of acids in alcoholic solution, is retarded to a very marked extent by traces of water; consistent results could be obtained only with alcohols distilled over metallic calcium. The following values for  $k + k'$  were obtained with hydrogen chloride as catalyst and anhydrous alcohols as solvents, at 20°, with  $c = 0.01N$ .

Methyl, 0.0067; ethyl, 0.0150; propyl, 0.0215; isobutyl, 0.0265; isoamyl, 0.0277; *n*-octyl, 0.0492; allyl, 0.0104; benzyl alcohol, 0.0335. The velocity is related to the molecular weight and structure of the alcohols in the same manner as with sodium alkyl oxides as catalysts.

The inhibiting influence of water on the inversion by means of hydrogen chloride increases with the molecular weight of the solvent alcohol, as is shown by the following values for  $k + k'$  obtained with aqueous alcohols; the percentages of water are given. Methyl, 0.05%, 0.0041; 0.1%, 0.0025; 10%, 0.000027. Ethyl, 0.05%, 0.0064; 0.1%, 0.0040; 10%, 0.000015; 40%, 0.0000068. Propyl alcohol, 0.1%, 0.0060.

On addition of benzene or carbon tetrachloride to the alcoholic solution, the inversion by means of hydrogen chloride is accelerated, at first slowly, then more rapidly, to a maximum with about 97% of benzene present, and finally falls sharply to the value for the indifferent solvent;  $k + k'$  for benzene,  $c = 0.01N$ , 0.0023;  $c = 0.005N$ , 0.0010; for carbon tetrachloride,  $c = 0.01N$ , 0.0053. The following values for  $(k + k') \cdot 10^4$  were obtained with mixtures containing 97% of the indifferent solvent. Methyl alcohol-benzene,  $c = 0.01N$ , 625; ethyl alcohol-benzene,  $c = 0.01N$ , 587; isobutyl alcohol-benzene,  $c = 0.005N$ , 283; ethyl alcohol-carbon tetrachloride,  $c = 0.01N$ , 700. The velocity of the reaction is accelerated to a very marked extent by the addition of small amounts of alcohols to the benzene solution; with  $c = 0.005N$ , in mixtures of 99% of benzene and 1% of alcohol,  $(k + k') \cdot 10^4$  had the values: methyl alcohol, 232; ethyl, 186; propyl, 142; isobutyl, 92; amyl, 83; *n*-octyl, 52. With  $c = 0.01N$ , the pure indifferent solvents gave for  $(k + k') \cdot 10^4$ : benzene, 23; xylene, 20; chlorobenzene, 69; ether, 4; ethyl bromide, 34; ethylene dibromide, 108; carbon tetrachloride, 53; chloroform, 471. The small value obtained with ether results probably from the formation of a stable additive compound of ether with hydrogen chloride, which does not act as a catalyst.

Whilst the velocity of the inversion under the influence of sodium

alkyloxides is not accelerated to any marked extent by the presence of neutral salts, the catalytic action of hydrogen chloride is increased considerably. The following values for  $k+k'$  were obtained with ethyl alcoholic solutions,  $c=0.01N$ , containing an equivalent amount of the salt: triethylamine hydrochloride, 0.0171; aniline hydrochloride, 0.0190; lithium chloride, 0.0190.

Picric and sulphosalicylic acids have only feeble inverting powers. Ethyl-alcoholic picric acid,  $c=0.1N$ , gives  $k+k'=0.0012$ ; chloroform is slightly more favourable to the catalytic action of picric acid than is benzene, but in both solvents inversion can be observed only after some days.

Sulphosalicylic acid in absolute ethyl-alcoholic solution gives the following velocity constants:  $c=0.01N$ , 0.0014;  $c=0.04N$ , 0.0041;  $c=0.1N$ , 0.0071;  $c=0.04N$  acid and 0.04*N* aniline sulphosalicylate, 0.0020;  $c=0.04N$  acid and 0.08*N* aniline sulphosalicylate, 0.0014;  $c=0.01N$  acid in 10% alcohol and 90% benzene, 0.0008.

The alcoholysis of salts has been studied further (compare Abstr., 1905, ii, 424) by means of the inversion of *l*-menthone. The following values have been obtained for the alcoholysis constant  $K$  with the aid of the equation:  $K = (k+k')[(k+k')_0(n-1) + (k+k')]/V[(k+k')_0(k+k')_0 - (k+k')]$ , in which  $(k+k')_0$  is the inversion constant for the given concentration of the sodium alkyloxide,  $(k+k')$  the corresponding value observed in presence of the base and the acid, and  $n$  the number of molecules of acid present per molecule of base.

Ethyl sodioethylacetoacetate: methyl alcohol, 0.27; ethyl alcohol, 0.011; propyl alcohol, 0.0050; *isobutyl* alcohol, 0.0015; amyl alcohol, 0.0011; ethyl alcohol and 33.3% benzene, 0.0083; and 66.6% benzene, 0.0024; and 91% benzene, 0.00074. Sodium ethyl sulphide: methyl alcohol, 0.0091; ethyl alcohol, 0.0019; *isobutyl* alcohol, 0.00073; amyl alcohol, 0.00068. Sodium phenoxide: methyl alcohol, 0.0031; ethyl alcohol, 0.00070.

The alcoholysis constants, which are greatest in methyl-alcoholic solution and decrease rapidly with the molecular weight of the solvent as also with the percentage of benzene in the alcohol-benzene mixtures, are approximately inversely proportional to the constants for the velocity of the inversion of menthone by means of hydrogen chloride.

The mechanism of the inversion of menthone is discussed and considered to consist of the formation of additive compounds of the carbonyl group with the catalyst alone or together with the solvent. The formation of such compounds would take place the more easily, and the velocity of the inversion would be therefore the greater, the smaller the hydrolytic power of the solvent. G. Y.

**Chemical Equilibrium of Several Bases in Simultaneous Contact with Phosphoric Acid.** ANTONIO QUARTAROLI (*Gazzetta*, 1907, 37, i, 198—200).—The author confirms his earlier observation (Abstr., 1905, ii, 821), that when one equivalent of lime and two of sodium hydroxide are added to 1 mol. of phosphoric acid, precipitation occurs of about one-third of the acid as tricalcium phosphate together with a little tetracalcium phosphate, and not, as Berthelot states



(Abstr., 1901, ii, 504 ; 1902, ii, 255 ; 1906, ii, 657), of about two-thirds of the acid as an insoluble double phosphate of calcium and sodium.

T. H. P.

**Formation of Ethyl Chloride.** ANTON KAILAN (*Monatsh.*, 1907, 28, 559—569. Compare Cain, Abstr., 1894, ii, 133).—It has been found necessary to determine the velocity of formation of ethyl chloride from alcohol and hydrogen chloride, not only in absolute alcohol (compare this vol., ii, 242), but also in alcohol containing water.

The constants for the formation of ethyl chloride are proportional to the concentration of the hydrogen chloride only in absolute alcohol. In alcohol containing water, even in 99.9% alcohol, an increase in the concentration of the hydrogen chloride is found to be accompanied by a greater increase in the velocity constant. The mean velocity constant for concentrations of hydrogen chloride between  $c_m = 0.1583$  and  $c_m = 0.6708$  and concentrations of water between  $w_m = 26.10^{-3}$  and  $w_m = 50.10^{-3}$  is  $k = 2.7.10^{-5}$ , or for natural logs.  $k = 6.2.10^{-5}$ . For concentrations of water between  $w_m = 0.305$  and  $w_m = 0.336$ , the values observed were :

$c_m$	=	0.1577	0.3120	0.3180	0.6217	0.6290
$10^5.k$	=	0.6	1.0	1.4	2.1	1.9

For concentrations of water between  $w_m = 0.601$  and  $0.644$  :

$c_m$	=	0.3016	0.3478	0.6237
$10^5.k$	=	0.4	0.3	1.2

The relation of the velocity constant (nat. logs.) to the molecular concentration of the hydrogen chloride and of the water is represented by the equation :  $1/k = 14780 + (20300 - 22020/c + 6575/c^2)w + (-259400 + 247300/c - 28330/c^2)w^2$ , which applies to solutions with the molecular concentration of the water between  $w = 0.02$  and  $w = 1.3$ , and that of the hydrogen chloride,  $c = 0.66$  ; for  $w = 0.02 - 0.6$  and  $c = 0.3$  ; and for  $w = 0.02 - 0.3$  and  $c = 0.16$ .

It is also shown that the velocity constant for the formation of ethyl chloride decreases much more quickly with increase in the concentration of water than the velocity constant for the formation of ethyl benzoate, so that, under identical conditions, the formation of ethyl chloride comes less into consideration when the alcohol contains fairly large quantities of water than when the concentration of the water is small.

W. H. G.

**Esterification of Dinitrobenzoic Acids by Means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Monatsh.*, 1907, 28, 571—588).—The velocities of esterification of the three mononitrobenzoic acids have been measured (this vol., ii, 242), and it has been shown that the introduction of the nitro-group retards the formation of the ester. The rates of esterification of the 2:4- and 3:5-dinitrobenzoic acids have been determined in the same manner as those of benzoic and the aminobenzoic acids (compare Abstr., 1906, ii, 659 ;

this vol., ii, 158), and it is found that the second nitro-group in both acids decreases the velocity of esterification far more, relatively, than the first.

In all cases, the influence of the formation of ethyl chloride has been taken into account, and it is then found that the velocity of esterification of 2:4-dinitrobenzoic acid in alcohol containing only very small quantities of water is proportional to the concentration of the hydrogen chloride. On the contrary, in the case of 3:5-dinitrobenzoic acid, the velocity of esterification, both in absolute alcohol and in alcohol containing water, increases more rapidly than the concentration of the hydrogen chloride. Although ethyl 3:5-dinitrobenzoate is shown to be hydrolysed by a solution of hydrogen chloride in mixtures of alcohol and water, still this reaction need not be considered in calculating the esterification velocity constants except when the esterification is nearing completion.

The relation of the esterification constant of 3:5-dinitrobenzoic acid to the concentration of the water ( $w$ ) and of the hydrogen chloride ( $c$ ) is represented by the equation:  $1/k = -13.3 + 81.28/c - 0.413/c^2 + (-450.1 + 271.9/c + 43.86/c^2)w + (-114.9 + 71.37/c - 2.714/c^2)w^2$ , which applies to solutions between  $w=0.03$  and  $w=1.3$ , and  $c=0.16$  and  $c=0.64$ .

The behaviour of 3:5-dinitrobenzoic acid on esterification is shown to be quite analogous to that of the other acids investigated by the author.

W. H. G.

**Esterification of Dihydroxybenzoic Acids by Means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Monatsh.*, 1907, 28, 673—703).—It has been shown in the case of the dinitrobenzoic acids that the introduction of the second nitro-group is accompanied by a reduction in the velocity of esterification (compare preceding abstract). The effect produced on the rate of esterification by the substitution of a second hydrogen atom by hydroxyl in the monohydroxybenzoic acids is not quite so simple. In the case of the monohydroxybenzoic acids, it was found (this vol., ii, 243) that the introduction of the first hydroxyl group in either the ortho- or para-positions produced a diminution, whilst substitution in the meta-position produced an acceleration in the rate of esterification. The results obtained in the present investigation show that the introduction of the second hydroxyl group in positions, either ortho- or para- to the carboxyl group, is accompanied by a marked decrease in the velocity of esterification, whilst introduction in the meta-position in the case of *m*-hydroxybenzoic acid produces an increase, and in the case of *p*-hydroxybenzoic acid, with hydrogen chloride concentration,  $c=0.1667$ , a slight increase, and with  $c=0.3333$  and  $c=0.6667$ , a slight decrease in the rate of esterification. This is shown by the following values for the velocity constants in solutions of hydrogen chloride concentration,  $c=0.3333$ , and of water concentration,  $w=0.052$ , taking that of benzoic acid = 1 :

Benzoic acid.	Hydroxybenzoic acids.			Dihydroxybenzoic acids.		
	<i>o</i> -.	<i>m</i> -.	<i>p</i> -.	2:4-.	3:4-.	3:5-.
1	0.0355	1.084	0.405	0.0074	0.387	1.135

The esterification constants for 2:4-dihydroxybenzoic acid in alcohol containing only traces of water are found to be directly proportional to the hydrogen chloride concentration, whilst the velocity of esterification of the 3:5- and 3:4-dihydroxybenzoic acids in alcohol containing but small quantities of water increases more slowly, and in alcohol containing fairly large quantities of water more rapidly, than the concentration of the hydrogen chloride.

The relation of the esterification constant of 3:5-dihydroxybenzoic acid to the concentration of the hydrogen chloride and of the water is represented by the equation:  $1/k = 5.25 + 12.83/c - 0.3375/c^2 + (-23.43 + 20.63/c + 8.018/c^2)w + (-63.97 + 77.73/c - 3.083/c^2)w^2$ , which applies to solutions in which the molecular concentration of the hydrogen chloride lies between  $c=0.16$  and  $c=0.66$ , and that of the water between  $w=0.01$  and  $w=1.3$ .

The expression for 3:4-dihydroxybenzoic acid is:  $1/k = 0.08 + 51.16/c - 3.343/c^2 + (131.5 - 117.2/c + 51.3/c^2)w + (-408.0 + 434.3/c - 45.64/c^2)w^2$ , which applies to solutions with  $w=0.03-1.3$  and  $c=0.16-0.66$ . No hydrolysis of ethyl 3:5-dihydroxybenzoate by solutions of hydrogen chloride in mixtures of water and alcohol could be detected.

The behaviour of the 3:5- and 3:4-dihydroxybenzoic acids on esterification with various concentrations of water and hydrogen chloride is shown to be analogous to that of the acids previously examined.

W. H. G.

**Esterification of Pyridinemonomonocarboxylic Acids by Means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Monatsh.*, 1907, 28, 705—738. Compare preceding abstracts).—The behaviour of the pyridinemonomonocarboxylic acids on esterification is found to be similar to that of the aminobenzoic acids (this vol., ii, 158) in that the velocity of esterification is greatest in the case of the para-acid (pyridine-4-carboxylic acid) and smallest in that of the ortho-acid (pyridine-2-carboxylic acid).

The esterification constants of picolinic acid (pyridine-2-carboxylic acid) at  $25^\circ$  in alcohol containing only traces of water, and with hydrogen chloride concentrations between  $N/6$  and  $N/3$ , increase more slowly than the hydrogen chloride concentration, and between  $N/3$  and  $2N/3$  are approximately proportional to the concentration of the hydrogen chloride.

The constants of the pyridine-3- and pyridine-4-carboxylic acids, on the contrary, increase more rapidly than the concentration of the hydrogen chloride.

The relation of the velocity constant at  $25^\circ$  to the concentration of the water and of the hydrogen chloride is expressed in the case of pyridine-3-carboxylic acid by the equation:  $1/k = -77.5 + 128.9/c - 0.5333/c^2 + (1451 - 1221/c + 247.8/c^2)w + (-4460 + 3566/c - 439.5/c^2)w^2$ , when the molecular concentration of the water lies between  $w=0.02$  and  $w=0.65$ , and that of the hydrogen chloride between  $c=0.16$  and  $c=0.66$ ; also when  $w$  is less than  $0.04$  for solutions with  $c=0.0-0.1$ . The rate of hydrolysis of ethyl nicotinate is

so small as to be negligible in comparison with the velocity of esterification.

The behaviour of the pyridinemonocarboxylic acids on esterification is shown to differ somewhat from that of benzoic acid and of the aminobenzoic acids.

The solubilities of picolinic acid and nicotinic acid in 99.93% alcohol at 25° were found to be respectively 0.544 gram and 0.073 gram per 10 c.c. of solution.

W. H. G.

**The Course of the Decomposition of Polypeptides by Ferments.** EMIL ABDERHALDEN and LEONOR MICHAELIS (*Zeitsch. physiol. Chem.*, 1907, 52, 326—337).—The decomposition of *D*-alanyl-*D*-alanine by pancreatic juice has been studied by the rotatory method described previously (this vol., ii, 488). By means of several series of experiments, it is shown that the velocity constant cannot be calculated by either of the two formulæ,  $K = x/t$  or  $K_1 = 1/t \log^a/a-x$ , but the formula  $K = \log^a/a-x + C^x/t$  gives fairly concordant values for  $K$ . When the first equation is used,  $K$  decreases with the time, and when the second is employed  $K_1$  increases with  $t$ . It is found that with equal amounts of fermentable substance, the decomposition curve tends to approximate to a straight line as the amount of ferment decreases, but, on the other hand, tends to approximate more closely to a logarithmic curve with increasing amounts of ferment.

Several series of experiments show that the velocity of decomposition increases with the amount of ferment present, and that at the beginning of each series the velocity is directly proportional to the amount of ferment. If, however, the initial point for the calculation is not the initial point of the reaction, but some intermediate point, then the proportionality disappears and a retarding effect is noticed.

J. J. S.

**Reversible Fermentation in a Heterogeneous System. Formation and Hydrolysis of Esters.** WILHELM DIETZ (*Zeitsch. physiol. Chem.*, 1907, 52, 279—325. Compare Pottevin, *Abstr.*, 1903, ii, 494; 1904, i, 284).—Pottevin's ester-forming and ester-hydrolysing ferment has been prepared by his method from the pancreas of the pig, but all attempts to purify the glycerol extract by filtration through a Pukall cell or by precipitation with alcohol, ether, acetone, &c., proved fruitless, as inactive products were obtained. The reactions between alcohols and acids in the presence of the ferment have been studied quantitatively at 35°; water was usually added and, as the ferment was insoluble, the reaction was heterogeneous and constant stirring was employed, care being taken that in removing portions of the mixture for titration an equal amount of the ferment was removed each time. The reaction proceeds in the ferment phase only, as it is immediately stopped by filtration. The velocity of diffusion is probably rapid compared with the velocity of the chemical reaction.

In the formation of ester, the constants have been calculated from the equation:  $K_1 + K_2 = 1/t \log^k/\xi - x$ , where  $t$  is the time in hours,  $x$

is the amount of acid used up (that is, of ester formed) after time  $t$ , and  $\xi$  is the value of  $x$  when equilibrium is established. The experiments made with oleic acid and ethyl alcohol do not yield very constant values for  $K_1 + K_2$ , as the reaction proceeds very slowly, requiring some six weeks before equilibrium is established and during this time the ferment probably undergoes change. When the initial concentration of the water is 10%, the formation of ester proceeds nearly to completion. Experiments made with  $n$ -butyric acid and amyl alcohol in the presence of 6.5% and 8% of water show that the same state of equilibrium is attained whether the original mixture is ester, water and alcohol, or acid, water, and alcohol. The equilibrium is also independent of the activity, age, or amount of the ferment used. When the amount of water is very small, the hydrolysis of the ester is practically nil. It is found that the value of  $K$  calculated from  $K = C_{\text{ester}} \times C_{\text{water}} / C_{\text{acid}} \times C_{\text{alcohol}}$  or from  $K = C_{\text{ester}} / C_{\text{acid}}$ , since the amount of alcohol and water can be assumed to remain constant, do not agree, but if the equation  $K = C_{\text{ester}}^{1/2} / C_{\text{acid}}$  is employed fairly constant values are obtained for  $K$ . The equilibrium in a similar homogeneous system, using hydrogen chloride or picric acid as catalyst, is entirely different from the equilibrium in this heterogeneous system.

Numerous determinations of velocity constants have been made; when the percentage of water is small, the reaction may be assumed to be non-reversible, and the equation  $K = 1/t \log a/a - x$  gives constant values for  $K$ . An increase in the amount of water from 3.5% to 5.5% practically doubles the value of  $K$ . This is entirely different from the catalytic action of acids, where an increase in the amount of water reduces the velocity of esterification.

When the percentage of water reaches 6.5%, the velocities of both ester formation ( $K_1$ ) and ester hydrolysis ( $K_2$ ) can be measured by means of the equations  $K_1 = \xi/a \cdot 1/t \log \xi/\xi - x$  and  $K_2 = \xi^2/a_1 \cdot 1/t \log \xi/\xi_1 - x_1$ . In any one series of experiments, the values for  $K_1$  and  $K_2$  agree fairly well, but in different sets, in which the initial concentrations differ, the mean values do not agree, and it appears that the velocity of hydrolysis is proportional to the square root of the ester concentration.

It is shown that the velocity is proportional to the amount of ferment present and that the equilibrium constant is equal to the ratio of the two velocity constants,  $K' = K'_1/K'_2$ .

The results are discussed from the point of view of the second law of thermodynamics. J. J. S.

**Are the Stoichiometrical Laws Intelligible without the Atomic Hypothesis?** O. KUHN (*Chem. Zeit.*, 1907, 31, 688—689. Compare Baur, *Abstr.*, 1906, ii, 661).—An adverse criticism of a paper by Wald (*Chem. Zeit.*, 1906, 30, 963, 978), in which this author claims to have shown that the stoichiometrical laws may be established by pure mathematical deduction. W. H. G.

**A New Portable Gas Generator.** ARTHUR W. BROWNE and M. J. BROWN (*J. Amer. Chem. Soc.*, 1907, 29, 859—864).—A portable

modification of Browne and Mehling's gas generator (Abstr., 1906, ii, 609), for which a number of advantages over the generators in common use are claimed, is described and figured. G. Y.

**A Constant Pressure Gas Generator for Use over a Wide Range of Pressure.** ARTHUR W. BROWNE and M. J. BROWN (*J. Amer. Chem. Soc.*, 1907, **29**, 864—867).—A simple arrangement of two calcium chloride towers is described, by means of which a gas may be generated from a liquid and a solid, under a constant pressure, the spent liquid escaping through a mercury trap. The original is to be consulted for details and diagram. G. Y.

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## Inorganic Chemistry.

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**Absolute Atomic Weight of Chlorine.** GUSTAV D. HINRICHS (*Compt. rend.*, 1907, 145, 58—60).—In support of his contention that the absolute atomic weights of silver and carbon are exactly 108 and 12 respectively, the author compares the values obtained, by the synthesis of silver chloride, for the absolute atomic ratio  $\text{AgCl}:\text{Ag}$ , commencing with those of Berzelius (1820) and concluding with the recent results of Richards. He deduces that the absolute atomic weight of chlorine is 35.5. E. H.

**Ignition Point of Sulphur.** R. H. MCCREA and A. WILSON (*Chem. News*, 1907, 96, 25).—The ignition temperature of sulphur, determined by means of a U-tube through which air or oxygen was slowly drawn, was found to be  $261^{\circ}$  ( $255^{\circ}$  uncorr.) in air at approximately atmospheric pressure, and  $257$ — $264^{\circ}$  (uncorr.) in oxygen. Hill (this vol., ii, 341) recently obtained  $248^{\circ}$  as the value in air at atmospheric pressure. G. S.

**Analysis of Selenium Hexafluoride.** PAUL LEBEAU (*Compt. rend.*, 1907, 145, 190—192. Compare this vol., ii, 540, 613).—On freeing the gaseous mixture, obtained by the action of fluorine on selenium, from silicon fluoride, and purifying it by liquefaction and evaporation, fractions are obtained having appreciably different densities. Attempts to determine the fluorine content of the gas by heating the latter in a Jena glass bell-jar yielded a mixture of silicon fluoride and oxygen having a volume about 1.5 times that of the original gas. Analyses of any one fraction of the gas gave discordant results, which were not in agreement with the formula  $\text{SeF}_6$ , part of the fluorine being probably retained by the glass in the form of metallic fluorides. The use of silica tubes led to results agreeing moderately well with the theoretical numbers, but the oxygen content of the gaseous mixture was always somewhat too high and the silicon fluoride

content somewhat too low. Decomposition of the gaseous fractions by means of a solution of sodammonium in liquid ammonia, which yields sodium fluoride and selenide and a small proportion of selenite, showed that all the fractions have a composition approximating to that of selenium hexafluoride, but that a certain amount of an oxyfluoride is always present. An appreciable purification of the gas is produced by prolonged manipulation in contact with glass and mercury.

T. H. P.

**Atomic Weight of Nitrogen.** DANIEL BERTHELOT (*Compt. rend.*, 1907, 145, 65—67).—In confirmation of his values 14·007 and 14·000 for the atomic weight of nitrogen deduced from the limit densities of this gas and of nitrous oxide (Abstr., 1898, ii, 502), the author cites the value 14·005, obtained by Leduc (Abstr., 1897, ii, 549) by the method of corresponding states, and the values 13·999 (from nitrous oxide), 14·006 (from nitric oxide), and 14·008 (from nitrogen) obtained by Gray (Trans., 1905, 87, 1601). He criticises the calculations made by Guye (Abstr., 1905, ii, 442) and by Jaquero and Perrot (*ibid.*, ii, 506) and considers that the results they obtained are inexact.

E. H.

**Fixation of Nitrogen.** NORMAN WHITEHOUSE (*J. Soc. Chem. Ind.*, 1907, 26, 738—739).—The investigation was undertaken with the object of finding a commercial method by which the nitrogen of the atmosphere could be combined as ammonia or nitrate, but has not led to conclusive results.

Experiments were made with magnesium, titanium, boron, cerium, molybdenum, and tungsten, but it was found either that the elements would not combine directly with nitrogen, or, if they did so, the nitrides could not be reduced directly with hydrogen, and when decomposed by steam the resulting oxides could not be economically reduced.

Cerium nitride can be converted directly into hydride by heating in a current of hydrogen, and the hydride into nitride and ammonia by heating in nitrogen, but as the hydrogen and nitrogen for this purpose must be absolutely free from oxygen, carbon monoxide, and water, a method based on these observations is not likely to be of commercial importance.

G. S.

**The Nature of Sulphammonium.** PAUL LEBEAU and P. DAMOISEAU (*Compt. rend.*, 1907, 144, 1422—1424. Compare Moissan, Abstr., 1901, ii, 234; Ruff and Geisel, Abstr., 1905, ii, 699).—When ammonia gas, dried by passing over fused potassium hydroxide and sodium wire, is liquefied in contact with pure sulphur, the latter dissolves to a purple solution, which, when evaporated in a vacuum, leaves a yellow residue containing red particles, whilst the last portions of gas proceeding from the evaporation blacken lead acetate paper. By dissolving the residue in water, a yellow solution is obtained, which gives a maroon-coloured precipitate with lead acetate. Thus both hydrogen sulphide and a non-volatile sulphide soluble in water are formed, but the amount of sulphur attacked is very small, since the weight of the residue exceeds that of the sulphur used by, at the most,



1.2%. If, however, an apparatus containing no rubber joints or stop-cocks is used and the sulphur is dried in a current of absolutely dry hydrogen, which is afterwards replaced by ammonia, then no hydrogen sulphide is obtained on evaporating the solution, and the residue has the same weight as the sulphur employed. The conclusion is drawn that the reaction described by Ruff and Geisel only takes place in presence of a trace of water. E. H.

**Transformation of Yellow into Red Phosphorus.** FILIPPO ZECCHINI (*Gazzetta*, 1907, 37, i, 422—423).—The transformation of yellow into red phosphorus may be readily demonstrated as follows: about 10 c.c. of the phosphorus, dried between filter paper, is introduced in small pieces into a glass tube having a length of about 30 cm. and a diameter of about 7—8 mm. and sealed at one end. The part of the tube containing the phosphorus is heated in a sulphuric acid bath to 180°. On allowing a flake of iodine to fall on to the surface of the molten phosphorus, the whole or the greater part of the latter passes immediately into the red modification. Investigations are being carried out to ascertain whether the phenomenon is catalytic or whether any intermediate reaction occurs. T. H. P.

**Causticising of Soda.** HEINRICH WALTER (*Monatsh.*, 1907, 28, 543—553. Compare Lunge and Schmid, *Abstr.*, 1886, 203).—Solutions of sodium carbonate, varying in concentration from 2*N* to 5*N*, were heated with lime in a nickel vessel under constant stirring at 106—110° until equilibrium, represented by the equation:  $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3$ , was established (after three hours), and the relative proportions of hydroxide and carbonate present in solution determined. The equilibrium was also reached by heating calcium carbonate with sodium hydroxide solutions.

It is found that the proportion ( $v$ ),  $(\text{NaOH})^2/\text{Na}_2\text{CO}_3$ , in which the concentrations of these substances in solution are represented in 0.1 equivalent per litre, is not a constant value, but increases with dilution; for 5*N* and 2*N* solutions, the values are roughly 200 and 400 respectively. The proportion  $v$  is, approximately, for solutions of total titre ( $T$ ) less than 4.7*N*, a linear function of  $T$ , and thus from the observed values is obtained the equation  $v = 596.2 - 7.927T$ . From the value  $v$  obtained by this equation, it is possible by aid of the formula  $P = \frac{100v}{T} \left( -\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{T}{v}} \right)$  to calculate the quantity of sodium hydroxide present in the equilibrium solution, in percentage of the total titre. The values for  $P$  obtained by this equation agree to within 1% of the observed values for solutions of concentration not greater than 4*N*.

The experiments were repeated at 80°, and from the observed values the following equations were obtained:  $v = 479.6 - 5.537T$  (for 4.9*N* to 5.4*N* solutions) and  $v = 1337.4 - 26.55T$  (for solutions of concentration less than 3.9*N*).

At 62°, equilibrium is not established after forty hours, so the investigation was not continued at this temperature.

In agreement with d'Anselme (Abstr., 1903, ii, 726), but not with Bodländer and Lucas (Abstr., 1905, ii, 634), the author finds that the causticising of the soda proceeds further at 80° than at 106–110°.

W. H. G.

**Causticising of Soda.** RUDOLF WEGSCHEIDER (*Monatsh.*, 1907, 28, 555–558).—From the formulæ:  $v_{108} = 58.44 - 8.624T$  and  $v_{80} = 133.74 - 26.55T$ , obtained by Walter (compare preceding abstract), may be deduced the formula:  $v_t = 348.88 - 2.6893t - (77.767 - 0.640214t)T$ , where  $T$  represents the total titre and  $t$  the temperature. The values calculated by this formula for 20° and 60°, for example, are in very close agreement with the values observed at these temperatures. However, the values observed by Le Blanc and Novotný (this vol., ii, 22) at 100°, which are almost identical with those observed by Lunge and Schmid (Abstr., 1886, 203), do not agree so well with the calculated values obtained by the above formula for 100° as with those calculated for 80°.

A reason for the slight difference in the extent to which the soda is causticised at 100° and slightly above this temperature cannot yet be given.

W. H. G.

**Sodium Selenides.** C. H. MATHEWSON (*J. Amer. Chem. Soc.*, 1907, 29, 867–880).—The existence of alkali sulphides of the six types,  $M'_2S$ ,  $M'_2S_2$ ,  $M'_2S_3$ ,  $M'_2S_4$ ,  $M'_2S_5$ , and  $M'_2S_6$ , has been proved by Biltz and Wilke-Dörfurt (Abstr., 1906, ii, 283). The close analogy of the selenides with the sulphides suggesting the possibility of a similar series of alkali selenides, the present work was undertaken with the object of describing all compounds of sodium and selenium which are formed by direct combination of the elements and are stable in contact with the liquid phase. The method of investigation was essentially that used previously in investigating the sodium-tin alloys (Abstr., 1905, ii, 634). Amorphous selenium was added in small quantities to molten sodium in an atmosphere of hydrogen, occasioning at first a violent, exothermic formation of the monoselenide, followed by formation of polyselenides, which takes place without any considerable development of heat. The rate of cooling of various concentrations of selenium in sodium was measured with the aid of a thermoelectric, platinum-platinum rhodium couple. The results obtained are tabulated and a freezing point curve constructed, which, starting from sodium monoselenide, has breaks representing the compositions of the di-, tri-, tetra-, and hexa-selenides. No indication of the formation of a penta-, or other, selenide has been obtained. The polyselenides decompose at their melting points, forming an equilibrium with the next lower selenide and a liquid phase containing a corresponding excess of selenium.

The white monoselenide,  $Na_2Se$ , m. p. above 875° (Hugot, Abstr., 1899, ii, 650), forms a colourless solution in water, becomes red on exposure to air, and dissolves selenium, becoming red, and, finally, dark and opaque.

Sodium diselenide,  $Na_2Se_2$  (Jackson, this Journ., 1875, 28, 533), has m. p. 495° (decomp.). The triselenide,  $Na_2Se_3$ , has m. p. 313° (decomp.). The tetraselenide,  $Na_2Se_4$  (Hugot, *loc. cit.*), has m. p. 290°

(decomp.). The *hexaselenide*,  $\text{Na}_2\text{Se}_6$ , has m. p.  $258^\circ$  (decomp.). These polyselenides are darker than grey, metallic selenium, become red and disintegrate on exposure to air in consequence of the separation of selenium, and are readily soluble in water, forming red solutions, the depth of colour increasing with the amount of selenium.

The melting point of sodium is lowered to only a very slight extent, not more than  $0.2^\circ$ , by the addition of selenium. After heating and supercooling of grey, metallic selenium, crystallisation does not take place, but the substance gradually solidifies to an amorphous mass. The addition of 0.1% of sodium is sufficient, however, to cause complete crystallisation at  $217^\circ$ . It is shown that the solubility of sodium hexaselenide in selenium at its melting point is extremely small, but the limited miscibility, which is not excluded by the experiments, may be the cause of the crystallisation. The possible nature of this solidification is discussed. G. Y.

**A New Method of Preparation of Anhydrous Lithium Oxide.** Its Heat of Solution. ROBERT DE FORCRAND (*Compt. rend.*, 1907, 144, 1402—1404).—When pure lithium carbonate, in quantities less than a gram, is heated in a platinum boat at  $780$ — $800^\circ$  in a current of hydrogen, it loses all its carbon dioxide in about three hours, giving pure lithium oxide,  $\text{Li}_2\text{O}$ , as a colourless, translucent fused mass. For the heat of dissolution of 1 gram-molecule of  $\text{Li}_2\text{O}$ , prepared from the crystallised hydrate,  $\text{LiOH} \cdot \text{H}_2\text{O}$ , in four litres of water at  $15^\circ$ , the author obtains a mean value of  $+31.2$  Cal. Using the oxide prepared by the above method, the value  $+31.00$  Cal. is obtained under the same conditions. The heat of dissolution increases by 0.098 Cal. per degree, being  $+30.71$  Cal. at  $10^\circ$  and  $+31.69$  Cal. at  $20^\circ$ . Dilution to 15 litres increases it by 0.306 Cal., to 20 litres by 0.390 Cal., and to 36 litres by 0.501 Cal. The large influence of dilution is contrary to what is observed with the other alkali oxides, but agrees with the behaviour of the alkaline earth oxides. E. H.

**Ammonium Amalgam.** ALFRED COEHN (*Ber.*, 1907, 40, 3192—3193).—Polemical. A reply to Smith (this vol., ii, 615). G. Y.

**Interaction of Dilute Solutions of Ammonium Salts and Various Filtering Media.** GILBERT J. FOWLER and PERCY GAUNT (*J. Soc. Chem. Ind.*, 1907, 26, 740—744. Compare Chick, *Abstr.*, 1906, ii, 245).—A series of experiments have been made to determine the extent to which certain filtering media and similar substances remove ammonia from dilute solutions of ammonium chloride under sterile conditions. Clinker, gravel, quartz, carbon, and various mixtures were employed, and in almost all cases a certain amount of ammonia was removed; the proportion was greatest with clinker and gravel, and least with mixtures containing quartz. The absorption is physico-chemical in nature, as the ammonia is not oxidised or volatilised, but can all be recovered by long-continued washing. Only the ammonia and not the negative radicle is absorbed, and in the majority of cases certain constituents of the medium, for example,

iron, calcium and magnesium, pass into solution. Change of temperature has practically no effect on the amount of absorption.

Absorption appears to facilitate nitrification in biological filters, but the results are not quite conclusive. G. S.

**Preparation of Colloidal Silver.** NICOLA CASTORO (*Gazzetta*, 1907, 37, i, 391—395).—Colloidal silver solutions may be readily prepared by boiling ammoniacal silver nitrate solution with acetaldehyde and a small quantity of gelatin solution. In this way, concentrated solutions of colloidal silver, having the colour of bromine, may be prepared. These solutions may be kept for years without losing their properties or changing their colour. T. H. P.

**Electrolysis of Very Dilute Solutions of Silver Nitrate and Oxide. Silver an Alkali Metal.** ANATOLE LEDUC and LABROUSTE (*Compt. rend.*, 1907, 145, 55—58).—When a solution of silver oxide, prepared by the action of baryta on the nitrate, is electrolysed between platinum electrodes at a pressure of 10—20 volts, a brown cloud is produced in the neighbourhood of the cathode, at the edges of which light filaments of silver are formed, while there is an abundant evolution of hydrogen. The brown cloud probably consists of a suboxide of silver, and a drop of phenolphthalein introduced near the cathode produces a pink colour. By substituting a silver anode, the evolution of oxygen is almost prevented, a bluish-black cloud being produced at the anode which has no action on phenolphthalein. A black powder is observed to fall from the anode and slowly disappear, each particle being replaced by a bubble of gas, from which the conclusion is drawn that the black powder is a peroxide of silver. When a mercury cathode and a silver anode are used, there is less evolution of hydrogen, but the cathodic cloud persists and only 20% of the silver corresponding with the quantity of electricity passing is taken up by the mercury, forming an amalgam which is not attacked by water. A solution of silver nitrate and oxide in about equal concentrations gives rise, on electrolysis, to the cathodic cloud, but does not evolve hydrogen, which is oxidised by the nitrate. But if the solution is rich in nitrate, the cathodic cloud is no longer produced. With relatively concentrated solutions of the nitrate alone, the cloud is produced, provided the voltage is sufficient. When a saturated solution of silver oxide diluted with nine times its volume of water is electrolysed, the cathodic cloud is not produced, and there is no appreciable deposit on the cathode, only hydrogen being evolved. After electrolysing a very dilute solution of silver nitrate, sulphate, or oxide for a few minutes in a voltameter partitioned by a paraffined Soxhlet filter, which prevents diffusion, the liquid in the cathodic compartment reacts alkaline to phenolphthalein. The conclusion is drawn that the silver liberated by electrolysis behaves as an alkali metal, reacting with water to form an oxide, which wholly or partially dissolves in the water, probably as AgOH. E. H.

**Preparation of Solid Ammonio-silver Nitrate.** NICOLA CASTORO (*Gazzetta*, 1907, 37, i, 310—312).—Solid ammonio-silver nitrate

may be obtained in crystals by adding absolute alcohol to concentrated ammoniacal silver nitrate solution, or as an amorphous precipitate by using ether in place of the alcohol. The salt, to which Hantzsch (Abstr., 1899, ii, 215) has given the formula  $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ , dissociates readily when dissolved in water, is precipitated by chlorine ions, and gives the ammonia reaction with Nessler's solution, so that the complex ion,  $\text{Ag}(\text{NH}_3)_2$ , is resolved to some extent into  $\text{Ag} + 2\text{NH}_3$ .

Silver nitrate also forms moderately stable complex salts with asparagine, carbamide, urethane, leucine, and other amino-derivatives. These will be studied and described later. T. H. P.

**Quantitative Synthesis of Silver Nitrate and the Atomic Weights of Nitrogen and Silver.** THEODORE W. RICHARDS and GEORGE S. FORBES (*J. Amer. Chem. Soc.*, 1907, 29, 808—826).—The composition of silver nitrate being of importance in connexion with the atomic weights of nitrogen and silver, the authors have repeated Stas's synthesis of silver nitrate. The silver nitrate, formed by dissolving pure silver in pure nitric acid, was fused until constant in weight. Of six experiments, four gave the ratio for  $\text{Ag} : \text{AgNO}_3 = 100,000 : 157.480$ , whilst two gave the value  $100,000 = 157.481$ . The fused silver nitrate was found to contain traces of water and ammonia, amounting in all to less than 0.002%, but neither air, nitrite, nor free nitric acid. When corrected for these errors, the ratio  $\text{Ag} : \text{AgNO}_3$  becomes  $100,000 : 157.479$ . The following relations between the atomic weights of nitrogen and silver, and the molecular weight of silver nitrate, are calculated from this result :

$$\text{Ag} = 107.880, \text{AgNO}_3 = 169.888, \text{N} = 14.008 ;$$

$$\text{Ag} = 107.883, \text{AgNO}_3 = 169.893, \text{N} = 14.010 ;$$

$$\text{Ag} = 107.890, \text{AgNO}_3 = 169.904, \text{N} = 14.014 ;$$

$$\text{Ag} = 107.930, \text{AgNO}_3 = 169.967, \text{N} = 14.037.$$

Hence, if the recent low values for the atomic weight of nitrogen are accepted, that of silver must have a value much lower than 107.93.

G. Y.

**The Molecular Weight of Silver Sulphate and the Atomic Weight of Sulphur.** THEODORE W. RICHARDS and GRINNELL JONES (*J. Amer. Chem. Soc.*, 1907, 29, 826—844).—The methods used by previous authors for determining the atomic weight of sulphur are reviewed and the results criticised.

Silver sulphate is prepared by conversion of the pure nitrate into the hydrogen sulphate by means of concentrated sulphuric acid and precipitation of the sulphate by addition of much water ; it is purified by alternate heating with concentrated sulphuric acid and treatment with water. When fused in a quartz tube, silver sulphate has D 5.45. In consequence, on the one hand, of its sparing solubility in water and, on the other, of the occlusion of the sulphate by the chloride in presence of an excess of sulphuric acid, silver sulphate is converted into silver chloride by reaction in solution only with great difficulty. Pure silver chloride is obtained, however, by passing hydrogen chloride over

the sulphate in a heated quartz tube. Ten experiments gave the ratio  $\text{Ag}_2\text{SO}_4 : \text{AgCl} = 100.000 : 91.933$ , the individual results varying from 91.929 to 91.936, from which the sulphate is calculated to contain 69.192% of silver. Stas, who reduced the sulphate in a current of hydrogen, found 69.203% of silver; the conclusion is drawn that Stas's silver sulphate was incompletely reduced. The following relations between the atomic weights of silver and chlorine and that of sulphur have been calculated from these results, the atomic weight of oxygen being taken as 16.00:

$\text{Ag} = 107.930$ ,  $\text{Cl} = 35.473$ ,  $\text{S} = 32.113$ ;

$\text{Ag} = 107.890$ ,  $\text{Cl} = 35.460$ ,  $\text{S} = 32.078$ ;

$\text{Ag} = 107.880$ ,  $\text{Cl} = 35.457$ ,  $\text{S} = 32.069$ .

The lowest of these values for sulphur is the one in agreement with the results of recent work on the densities of gases. G. Y.

### Conditions of Existence of Sodium Calcium Carbonates.

RUDOLF WEGSCHEIDER and HEINRICH WALTER (*Monatsh.*, 1907, 28, 633—672).—A detailed account of work previously published (this vol., ii, 259). A description of experiments carried out with the object of obtaining double compounds of calcium and sodium hydroxides is also given. The existence of such compounds could not, however, be detected. W. H. G.

### Chemical Investigations for a Cement Quarry.

ROBERTO SALVADORI and CESARE SPERONI (*Gazzetta*, 1907, 37, i, 234—250).—Different strata of a quarry often vary widely in composition, so that, in order to obtain a cement uniform in qualities, limestone obtained from only one stratum should be employed. In the particular quarry examined, it was found that the best slow-setting cements were obtained from stones which contain, after burning, 15.5—16.5% of their original weight of matter insoluble in hydrochloric acid and in which the ratio of the matter soluble to that insoluble in the acid is about 3; for quick-setting cements, the insoluble matter is 19—20% and the ratio about 2.4. The chemical composition of cement obtained directly from the stone corresponds with the composition of the latter, excepting for those small amounts of silica, iron, sulphates, &c., derived from the fuel. T. H. P.

### Changes Involved in the Production and Setting of Plaster

of Paris. WILLIAM A. DAVIS (*J. Soc. Chem. Ind.*, 1907, 26, 727—737).—It is pointed out that, in spite of the work of Le Chatelier (1887), van't Hoff and his pupils (1900—1903), and others, there is still much uncertainty with regard to the relationship between gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , the half-hydrate,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , soluble anhydrite,  $\text{CaSO}_4$ , which sets rapidly, and ordinary anhydrite, which sets very slowly with water. In the present paper, it is shown that a second modification of the dihydrate exists, and, further, that there is probably a second form of the half-hydrate; for these and other reasons, many of the results obtained by van't Hoff are of doubtful value.

Experiments with gypsum in a current of air at temperatures from 98° to 130° showed that dehydration proceeded continuously and was

finally complete, the product in all cases being soluble anhydrite. As previously found by Shenstone and Cundall (*Trans.*, 1888, 53, 544), there is an initial retardation in the rate of dehydration, which is most marked at the lower temperatures. Evidence is adduced to show that this retardation is due to the gradual change of (monoclinic) gypsum to another form which occurs in orthorhombic crystals, only the latter form undergoing dehydration. Conversely, when the half-hydrate or soluble anhydrite sets, observations with a polarising microscope indicate that at first only the orthorhombic crystals are formed, these slowly changing to monoclinic crystals of gypsum. Calcium chromate dihydrates of corresponding crystalline form are known.

When gypsum is heated in an open crucible at  $98^{\circ}$ , the half-hydrate is formed, and it is probable that the latter is also an intermediate product when gypsum is heated in a current of air. Although the half-hydrate undergoes no further change at  $98^{\circ}$ , it is dehydrated completely on prolonged heating at  $107$ – $108^{\circ}$ . The change half-hydrate  $\rightleftharpoons$  soluble anhydrite + water vapour is completely reversible, the change indicated by the lower arrow taking place rapidly at the ordinary temperature. For this reason, the method used by van't Hoff to determine the equilibrium pressures in the system gypsum-soluble anhydrite is open to objection. When freshly prepared crystals of gypsum are heated for three to four hours with water at  $100^{\circ}$ , a half-hydrate, which sets very slowly, is obtained. This appears to be identical with a half-hydrate obtained by Le Chatelier in a similar way at  $130$ – $150^{\circ}$ , and is probably a second modification.

It is pointed out that the available data for the solubility of gypsum in water and its variation with temperature are somewhat uncertain. G. S.

**Reduction of Cadmium Oxide.** F. O. DOELTZ and C. A. GRAUMANN (*Metallurgie*, 1907, 4, 419–420).—The reduction of cadmium oxide by carbon in an atmosphere of nitrogen begins at about  $580^{\circ}$ , increasing with the temperature. It is therefore more easily reducible than zinc oxide (this vol., ii, 619). C. H. D.

**Reduction of the Oxides of Lead, Copper, and Tin by Carbon.** F. O. DOELTZ and C. A. GRAUMANN (*Metallurgie*, 1907, 4, 420–421).—The reduction of lead oxide by carbon begins at about  $550^{\circ}$ , and is considerable at  $700^{\circ}$ . The reduction of copper and tin oxides is slight, but recognisable, at  $700^{\circ}$  and  $830^{\circ}$  respectively. C. H. D.

**Freezing Point Diagrams of the Binary Systems Lead Sulphide-Ferrous Sulphide and Lead Sulphide-Silver Sulphide.** K. FRIEDRICH (*Metallurgie*, 1907, 4, 479–485).—Freezing point curves of binary mixtures of metallic sulphides are really sections through the surface of a ternary system, such as Pb, Ag, S. This section will only be a plane when the proportion of sulphur present is throughout that necessary to combine with the two metals. This condition is fulfilled for the system PbS–Ag<sub>2</sub>S, it is not exactly fulfilled for the system PbS–FeS, but the error involved in assuming the section to be plane is probably small.

Pure lead sulphide melts at  $1114^{\circ}$  (compare Friedrich and Leroux, *Abstr.*, 1906, ii, 355). Ferrous sulphide melts at  $1187^{\circ}$ , and the two branches of the freezing point curve intersect in a eutectic point at 70% PbS and  $863^{\circ}$ . Solid solutions are not formed.

Silver sulphide melts at  $835^{\circ}$ , and the freezing point curve of mixtures with lead sulphide consists of two branches intersecting at 77%  $\text{Ag}_2\text{S}$  and  $630^{\circ}$ . The horizontal line at  $175^{\circ}$  indicates the transformation of silver sulphide (*Abstr.*, 1906, ii, 751). C. H. D.

**Thallium Sulphides, Selenides, and Tellurides.** HENRI PÉLABON (*Compt. rend.*, 1907, 145, 118—121).—An account of the behaviour on fusion of mixtures of thallium with sulphur, selenium, and tellurium. When fused, mixtures containing more than 2 atoms of thallium for 1 atom of sulphur form two layers; the upper layer consists of thallium sulphide,  $\text{Tl}_2\text{S}$ , containing 7.26% of sulphur, and solidifying at  $448^{\circ}$ , whilst the lower is pure thallium, solidifying at  $302^{\circ}$ . The portion of the melting point curve corresponding with such mixtures is horizontal. The curve for mixtures containing 7.26% to 28.2% of sulphur corresponds with the separation of  $\text{Tl}_8\text{S}_7$ , m. p.  $295^{\circ}$ . The melting point curve becomes again horizontal for mixtures containing a greater proportion of sulphur; these, on fusion, form two layers, the lower consisting of the pentasulphide,  $\text{Tl}_2\text{S}_5$ , m. p.  $127^{\circ}$ , and the upper of sulphur.

The melting point curve for mixtures of thallium and selenium resembles that for thallium and sulphur, but has a eutectic point at  $315^{\circ}$  corresponding with the composition  $\text{Tl}_4\text{Se}_3$ , from which the curve rises to a maximum at  $338^{\circ}$ , representing the mixture  $\text{Tl}_2\text{Se}, \text{Tl}_2\text{Se}_3$ , and finally falls to the m. p.  $195^{\circ}$  of the pentasulphide,  $\text{Tl}_2\text{Se}_5$ . Mixtures containing more than 50% of selenium solidify between  $178^{\circ}$  and  $195^{\circ}$ , one of the liquid phases being the pentasulphide, the other a solution of this in selenium. The curve has no break corresponding with the triselenide.

Mixtures of thallium and tellurium containing more than 24% of thallium, correspond with the solidification of  $\text{Tl}_2\text{Te}$ , which has m. p.  $412^{\circ}$ ; as the proportion of thallium diminishes, the melting point curve rises to a maximum at  $442^{\circ}$ , representing a compound  $\text{Tl}_5\text{Te}_3$  or  $\text{Tl}_2\text{Te}_3, 9\text{Tl}_2\text{Te}$ , falls to a minimum at  $214^{\circ}$ , the m. p. of the pentatelluride,  $\text{Tl}_2\text{Te}_5$ , and finally rises to the m. p.  $452^{\circ}$  of pure tellurium. The temperatures of complete solidification of mixtures of the composition,  $3\text{Tl}_2\text{Te}_3, \text{Tl}_2\text{Te}$  and  $\text{Tl}_2\text{Te}$ , are indicated by corresponding points on the melting point curve. G. Y.

**Relation of Thallium to the Alkali Metals: Thallium Sulphate and Selenate.** ALFRED E. H. TUTTON (*Proc. Roy. Soc.*, 79, A, 351—382. Compare *Trans.*, 1894, 65, 628; 1897, 71, 846; 1903, 83, 1049; 1906, 89, 1059).—A comparison of the crystals of thallium sulphate and selenate with those of potassium, rubidium, and caesium sulphates and selenates and ammonium sulphate shows that the thallium salts fall in the same orthorhombic isomorphous series, and that thallium occupies a position near to those of rubidium and ammonium and between those of potassium and caesium. The optical refraction and dispersion are, however, far higher than those of the



alkali salts. The solubility of the thallium salts is much lower than that of the alkali salts, and is lower for the selenate than for the sulphate.

A "eutropic" series is defined as one in which the small angular differences of the crystals, and also their structural and physical properties, obey the law of progression according to the atomic weight of the elements which give rise to the series and belong to the same group. Thus thallium sulphate and selenate and ammonium sulphate belong to the isomorphous series, but not to the eutropic series of the sulphates and selenates of the alkali metals. C. H. D.

**The Copper Bessemer Reaction.** F. O. DOELTZ and C. A. GRAUMANN (*Metallurgie*, 1907, 4, 421—422).—Mixtures of cuprous sulphide with cuprous or cupric oxide were heated in an atmosphere of nitrogen at varying temperatures, the sulphur dioxide evolved being estimated by titration. The reactions,  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = \text{SO}_2 + 6\text{Cu}$  and  $\text{Cu}_2\text{S} + 2\text{CuO} = \text{SO}_2 + 4\text{Cu}$ , begin at about  $500^\circ$ , increase rapidly from  $600^\circ$  onwards, and are practically complete at  $800^\circ$ . C. H. D.

**Cuprous Iodide.** MARCEL GUICHARD (*Compt. rend.*, 1907, 144, 1430—1432).—By passing dry hydrogen iodide over anhydrous cupric chloride at the ordinary temperature, iodine is liberated with development of heat, and, after subliming the iodine, a white residue of cuprous iodide remains. If cupric chloride, dehydrated by heating at  $200^\circ$  in a current of dry hydrogen chloride, is cooled at  $-40^\circ$  in a current of hydrogen iodide, the latter liquefying on the chloride is immediately coloured violet-red by the liberation of iodine. The latter may be removed by cold dry ether, leaving grey cuprous iodide. Thus the reaction produced in the dry state and at low temperatures is the same as at the ordinary temperature in aqueous solution. Cuprous iodide, dried to constant weight in air at  $20^\circ$ , does not lose weight when exposed in a vacuum for twenty-four hours, or when heated at  $130^\circ$  for several days, but loses 0.2% water when heated at  $300^\circ$  in a vacuum; it oxidises below  $200^\circ$  when heated in air.

For the analysis of cuprous iodide, a method applicable also to other iodine compounds is employed. This consists in heating a weighed quantity of the iodide in a current of dry air in a weighed tube of which the posterior end is cooled at  $-60^\circ$ ; the iodine is wholly condensed in the cool part of the tube. Then, by weighing the tube after the decomposition, heating to expel the iodine, and again weighing, the weights of cuprous iodide, cuprous oxide, and iodine are obtained. The method gives quite accurate results. E. H.

**Reduction of Cupric Compounds by Ferrous Salts in Ammoniacal Solution.** FELIX HERRMANN (*Chem. Zentr.*, 1907, i, 1394—1395; from *Chem. Ind.*, 1907, 30, 152—155).—When an excess of ammonia is added to a solution containing copper sulphate (1 mol.) and ferrous sulphate (1 mol.) from which air is excluded, ferric hydroxide is precipitated and the supernatant liquid becomes almost colourless. When an excess of ferrous sulphate (1.02 mols.) is used, the liquid is completely colourless. If the mixture is kept for a long

time and then filtered, the filtrate is free from iron and becomes blue on exposure to the air; on the addition of acid, a precipitate of cuprous oxide or of a cuprous salt is formed. By the action of ammonia (10 mols.) on copper sulphate (2 mols.) and ferrous sulphate (2 mols.) in presence of water, cuproammonium sulphate,  $[\text{Cu}(\text{NH}_3)_2]_2\text{SO}_4$  (1 mol.), ferric hydroxide (1 mol.), and ammonium sulphate (3 mols.) are formed. If the mixture of ferric hydroxide and the solution of the cuprous salt is poured into an excess of cold dilute sulphuric acid, a clear blue solution is obtained. Since ferric hydroxide is practically insoluble in the acid, the original cupric salt and ferrous sulphate must be regenerated. When a larger excess of ferrous sulphate is used, however, a deep blackish-brown precipitate of ferrous and ferric hydroxides is formed. In testing ferrous sulphate for copper sulphate by adding ammonia, a blue solution and a brown precipitate can only be obtained therefore when a large excess of copper sulphate is present.

The reaction affords a method for preparing concentrated cuprous solutions for gas analysis (compare Level, *Ann. Chim. Phys.*, 1837, [ii], 65, 320).  
E. W. W.

**Formation of Cupric Acid.** BOHUSLAV BRAUNER and BOHUMIL KUZMA (*Ber.*, 1907, 40, 3362—3371).—See this vol., ii, 716.

**Slow Decomposition of the Solutions of Some Very Stable Mineral Salts and the Influence of Light on these Changes.** A. VERDA (*Chem. Zentr.*, 1907, i, 1392; from *Schweiz. Woch. Chem. Pharm.*, 1907, 45, 179—180).—Aqueous solutions of mercuric chloride decompose slowly in the dark, thus:  $3\text{HgCl}_2 + \text{H}_2\text{O} + \text{O}_2 = 3\text{HgO} + 2\text{HCl} + 2\text{Cl}_2$ ; but when the solution is exposed to light, mercurous chloride is deposited,  $4\text{HgCl}_2 + 2\text{H}_2\text{O} = 2\text{Hg}_2\text{Cl}_2 + 4\text{HCl} + \text{O}_2$ . Solutions of zinc sulphate remain, at least for some time, more clear when exposed to light than when kept in the dark.  
E. W. W.

**Rapid Method for Obtaining Certain Cerous Salts Directly from Cerium Dioxide.** LUIGI MARINO (*Gazzetta*, 1907, 37, i, 51—54).—Cerium dioxide may be readily converted into cerous salts by the use, as reducing agent, of quinol, which becomes converted partly into quinhydrone and partly into benzoquinone. Thus cerous sulphate,  $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , is obtained by heating a mixture of equal amounts of cerium dioxide and quinol with rather more than the calculated quantity of dilute sulphuric acid. Cerous chloride may be prepared in a similar manner.

This reaction may be advantageously employed in the separation of cerium from thorium, since calcined thorium dioxide is difficultly soluble in dilute acids.  
T. H. P.

**Action of Chlorine and Sulphur Chloride on Some Oxides.** FRANÇOIS BOURION (*Compt. rend.*, 1907, 145, 62—64. Compare Matignon and Bourion, *Abstr.*, 1904, ii, 340).—By the simultaneous action of chlorine and sulphur chloride on zirconium oxide heated at a little below redness, zirconium chloride,  $\text{ZrCl}_4$ , is formed in crystals which are coloured red by adhering sulphur chloride, but are obtained white by sublimation in a current of hydrogen.

Similarly, glucinum oxide gives white needles of the chloride,  $\text{GlCl}_2$ , lanthanum oxide,  $\text{La}_2\text{O}_3$ , the white chloride,  $\text{LaCl}_3$ , and yellow cerium oxide,  $\text{CeO}_2$ , the white chloride,  $\text{CeCl}_3$ . The oxides of europium,  $\text{Eu}_2\text{O}_3$ , gadolinium,  $\text{Gd}_2\text{O}_3$ , terbium,  $\text{Tb}_4\text{O}_7$ , and dysprosium,  $\text{Dy}_2\text{O}_3$ , give chlorides of the type  $\text{MCl}_3$ , of which dysprosium chloride is yellow, the others white. These four chlorides form colourless dilute solutions, which are neutral to methyl-orange, but, like ytterbium chloride, give a wine-red colour with litmus. Contrary to the statement of Matignon, ytterbium chloride is not green, but white. By passing a current of dry air over fused gadolinium and dysprosium chlorides, they are oxidised; the oxidation takes place in two stages, the first products being the oxychlorides,  $\text{GdOCl}$  and  $\text{DyOCl}$ . The latter forms greenish, yellow scales; the former, a white, amorphous mass; neither is volatile at a red heat. Both are dissolved by dilute sulphuric and nitric acids, that of dysprosium more rapidly than that of gadolinium, which slowly becomes crystalline before dissolving E. H.

**Action of Metallic Aluminium on Insoluble or Sparingly Soluble Mercury Compounds.** C. REICHARD (*Pharm. Zentr.-h.*, 1907, 40, 569—571).—Aluminium has no action on mercury, mercurous chloride, mercuric oxide (red and yellow), mercurous oxide, mercuric sulphide, or mercuric ammoniochloride, either in the cold or at the temperature of volatilisation or decomposition. On rubbing aluminium with these compounds, however, the sulphide excepted, amalgam is formed; if mixed with iron turnings, this interaction also takes place. As compared with the chloride and sulphide, the oxides and ammoniochloride are very reactive; when the solids mixed with water are ground with the metal, interaction takes place at once with formation of aluminium oxide, whereas no reaction occurs with the chloride. W. R.

**Aluminium Nitride.** FRITZ FICHTER (*Zeitsch. anorg. Chem.*, 1907, 54, 322—327).—Aluminium nitride can be obtained in an impure condition by raising to a high temperature in a covered crucible a mixture of aluminium and 4—5% of soot and then removing the lid; the combustion proceeds with great vigour, and greyish-blue masses containing up to 80% of aluminium nitride are obtained on cooling.

The pure nitride was obtained by heating the finely-divided metal in a current of nitrogen at  $720\text{--}740^\circ$ , but in order to effect complete conversion to the nitride it was found necessary to powder finely the product first obtained and repeat the heating in nitrogen.

Aluminium nitride is a bluish-grey, amorphous powder, which is acted on slowly by water vapour, but rapidly by alkalis.

An attempt was made to determine the heat of formation of the nitride indirectly by burning it in oxygen in a calorimetric bomb, but owing to incomplete combustion the results were not conclusive.

G. S.

**Preparation and Properties of the Manganese Borides,  $\text{MnB}$  and  $\text{MnB}_2$ .** ARMAND BINET DU JASSONNEIX (*Ber.*, 1907, 40, 3193—3199. Compare Abstr., 1905, ii, 90; 1906, ii, 520).—A claim

for priority, partly on behalf of Troost and Hautefeuille (this Journ., 1876, i, 883), and a criticism of Wedekind's work (this vol., i, 353). G. Y.

**Non-metallic Impurities in Steel.** EDWARD F. LAW (*J. Iron Steel Inst.*, 1907, 74, 94—105).—The non-metallic impurities in steel, described as "slag," may consist of the sulphides or silicates of iron or manganese or of iron oxide. Of these, ferrous sulphide rarely occurs in steel, and only when the proportion of manganese is low. Manganese sulphide occurs in grey patches, readily identified by coating the specimen with gelatin containing an acid solution of a lead or cadmium salt. In steels low in manganese and high in sulphur, the patches are lighter in colour and more fusible, and probably contain some dissolved ferrous sulphide. Manganese and iron silicates are darker in colour and brittle, being much broken up in rolling.

Oxides also occur in steel in minute specks, and may be estimated by careful ignition in a current of hydrogen. The presence of oxide greatly increases the corrosion of steel, ferrous oxide being electro-positive to iron, the other impurities being electro-negative.

The paper is illustrated with photo-micrographs.

C. H. D.

**Preparation and Properties of the Borides of Iron,  $\text{Fe}_2\text{B}$  and  $\text{FeB}_2$ .** ARMAND BINET DU JASSONNEIX (*Compt. rend.*, 1907, 145, 121—123. Compare Moissan, Ab-tr., 1895, ii, 270).—Two new borides of iron have been obtained by heating mixtures of iron, prepared by reduction of the oxide by means of hydrogen, and boron, in varying proportions, in a porcelain tube in a current of hydrogen or in the electric furnace.

The boride,  $\text{Fe}_2\text{B}$ ,  $D^{18}$  7.37, is obtained in steel-grey prisms, is oxidised by dry air only at a dull red heat, but is attacked by moist air readily at the ordinary temperature, and is dissolved by hot hydrochloric, sulphuric, or dilute nitric acids, or by cold concentrated nitric acid.

The boride,  $\text{FeB}_2$ ,  $D^{18}$  5, contains 2% of carbon boride, resembles cast iron, and is slightly yellow, hard, scratching quartz, friable, oxidised by moist air, and is dissolved by hot concentrated hydrochloric or nitric acid, leaving a residue of carbon boride. This boride represents the maximum limit of combination of boron with iron.

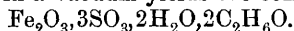
G. Y.

**Hydrolysis of Ferric Chloride.** G. MALFITANO and L. MICHEL (*Compt. rend.*, 1907, 145, 185—188).—The molecular conductivity of ferric chloride is less than that of barium chloride or potassium chloride at high concentrations, but increases rapidly with the dilution and outstrips first that of barium chloride and later that of the potassium salt. Solutions of ferric chloride must hence contain hydrogen ions. So that, on dissolving in water, ferric chloride undergoes an immediate hydrolysis, which reaches a state of definite and reversible equilibrium and is maintained for a period varying with the temperature and concentration. When this equilibrium is destroyed, the hydrolysis tends to progress continu-

ously towards unstable and irreversible states. It is probable that the products  $\text{FeCl}_2 \cdot \text{OH}$  and  $\text{FeCl}(\text{OH})_2$  exist, whilst the insoluble  $\text{Fe}(\text{OH})_3$  can only have a transitory existence in solution, and, since it is not precipitated, must form complex ions with hydrogen or iron.

T. H. P.

**Different Molecular States of Anhydrous and Hydrated Ferric Sulphate.** ALBERT RECOURA (*Compt. rend.*, 1907, 144, 1427–1430. Compare this vol., ii, 552).—By keeping the white hydrated ferric sulphate at a temperature a little below  $100^\circ$ , it loses  $6\text{H}_2\text{O}$ ; if then the temperature is gradually raised to  $175^\circ$ , it is completely dehydrated, giving a light brownish-yellow sulphate, which differs from the canary-yellow hydrated sulphate previously described (*Abstr.*, 1905, ii, 590) in that it dissolves in water in a few minutes. The difference is not due merely to the temperature at which the sulphate is prepared, since dehydration of the white hydrated sulphate and decomposition of ferrisulphuric acid under the same conditions give two sulphates of which the first dissolves in water in ten minutes, whilst the second requires forty-eight hours. The new anhydrous sulphate, when exposed to moist air, is converted into a new brownish-yellow hydrated sulphate,  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , which is also formed by loss of  $6\text{H}_2\text{O}$  from the white hydrated sulphate at a temperature a little below  $100^\circ$ . It dissolves rapidly in 96% alcohol, whilst the white sulphate dissolves very slowly and the yellow sulphate is decomposed. What constitutes the difference in constitution between these two sulphates and those previously described has not yet been determined, since they all give identical solutions in water, and in alcohol the yellow sulphate is decomposed, whilst the other four give the same solution which on evaporation in a vacuum yields the compound:



Besides these five varieties, other forms of ferric sulphate result from heating the yellow hydrated sulphate. E. H.

**Alloys of Cobalt and Tin.** F. DUCELLIEZ (*Compt. rend.*, 1907, 144, 1432–1434. Compare Vigouroux, this vol., ii, 354).—The author has prepared alloys of cobalt and tin containing from 66 to 100% of the latter metal by heating powdered cobalt contained in a boat of magnesia and covered with an ingot of tin in a current of hydrogen in a Schloesing furnace. Of these, (1) containing 80.89% Sn is of a grey colour and brittle; (2) containing 89.28% Sn, has a reticulated surface, is malleable, and can be cut; (3) containing 92.91% Sn, has the appearance and malleability of tin. Either of these, after being powdered, boiled with 25% nitric acid, the metastannic acid removed by levigation, the residue fused with potassium hydroxide, and the product washed with water, alcohol, and ether, gives a substance having the composition  $\text{CoSn}$ .

This compound can be prepared directly by heating a mixture of powdered cobalt and tin in atomic proportions in a current of hydrogen. Combination occurs with incandescence. The product forms a dark grey powder,  $D^{20}_4$  8.950, which at a red heat is attacked by chlorine, oxygen, and sulphur vapour. It is completely dissolved by hydrochloric or sulphuric acid, but is not attacked by

boiling dilute nitric acid, and only slowly by the concentrated acid. Fused alkali hydroxides, carbonates, nitrates, and chlorates attack it slowly. E. H.

**Change of Colour of the Chlorides of Cobalt and Copper in Solution.** ALFRED BENRATH (*Zeitsch. anorg. Chem.*, 1907, 54, 328—332).—Donnan and Bassett (*Trans.*, 1902, 81, 939) have shown that the red solutions of cobalt salts contain positive  $\text{Co}^{++}$  ions, whilst the blue solutions contain complex negative ions of the formula  $\text{CoCl}_3'$  and  $\text{CoCl}_4''$ , and have expressed the view that the change of colour from red to blue is due to the production of these complex ions; Hartley (*Trans.*, 1903, 83, 401) and Lewis (*Abstr.*, 1906, ii, 657), on the other hand, consider that the colour change from blue to red is connected with the hydration of the salt. In the present paper, fresh evidence is brought forward which appears to support the association view of the phenomenon.

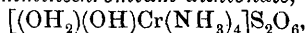
It is shown, by boiling point determinations in aqueous solution, that salts such as mercuric chloride, which favour the production of the red colour, form complexes with cobalt chloride, whereas salts such as calcium chloride, which favour the production of the blue colour, do not form complexes. With cupric chloride, the results are qualitatively, but not quantitatively, the same as for cobalt salts. Further, the dissociation is only slightly greater at the freezing point than at the boiling point of water, and appears to increase slowly as the concentration increases; the latter phenomenon is best accounted for by hydrate formation (compare Jones, *Abstr.*, 1905, ii, 687).

From a solution of anhydrous cobalt chloride in methyl alcohol, a blue alcoholate,  $\text{CoCl}_2 \cdot 2\text{MeOH}$ , has been obtained, which supports Hartley's view that the blue colour of alcoholic solutions of cobalt salts is connected with the formation of alcoholates. G. S.

**Alloys of Nickel and Lead.** A. PORTEVIN (*Rev. Métall.*, 1907, 4, 814—818).—Nickel and lead do not form solid solutions, and in the liquid state are only partially miscible, separation into two liquid phases occurring between the limits of 7% and 60% of nickel at  $1365^\circ$ . The eutectic alloy contains 0.07% of nickel. The microscopic examination confirms the conclusions drawn from the freezing-point curve. C. H. D.

**Diaquotetra-amminechromium Salts.** PAUL PFEIFFER (*Ber.*, 1907, 40, 3126—3134).—Of the aquoamminechromium salts intermediate between the violet hydrated chromium salts,  $[(\text{OH}_2)_6\text{Cr}]\text{X}_3$ , and hexa-amminechromium salts,  $[\text{Cr}(\text{NH}_3)_6]\text{X}_3$ , the penta-aquo-ammine- and diaquotetra-ammine-chromium salts have been hitherto unknown. The preparation and properties of the diaquotetra-ammine salts,  $[(\text{OH}_2)_2\text{Cr}(\text{NH}_3)_4]\text{X}_3$ , are now described; in their colour and reactions, these lie between the aquopenta-ammine and triaquotri-ammine salts.

*Hydroxo-aquotetra-amminechromium dithionate,*



prepared by the action of sodium dithionate and pyridine on chloro-

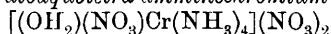
aquotetra-amminechromium chloride (Abstr., 1905, i, 854) in aqueous solution, forms Bordeaux-red crystals, dissolves in water forming a rose-coloured, neutral solution which gradually deposits a violet powder, is soluble in aqueous ammonium chloride or sulphate, and on treatment with mineral acids is converted into diaquotetra-amminechromium salts.

*Diaquotetra-amminechromium chloride*,  $[(\text{OH}_2)_2\text{Cr}(\text{NH}_3)_4]\text{Cl}_3$ , is obtained as a scarlet, crystalline powder, forms an orange, aqueous solution having an acid reaction, yields orange-red crystals with potassium cobalticyanide in concentrated aqueous solution, yields 3 mols. of silver chloride with silver nitrate in nitric acid solution at  $0^\circ$ , and when treated with pyridine in aqueous solution forms *hydroxo-aquotetra-amminechromium chloride*, which resembles the corresponding bromide. The diaquotetra-ammine chloride is converted into chloro-aquotetra-amminechromium chloride on slow evaporation of the hydrochloric acid solution.

*Diaquotetra-amminechromium bromide*,  $[(\text{OH}_2)_2\text{Cr}(\text{NH}_3)_4]\text{Br}_3$ , crystallises in orange-red plates, forms an orange, acid, aqueous solution, yields silver bromide quantitatively with silver nitrate in cold nitric acid solution, and changes slowly into the reddish-violet bromoaquotetra-amminechromium bromide. The *nitrate*,

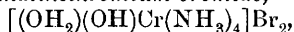


forms orange, prismatic needles, loses nitric acid and becomes red on exposure to air or on treatment with alcohol, and in a vacuum over soda-lime yields *nitratotetra-amminechromium nitrate*,



as a red, crystalline powder.

*Hydroxo-aquotetra-amminechromium bromide*,



prepared by the action of pyridine on the diaquotetra-ammine bromide in concentrated aqueous solution, crystallises in red leaflets, forms a red, aqueous solution which is not distinctly alkaline, with silver nitrate yields silver bromide free from silver oxide, and is converted into the diaquotetra-ammine salts by treatment with mineral acids or into the hydroxo-aquotetra-ammine dithionate by concentrated aqueous sodium dithionate. G. Y.

**Condition of Chromates and of Chromic Acid in Aqueous Solution.** EUGEN SPITALSKY (*Zeitsch. anorg. Chem.*, 1907, 54, 265—314. Compare this vol., ii, 338).—For some time there has been a difference of opinion as to the constitution of chromic acid and the dichromates; whilst Ostwald considers the chromic acid solutions to contain the strong acid  $\text{H}_2\text{Cr}_2\text{O}_7$ , which forms normal salts not appreciably hydrolysed in aqueous solution, Abegg and Cox (Abstr., 1904, ii, 662) have brought forward evidence to show that the  $\text{Cr}_2\text{O}_7^{=}$  ion is weak, splitting up almost completely into  $\text{CrO}_4^{=}$  ions and  $\text{CrO}_3$  in solutions of moderate strength. In the present paper, fresh evidence is brought forward which supports Ostwald's view. It is pointed out that the deductions of Abegg and Cox are not valid, as on one essential point an unjustifiable assumption has been made.

The experimental investigation has been carried out by measuring

the  $H^+$  ion concentration in solutions of free chromic acid and in mixtures containing chromates in varying proportions by the method suggested by Bredig and Fraenkel (Abstr., 1905, ii, 692), depending on the catalytic decomposition of ethyl diazoacetate. From these results and a knowledge of the total concentrations, the constitution of the solutions has been elucidated (compare Sand and Kaestle, this vol., ii, 178).

Dilute solutions of chromic acid contain almost exclusively the dibasic acid  $H_2Cr_2O_7$ , which in a dilution of 500 litres is dissociated almost completely into  $H^+$  and  $Cr_2O_7^{''}$  ions. Dilute solutions of potassium dichromate contain almost exclusively the ions of the normal salt  $K_2Cr_2O_7$ . In accordance with this view, dilute solutions of potassium chromate,  $K_2CrO_4$ , behave like alkalis to chromic acid, inasmuch as the  $CrO_4^{''}$  ions are changed practically quantitatively into  $Cr_2O_7^{''}$  ions, and the solution remains neutral. Strong solutions of potassium dichromate are slightly acid, probably owing to slight hydrolysis according to the equation:  $Cr_2O_7^{''} + H_2O \rightleftharpoons 2CrO_4^{''} + 2H^+$ ; the corresponding equilibrium constant  $k_1 = [CrO_4^{''}]^2[H^+]^2/[Cr_2O_7^{''}]$  is  $5.1 \times 10^{-12}$ . In a 0.1 molar solution of the dichromate, the  $Cr_2O_7^{''}$  ions are hydrolysed to the extent of 0.13% and in a 0.017 molar solution to 0.28%, so that the degree of hydrolysis does not alter much with dilution. Besides the above hydrolysis, another reaction represented by the equation  $CrO_4^{''} + H^+ \rightleftharpoons HCrO_4'$  takes place to some extent in dichromate solutions; the corresponding constant

$$k_2 = [CrO_4^{''}][H^+]/[HCrO_4']$$

is  $2.7 \times 10^{-7}$ . This is no evidence of the existence in dichromate solutions of complex ions such as  $Cr_3O_{10}^{''}$ .

In the light of the above results, the conditions which should be observed in preparing acid and other chromates are discussed. G. S.

**The Reducing Action of Hydrogen. Reduction of Molybdic and Vanadic Acids.** ALFRED C. CHAPMAN and HERBERT D. LAW (*Analyst*, 1907, 32, 250—254).—Molybdenum trioxide is completely reduced to the sesquioxide by the action of zinc or magnesium in sulphuric or hydrochloric acid solution; zinc coated with nickel, silver, cadmium, or platinum also effects complete reduction, but zinc coated with cadmium has the most rapid action. The authors' experiments with vanadium pentoxide confirm Roscoe's observation (this Journ., 1868, 322) that, in sulphuric acid solution, the pentoxide is reduced to the dioxide by the action of zinc, but to the trioxide only by magnesium. Zinc coated with cadmium reduced the quantity of pentoxide employed almost to the state of dioxide within eight minutes, whilst zinc coated with platinum was much slower in its action. Some electrolytic experiments with vanadium pentoxide are also described, from the results of which it is seen that when using a platinised platinum cathode the reduction did not proceed even as far as the trioxide stage, but with zinc, cadmium, or lead it approached the lowest point possible, that is, the dioxide. W. P. S.

**Compounds of Silicon and Molybdenum. Molybdenum Disilicide.** EDOUARD DEFACQZ (*Compt. rend.*, 1907, 144, 1424—1427. Compare this vol., ii, 475; Moissan, Abstr., 1895, ii, 501; Warren,



Abstr., 1899, ii, 158; Vigouroux, Abstr., 1900, ii, 144).—When a mixture of copper silicide, containing 50% Si, and amorphous molybdenum, prepared by reduction of the oxide with hydrogen, is heated in an electric furnace (Lebeau, Abstr., 1899, ii, 427) for one hundred seconds by a current of 800–900 amperes at 50 volts, a steel-grey ingot is formed, which breaks into large, brilliant plates. The latter, after successive treatment with nitric acid, dilute sodium hydroxide, hydrochloric acid, hydrofluoric acid (on a water-bath), and water, gives *molybdenum disilicide*,  $\text{MoSi}_2$ , in the form of non-magnetic, grey, microcrystalline needles,  $D^{20}_4$  6.2. The silicide is not altered by heating in a blowpipe flame, and is not attacked by hydrofluoric, hydrochloric, nitric, and sulphuric acids, by aqua regia, or by fused hydrogen sulphates. It is acted on by chlorine at 350–400°, giving silicon chloride and molybdenum pentachloride, by aqua regia containing hydrofluoric acid at the temperature of the water-bath, giving molybdic acid, and by fused alkali hydroxides or carbonates, or a mixture of these with alkali nitrates or chlorates. The authors have further isolated a series of compounds of silicon and molybdenum by the aluminothermic method. E. H.

**A Molybdo-Uranic Compound.** ANDRÉ LANCIEU (*Compt. rend.*, 1907, 144, 1434–1435).—By the addition of ammonium molybdate to uranyl nitrate solution, a precipitate is produced having the composition  $\text{UO}_2\text{MoO}_4$ . When prepared in the dark, this forms a white, amorphous powder, which is reduced by ethyl and methyl alcohols or acetic acid to the green uranous molybdate, is changed to a brick-red and then converted into the green oxide by prolonged boiling with alkalis, and is rapidly dissolved with a yellowish-green fluorescence by hydrochloric, sulphuric, and nitric acids. When exposed to sunlight for thirty hours, it becomes golden-yellow in colour, insoluble in nitric acid, which merely whitens it, and is no longer reduced by alcohol. Uranyl molybdate is radioactive, having an activity greater than that of the nitrate and equal to that of barium bromide of activity 40. E. H.

**The Melting Point of Pure Tungsten.** H. VON WARTENBERG (*Ber.*, 1907, 40, 3287–3291).—The high m. p. of this metal necessitates a special apparatus. The apparatus consisted of a Geissler tube, which was evacuated by a Gaede pump; the cathode was made of two water-cooled copper tubes, which were connected by a piece of platinum foil, 6 cm. long  $\times$  1 cm. broad, covered with a thin layer of lime obtained by passing an alternating current through the foil after smearing it with calcium nitrate. The anode consisted of a 4 mm. iron wire insulated by a glass tube, on the top of which a magnesia tube was cemented, and into which magnesia tubes of 5 mm. diameter and of differing lengths could be placed. A rod of tungsten was inserted in the magnesia tube. This rod was made by mixing pure tungsten with 10% tungstic acid in a paste, pressing into rod, and reducing in hydrogen at a red heat. The experiment was carried out by first evacuating the vessel to at least 0.01 mm. pressure and then gradually increasing the current density. With 20 amperes, the

tungsten begins to sink. With 800 watts on a surface of 70 sq. mm., it finally melts to a ball. It is allowed to cool, the tube opened, a shorter magnesia cylinder inserted, so that the rod with its head protrudes about 5 mm., and the melting repeated thus three or four times.

The temperature was measured by a Wanner pyrometer; the smoked glass was standardised by determining the m. p. of gold, the calculation from the intensity of the light being made by the Wien-Planck law.

The m. p. is at least 2800° and probably not more than 2850°. The temperature of the positive crater of the arc was 3350°; Reich found 3430°.

The tungsten so obtained is like highly polished platinum, can be indented by a knife, and is brittle. It is radio-crystalline in structure, D 17.6—18.3; powdered tungsten has D 19.0—19.2.

W. R.

**Electrolytic Oxidation of Platinum.** CHARLES MARIE (*Compt. rend.*, 1907, 145, 117—118).—The brown coloration observed on the anode during the electrolysis of platinum chloride solutions (Kohlrausch, *Abstr.*, 1898, ii, 203) suggests that the platinum is oxidised at least superficially. This has proved to be the case. On treatment of the brown anode with a dilute solution of potassium iodide acidified with hydrochloric acid, a red solution is obtained which resembles the solution formed on addition of potassium iodide to aqueous platinum chloride; from it a small amount of free iodine can be extracted by means of chloroform. The platinum is oxidised only slightly; thus, on electrolysis of *N*-sulphuric acid with a current of 2 amperes for twelve hours, square platinum anodes of 100, 40, 6, and 0.3 sq. cm. area, when treated with potassium iodide and hydrochloric acid, lost only 0.8, 0.5, 0.25, and 0.1 mg. respectively. The weight of the cathode remained unchanged in each case.

Similar results are obtained on electrolysis of nitric or hydrochloric acid or of aqueous sodium hydroxide with platinum anodes. The oxide formed is decomposed at a red heat, and is insoluble in nitric acid or in hydrochloric acid except in presence of an iodide. The liberation of iodine points to the presence of a peroxide (compare Engler and Wöhler, *Abstr.*, 1902, ii, 127). It is probable that platinum can be oxidised superficially, even in absence of an electric current, by contact with cold solutions of oxidising agents such as permanganate or sodium persulphate.

G. Y.

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### Mineralogical Chemistry.

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N'hangellite from Portuguese East Africa. SIR BOVERTON REDWOOD (*Bull. R. Bot. Gardens, Kew*, 1907, 151—153).—This elastic bitumen is found as a layer about half an inch in thickness on the

surface of the ground in the neighbourhood of Lake N'hangella in Portuguese East Africa. In thin flakes it is translucent with a light brown colour. Deducting 5.94% of ash and 0.06% of sulphur, the composition of the air-dried material is:

C.	H.	N.	O.	Total.
69.63	10.35	2.50	[17.52]	100.00

Benzene extracts 10.5–12%. The oil (D 0.857) yielded on destructive distillation amounts to 46.2–56.9%.

L. A. BOODLE (*ibid.*, 145–151), from a microscopical examination of the material, concludes that it has been derived from masses of a gelatinous alga, and that it is very similar to the coorongite of South Australia (Abstr., 1903, ii, 433).

L. J. S.

**Red Silver Minerals from the Binnenthal, Switzerland.** G. F. HERBERT SMITH and GEORGE T. PRIOR (*Min. Mag.*, 1907, 14, 283–307).—A detailed description is given of the red silver minerals discovered by R. H. Solly in 1903 (*Ann. Rep.*, 2, 279–281) in the white, crystalline dolomite of the Binnenthal in Switzerland. The crystals are minute, and only very small amounts of material were available for analysis. The characters of the three species are summarised as follows.

*Hutchinsonite*.—Orthorhombic;  $a : b : c = 1.6343 : 1 : 0.7549$ . Crystals, prismatic in habit. Cleavage,  $a$  (100) good. Fracture, conchoidal. Brittle. Hardness,  $1\frac{1}{2}$ –2. D 4.6. Lustre, adamantine. Colour and streak, scarlet-vermilion to deep cherry-red. Transparent to translucent. Optic axial plane parallel to  $a$  (100), acute bisectrix perpendicular to  $b$  (010); double refraction, negative and fairly strong. Pleochroism, weak. Composition,  $(\text{Ti, Ag, Cu})_2\text{S, As}_2\text{S}_3 + \text{PbS, As}_2\text{S}_3$  (Anal. I and II).

*Smithite*.—Monoclinic;  $a : b : c = 2.2206 : 1 : 1.9570$ ;  $\beta = 101^\circ 12'$ . Crystals, hexagonal in habit, tabular and occasionally modified. Cleavage,  $a$  (100), highly perfect. Fracture, conchoidal. Brittle. Hardness,  $1\frac{1}{2}$ –2. D 4.88. Lustre, adamantine. Colour and streak, scarlet-vermilion, altering to orange-red on exposure. Transparent. Optic axial plane parallel to  $b$  (010); acute bisectrix inclined at  $6\frac{1}{2}^\circ$  (Na) and  $4^\circ$  (Li) to normal to  $a$  (100) in the obtuse angle (100 : 001);  $2E$  about  $65^\circ$ . Double refraction, negative and fairly strong. Pleochroism, weak. Mean refractive power, 3.27 approximately. Composition,  $\text{Ag}_2\text{S, As}_2\text{S}_3 = \text{AgAsS}_2$  (Anal. III).

*Trechmannite*.—Rhombohedral, diplohedron;  $a : c = 1 : 0.6530$ . Crystals, prismatic in habit, often irregular; sometimes corroded in parts. Cleavage,  $r$  good,  $c$  distinct. Fracture, conchoidal. Brittle. Hardness,  $1\frac{1}{2}$ –2. Lustre, adamantine. Colour and streak, scarlet-vermilion. Transparent to translucent. Double refraction, fairly strong; negative. Pleochroism, weak. Composition, probably a sulpharsenite of silver.

	Ag.	Tl.	Pb.	Cu.	Fe.	As.	Sb.	S.	Total.
I.	9	25	12½	—	—	30.5	—	26	103
II.	2	18	16	3	½	29.5	2	26.5	97.5
III.	43.9	—	—	—	—	28.9	0.4	26.0	99.2

L. J. S.

**Bolivian Minerals (Jamesonite, Andorite, Valentinite, Miargyrite, &c.).** LEONARD J. SPENCER, with analyses by GEORGE T. PRIOR (*Min. Mag.*, 1907, 14, 308—344).—Descriptions are given of several new mineral occurrences in Bolivia; the following points are of chemical interest.

*Jamesonite*.—Acicular crystals occurring with iron-pyrites at the Cerro de Ubina, near Huanchaca, gave anal. I; the needles have a good cleavage, perpendicular to their length, and a prism-angle of  $78^{\circ}38'$ . Anal. II is of the associated fibrous jamesonite, which also exhibits the basal cleavage. These analyses, as well as the few that have been made previously on cleavable jamesonite, give the formula  $7(\text{Pb}_4\text{Fe}_4)\text{S}_4\text{Sb}_2\text{S}_3$ ; in all cases, iron is present to the extent of 2—3%. The formula  $2\text{PbS}_2\text{Sb}_2\text{S}_3$ , given in the text-books for jamesonite, belongs, not to this species, but to the flexible “feather-ore” or plumosite.

*Semseyite*.—Some indistinct and curved crystals of a sulphantimonite of lead, occurring with plumosite and galena at Oruro, were determined to belong to the plagionite group of minerals (Abstr., 1899, ii, 431), but to which member (plagionite, heteromorphite, or semseyite) could only be decided by analysis (III). The crystals are rather more basic than the two semseyites, from Hungary and the Harz, previously described;  $(\text{Pb}, \text{Ag}_2) : \text{Sb} = 1.28 : 1$ .

	S.	Sb.	Pb.	Fe.	Cu.	Ag.	Total.	Sp. gr.
I.	20.52	34.53	41.18	2.76	0.26	0.01	99.26	5.519
II.	21.37	34.70	40.08	2.79	0.22	0.13	99.29	5.546
III.	18.7	24.8	52.9	—	—	1.6	98.0	5.82

*Andorite*.—Although andorite (Abstr., 1890, ii, 120) is orthorhombic, it bears no crystallographic relationship to the orthorhombic zinckenite,  $(\text{PbSb}_2\text{S}_4)$ , and the few analyses all agree with the formula  $\text{PbAgSb}_2\text{S}_6$ . The mineral is therefore a double salt, and is not an isomorphous member of the zinckenite group as represented by the formula  $(\text{Pb}, \text{Ag}_2)\text{Sb}_2\text{S}_4$ .

*Valentinite*.—Taking a new pyramid for the parametral plane, the axial ratios of orthorhombic crystals from Tatasi are deduced as  $[a : b : c = 0.3938 : 1 : 0.4344]$ . The crystals contain 82.79% Sb, corresponding with the formula  $\text{Sb}_2\text{O}_3$ . The mineral had not previously been analysed. D 5.76.

*Miargyrite*.—The following analysis of a massive mineral from Tatasi was made in order to determine whether it was miargyrite or an argentiferous tetrahedrite. The numbers correspond with the miargyrite formula  $\text{AgSbS}_2$ , with part of the silver replaced by copper ( $\text{Ag} : \text{Cu} = 8 : 1$ ).

S.	Sb.	Ag.	Cu.	Fe.	Pb.	As.	Total.	Sp. gr.
21.9	40.5	33.9	2.6	1.0	0.6	trace	100.5	5.20

L. J. S.

**Manganese in India.** L. LEIGH FERMOR (*Trans. Mining and Geol. Inst., India*, 1906, 1, 69—131).—An account of Indian manganese-ore deposits, their origin, mode of occurrence, localities, and

mining, is prefaced by a general account of manganese minerals and ores. The Indian deposits are classified as follows.

*A*—Braunite, psilomelane, and pyrolusite associated with, and derived from, manganese-bearing silicates (such as spessartite, rhodonite, and, less frequently, piemontite) occurring as bands and lenticles in Archaean schists and gneisses.

*B*.—Psilomelane and pyrolusite superficially formed on outcrops of rocks of Dharwar age.

*C*.—Psilomelane and pyrolusite associated with, or contained in, laterite.

Amongst the minerals occurring in deposits of the first class, the three following are briefly described as new.

*Hollandite*.—This occurs at Kájlidongri, Jhábua State, Central India, as black crystals with a shining metallic lustre; the crystals are pseudo-tetragonal in form and have perfect prismatic cleavages. Analysis by H. J. WINCH shows it to be a manganate with the formula:  $m(\text{Ba}, \text{Mn})_2\text{MnO}_5 + n\text{Fe}_4(\text{MnO}_5)_3$ .

$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{MnO}_2$ .	$\text{MnO}$ .	$\text{BaO}$ .	$\text{SiO}_2$ .	Total.	Sp. gr.
10.56	0.94	65.63	5.12	17.59	trace	99.84	4.95

A similar mineral occurs as cleavage masses at Sitapár, Chhindwára district, Central Provinces; it has  $D\ 4.70$ , and is a manganate of barium, iron, and manganese, with a considerable amount of calcium.

*Blanfordite*.—A monoclinic pyroxene containing some sodium, manganese, and iron. A prominent character is the strong pleochroism (rose-pink to sky-blue).

*Winchite*.—A blue amphibole closely allied to tremolite, but containing also iron, sodium, potassium, and manganese.

L. J. S.

**Isomorphism as Illustrated by Varieties of Magnetite.**  
BERNARD J. HARRINGTON (*Min. Mag.*, 1907, 14, 373—377).—Some specimens of magnetite from St. Joseph du Lac in Two Mountains Co., Quebec, are remarkable in containing considerable amounts of titanium, manganese, and magnesium (anal. I); the crystals are also unusual in showing the faces of the icositetrahedron  $\{311\}$  in combination with the octahedron. Crystals of similar habit also occur at Magnet Cove in Arkansas (anal. II). Analysis III is of crystals ( $\{111\}$ ,  $\{110\}$ ) of magnetite from Digby, Annapolis Co., Nova Scotia.

	$\text{Fe}_2\text{O}_3$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{MgO}$ .	$\text{SiO}_2$ .	Total.	Sp. gr.
I.	59.71	5.32	0.62	22.70	8.46	3.24	0.16	100.21	4.913
II.	59.01	2.40	10.37	16.82	2.10	9.47	—	100.17	4.558
III.	70.64	0.24	—	26.13	trace	2.97	—	100.01	5.067

In each of these analyses, the atomic ratio of metals to oxygen is the normal one of 3 : 4. The titanium may be regarded as being present as  $\text{Ti}_2\text{O}_3$  or as  $\text{FeTiO}_3$ , isomorphously replacing  $\text{Fe}_2\text{O}_3$ . In anal. I,  $\text{RO} : (\text{R}_2\text{O}_3 + \text{Ti}_2\text{O}_3) = 1 : 3.022$  and  $\text{RO} : (\text{R}_2\text{O}_3 + \text{FeTiO}_3) = 1 : 2.975$ . In anal. II, however,  $\text{RO} : (\text{R}_2\text{O}_3 + \text{Ti}_2\text{O}_3) = 1 : 3.19$ , possibly because of partial oxidation of the ferrous iron.

L. J. S.

**Baddeleyite from Ceylon.** GEORGE S. BLAKE and G. F. HERBERT SMITH (*Min. Mag.*, 1907, 14, 378—384).—A crystallographic description is given of two black, well-developed crystals, one simple and the other twinned, of baddeleyite from the gem-gravels of the Balangoda district in Ceylon. A third crystal gave on analysis :

ZrO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> , FeO.	CaO.	SiO <sub>2</sub> .	Loss on ignition.	Total.	Sp. gr.
98.90	0.82	0.06	0.19	0.28	100.25	5.72.

L. J. S.

**New Method of Representing van't Hoff's Investigations [on Oceanic Salt Deposits].** Supplement. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1907, 54, 319—321. Compare Abstr., 1906, ii, 833 ; this vol., ii, 278, 480).—An amplification, and in one respect a slight correction, of the results already communicated. G. S.

**Formation of Oceanic Salt Deposits. LI. Borocalcite and the Artificial Preparation of Ascharite.** JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 652—663. Compare Abstr., 1906, ii, 456, 619, 863 ; this vol., ii, 363).—All attempts to procure borocalcite, CaO, B<sub>2</sub>O<sub>3</sub>, 4H<sub>2</sub>O, from natural sources have been unsuccessful ; various specimens from collections have been shown to be boronatrocalcite, pandermite, &c. Experiments to prepare it have also been without the desired result. An aqueous solution of lime and boric acid, kept at 40° for three weeks, deposits a substance of the approximate composition demanded by the formula ; it is really, however, a mixture of calcium triborate, CaO, 3B<sub>2</sub>O<sub>3</sub>, 4H<sub>2</sub>O, and dicalcium triborate, 2CaO, 3B<sub>2</sub>O<sub>3</sub>, 9H<sub>2</sub>O. At 83°, however, this solution deposits, after two months, colemanite ; this is the best method of obtaining artificial colemanite. Borocalcite, if capable of existence, is therefore very difficult to prepare.

The limits of formation of colemanite, pandermite, boronatrocalcite, and the tetrahydrate, NaCaB<sub>5</sub>O<sub>9</sub>, 4H<sub>2</sub>O, are graphically represented in conjunction with those of sylvite, borax, calcium chloride, &c.

The rule that the difficulty of forming artificial minerals increases from the chlorides to the sulphates and to the borates is given a quantitative significance, in which the idea of "mean valence" is introduced. "Mean valence" is a quotient of two totals ; the values for Na, K, Cl are 1 ; Ca, Mg, SO<sub>4</sub>, 2 ; B<sub>2</sub>O<sub>3</sub>, 6, and H<sub>2</sub>O, 4, in the numerator, those in the denominator being Na, K, Cl, Ca, Mg, SO<sub>4</sub>, 1 ; B<sub>2</sub>O<sub>3</sub>, 2, and H<sub>2</sub>O, 3 ; thus, for ascharite, MgHBO<sub>3</sub> or  $2\text{MgO}, \text{B}_2\text{O}_3, \text{H}_2\text{O} = \frac{4+6+4}{2+2+3} = 2$ . A number of examples are given and the value of the numbers explained ; 1.33, the mean valence of Glauber salt, for example, indicates that its separation from a super-saturated solution is easy, whereas with ascharite the difficulties would be much greater.

Consideration of the occurrence of ascharite in nature and the limits of formation for magnesium borate indicated that probably the easiest method of preparing this mineral would be to heat pinnoite in

saturated salt solution. This was carried out at 150° for eight days, and the product obtained had the composition and characteristic sparing solubility in dilute hydrochloric acid of ascharite. W. R.

**Hamlinite from the Binnenthal, Switzerland.** HERBERT L. BOWMAN (*Min. Mag.*, 1907, 14, 389—393).—A complete determination of the supposed new mineral, bowmanite (*Ann. Rep.*, 2, 278), establishes its identity with hamlinite. The mineral occurs as minute, honey-yellow, rhombohedral crystals in the dolomite of the Binnenthal. Although the crystals are sometimes optically uniaxial, they usually show optical anomalies with a division into six sectors. The calcium and magnesium previously found are doubtless due to the presence of dolomite. Some of the several determinations made on various small amounts of material are :

$P_2O_5$ .	$Al_2O_3$ .	SrO.	BaO.	Loss on ignition ( $H_2O + F$ ).	Sp. gr.
26.1	35.6	20.5	0.1	16.0	3.219—3.266.

L. J. S.

**A New Mineral Species from the High-temperature Fumaroles of the Recent Eruption of Vesuvius.** ALFRED LACROIX (*Compt. rend.*, 1907, 144, 1397—1401).—White, yellow, green, or brownish-red crusts have been collected from the lava-flow revealed after the washing away of the superficial layer of solid material (this vol., ii, 33) deposited by the fumaroles of the recent eruption of Vesuvius. The first specimens consist mainly of chlorides, those collected afterwards of sulphates. The chief constituent of the latter is apthitalite,  $KNa_3(SO_4)_2$ , recognised in a thin lamina of the crust by its uniaxial, optically positive, rhombohedral crystals, which show a feeble double refraction, but some specimens contain a considerable quantity of very thin, uniaxial, optically negative, highly double-refracting lamellæ, which can be isolated by dissolving away the apthitalite by cold water. These lamellæ are sometimes hexagonal in shape, are anhydrous and easily melted in a blowpipe flame, and are decomposed by boiling water leaving a dense residue. The analysis agrees approximately with the composition  $(NaK)_2SO_4 \cdot PbSO_4$ , and by fusion of lead sulphate with excess of the alkali sulphates, hexagonal crystals are obtained having all the properties of the natural mineral. The latter, to which the name *palmiërite* is given, belongs to the group of double sulphates of which the previously known members are glauberite, vanthoffite,  $(3Na_2SO_4, MgSO_4)$ , and langbeinite,  $(K_2SO_4, 2MgSO_4)$ . Its existence in the fumarole crusts affords an explanation of the presence of anglesite.

The author confirms Scacchi's discovery of the occurrence of aluminium chloride as the definite mineral chloraluminite,  $AlCl_3 \cdot 6H_2O$ . E. H.

**Isomorphism of Calcium Sulphate with Barytes and Celestite.** ERNST SOMMERFELDT (*Jahrb. Min.*, 1907, i, 139—146).—Crystals of calcium sulphate and of barytes and celestite were obtained



artificially by dissolving the precipitated sulphates of the alkaline earths in concentrated sulphuric acid and then slowly evaporating the acid. The crystals of calcium sulphate so obtained measure 1.5 mm. across; they are orthorhombic with a prism (prism-angle,  $67^{\circ}10'$ ), a brachydome ( $67^{\circ}28'$ ), and small faces of the macropinacoid and basal pinacoid. These angles can only be referred to the axes of anhydrite if complex indices be assigned to the faces; on the other hand, they agree (within  $10^{\circ}$ ) with the angles of barytes, and the crystals also resemble barytes in habit. These crystals therefore appear to represent a labile modification of calcium sulphate isomorphous with barytes, and to differ from the stable form represented by anhydrite; for this form of calcium sulphate, the name *metanhydrite* is proposed. The density and cleavages of the artificial crystals are, however, the same as those of anhydrite, but the optical interference-figure seen through one of the rectangular cleavages is almost always distorted. This seems to be a case of dimorphism only as concerns the external form and the state of internal strain of the crystals, the chemical composition and the physical characters being identical in the two modifications.

The calcium sulphate of volcanic origin found at Santorin, and possibly also at Vesuvius, seems to be identical with *metanhydrite* rather than with anhydrite. L. J. S.

**A New Yttrium Columbium Mineral.** OTTO HAUSER (*Ber.*, 1907, 40, 3118—3119).—A Norwegian mineral, supposed to be an orangite resembling euxenite, is shown by the following analyses to be an yttrium columbate, which in its composition approximates to ferugsonite, but differs from this in the amount of titanate acid, the abnormal loss on heating, and the absence of uranium.

Cl <sub>2</sub> O <sub>5</sub> .	TiO <sub>2</sub> .	Y <sub>2</sub> O <sub>3</sub> .	La[Ce,Di] <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	PbO.	SnO <sub>2</sub> ,ThO <sub>2</sub> .	Loss on heating.
38.52	6.48	36.99	4.01	0.98	2.34	1.93	0.26	traces	8.76
45.23		41.19		0.80	2.51	1.80	0.19	traces	8.40

The yttrium group consists chiefly of the colourless earths; amongst the erbium earths, dysprosium and holmium are present in relatively large amounts, terbium only in traces; the cerium group is represented by lanthanum, cerium, and neodymium, with traces of praseodymium. G. Y.

**Molybdate from Ilmen Mountains.** PRINCE G. GAGARINE (*Bull. Acad. Sci. St. Pétersbourg*, 1907, 287—288).—In reference to the recent determination by Schaller (this vol., ii, 480) that molybdate is a hydrous ferric molybdate and not molybdenum trioxide, attention is called to the fact that the Comte de Bournon, in 1813, distinguished two kinds of molybdate: (1) a citron-yellow powder, and (2) a pale green or white mineral, coating surfaces of, and lining cavities in, molybdenite. The former of these appears to be the mineral examined by Schaller, and it should receive a new name. The latter occurs in the Ilmen Mountains as white or grey pseudomorphs after molybdenite; it is semi-transparent with a pearly lustre, is difficultly fusible, and is

soluble in nitric acid; it appears to be pure molybdic oxide containing no iron or water. The associated molybdenite from the Ilmen Mountains is pure molybdenum sulphide without a trace of iron.

L. J. S.

**Benitoite, a New Gem-mineral from California.** GEORGE DAVIS LOUDERBACK, with analysis by WALTER C. BLASDALE (*Bull. Dept. Geol. Univ. California*, 1907, 5, 149—153).—The new mineral occurs as colourless to blue, transparent crystals embedded in zeolitic veins in a basic igneous rock near the head-waters of the San Benito River in San Benito Co., California. The crystals belong to the hexagonal system and have the form of trigonal pyramids with a trigonal prism and basal planes; the angle between the pyramid and the base is  $40^{\circ}14'$ . The refractive indices are  $\omega = 1.77$  and  $\epsilon = 1.80$  (Na); the pleochroism is strong ( $\omega$ , colourless;  $\epsilon$ , blue). Faceted stones resemble sapphire in colour, but exceed it in brilliancy. The hardness is  $6\frac{1}{4}$ — $6\frac{1}{2}$ ; D 3.64—3.65. The mineral is nearly insoluble in hydrochloric acid, but is readily attacked by hydrofluoric acid. The following mean of two analyses corresponds with the formula  $\text{BaTiSi}_3\text{O}_9$ :

$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{BaO}$ .	Total.
43.68	20.09	36.33	100.10

Associated with the benitoite is another new mineral, called *carlosite*, occurring in blackish-brown, prismatic (monoclinic?) crystals which have not yet been completely determined.

L. J. S.

**Apophyllite from Traversella.** LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 966—975).—The author describes crystals of apophyllite found, for the first time, in the deposits of Traversella. Analysis of the crystals gives the results:

$\text{SiO}_2$ .	$\text{CaO}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	F.	Total.
53.63	26.06	4.29	15.85	0.87	100.10

The structural formula is probably  $\text{H}_{14}\text{Ca}_{10}\text{K}_2\text{Si}_{19}\text{O}_{56}\text{F}, 12\text{H}_2\text{O}$ , or  $10\text{CaSiO}_3, \text{K}_2\text{SiO}_3, 7\text{H}_2\text{SiO}_3, \text{SiO}(\text{OH})\text{F}, 12\text{H}_2\text{O}$ .

T. H. P.

**Crocidolite from Siberia.** PETER TSCHIRWINSKY (*Centr. Min.*, 1907, 435—438).—Crocidolite occurs as plate-like masses, 3—5.5 cm. in thickness, in Devonian marls in the Minussinsk district, govt. Yeniseisk, Siberia. It is blue, or greyish-blue, and has a fibrous structure perpendicular to the surfaces of the plates. The fibres are optically positive with very nearly straight extinction. The following analysis gives the formula:  $2\text{Na}_2\text{O}, \text{FeO}, \text{Fe}_2\text{O}_3, 6\text{SiO}_2$ , or  $2\text{NaFe}''(\text{SiO}_3)_2 + \text{Fe}''\text{SiO}_3 + \text{Na}_2\text{SiO}_3$ .

$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	$\text{Na}_2\text{O} (+ \text{K}_2\text{O})$ .	Total.	Sp. gr.
53.90	trace	16.89	7.92	0.44	1.12	0.96	[18.77]	100.00	3.16

This occurrence of crocidolite is very similar to that on the Orange River in South Africa.

L. J. S.

**Analyses of Iron Meteorites.** OLIVER C. FARRINGTON (*Field Columbian Museum, Geol. Ser.*, 1907, 3, 59—110).—About 360 published analyses of 248 meteoric irons are collected together and tabulated in different classes according to the structure of the iron. It is seen that there is a close relation between chemical composition and structure. All irons with a hexahedral structure are very uniform in composition, whilst in those with an octahedral structure the amount of nickel increases with the fineness of the structure :

Class.	No. of Analyses.	Width of lamellæ in mm.	Fe%.
Hexahedrites .....	29	—	94·12
Coarsest octahedrites .....	12	2·5 and over	93·18
Coarse            "       .....	22	2·0—1·5	92·28
Medium           "       .....	88	1·0—0·5	90·64
Fine             "       .....	41	0·4—0·2	90·18
Finest           "       .....	13	0·2 and less	88·51

The ataxites, in which the structure is finely granular to compact, show more variation in composition, the nickel ranging from 6% to 16%, and in the doubtful Oktibbeha iron to 62%.

The averages for all irons are approximately : Fe, 90 ; Ni, 9 ; Co, 0·9 ; Cu, 0·02% ; the fact that the percentage of these metals decreases with increase in atomic weight may be a mere coincidence. Phosphorus, sulphur, and carbon appear to be invariably present.

L. J. S.

## Physiological Chemistry.

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**Saliva of the Dog.** WALTER E. GARREY (*Proc. Amer. Soc. Biol. Chemists*, 1907, xl.—xli., *J. Biol. Chem.*, 3).—The dog's saliva is free from fat-splitting and protein-splitting ferments. As a rule, phyalin is absent also, and the amount when present is small. No activation of the saliva occurs in œsophagus or stomach, and no adaptation of the secretion occurs to meet the digestive requirements of the diet.  
W. D. H.

**Physiology of Digestion. I. Gastric Juice obtained from a Dog by Sham-Feeding.** RUDOLF ROSEMAN (*Pflüger's Archiv*, 1907, 118, 467—524).—The juice was obtained from a gastric fistula, and the dog was sham-fed by Pawloff's method. The quantity of juice obtained per hour varied from 18 c.c. to 270 c.c. It is colourless and slightly opalescent, levorotatory, and has  $D_{1.002}$  to 1.004. The lowering of its freezing point varies from  $0.49^{\circ}$  to  $0.64^{\circ}$ . It contains on the average 0.43% of solids, of which 0.13% is ash. The organic substance is principally protein (0.25%); thiocyanic acid is present. In relation to its total molecular concentration, only the electrolytes play an important part. The percentage of hydrochloric acid averages

0.55. The total chlorine varies from 0.54% to 0.64%, or more than twice as great as in the blood. In three and a half hours, as much chlorine can be separated out in the juice as is contained in the whole blood of the animal, or a quarter of the total chlorine of the body.

W. D. H.

**Carbohydrate Metabolism in a Dog with an Eck's Fistula.** FILIPPO DE FILIPPI (*Zeitsch. Biol.*, 1907, 49, 511—557).—If a dog has performed upon it the operation known as Eck's fistula, so that the blood coming from the digestive apparatus passes into the general circulation without passing through the liver, it is able to utilise starch like a normal animal, and shows no trace of glycosuria. It exhibits a lowered tolerance for sugars given in solution, or for lactose in milk, a smaller dose leading to glycosuria than in a normal dog, probably because they pass more rapidly into the circulation. It is quite intolerant for lævulose. Such results render doubtful the clinical view that alimentary glycosuria is a symptom of hepatic insufficiency; pathological changes in the liver of such cases are usually absent.

W. D. H.

**Protein Metabolism in Exophthalmic Goitre.** PHILIP SHAFFER (*Proc. Amer. Soc. Biol. Chemists*, 1907, xiii.—xiv., *J. Biol. Chem.*, 3).—Observations are recorded on twelve cases; the diet was free from meat. In spite of increased tissue catabolism, the amount of creatinine excreted was very low. The normal excretion is 20—30 mg. per day per kilogram of body-weight; in exophthalmic goitre, this drops to 7—16. Creatinine is evidently the product of certain normal processes, which may be sluggish in diseases, even though total catabolism is high. The disease is one in which muscular weakness is a prominent symptom; creatinine appears to be an index of muscular efficiency. Eight of the twelve cases excreted creatine; this was sometimes in excess of the creatinine. There is no basis for the assumption that the two substances have a close physiological relationship.

W. D. H.

**Protein Catabolism during Digestive Activity.** WILHELM ROEHL (*Pflüger's Archiv*, 1907, 118, 547—550).—No increase of urinary nitrogen occurs during digestive work any more than in muscular work. If the food contains nitrogen, any increase of nitrogen in the urine comes from the food. If the food is free from nitrogen, the amount of nitrogen in the urine sinks after some days to a constant level (about 2.5 grams per diem). The intake of 3 grams of nitrogen per diem is the lowest limit of nitrogenous equilibrium.

W. D. H.

**Catalases.** II. ERNST J. LESSER (*Zeitsch. Biol.*, 1907, 49, 575—583. Compare Abstr., 1906, ii, 562).—A comparison of the amount of catalases in various animals, &c., does not support the view that the amount varies with the amount of oxygen needed by the animal or plant. Other views relating to the biological rôle of catalases are also shown to be untenable. A catalase is to be regarded as a substance which is capable of taking up oxygen and of giving it up again under certain circumstances.

W. D. H.

**Phenolphthalin as a Reagent for Oxydases in Plant and Animal Tissues.** JOSEPH H. KASTLE (*Proc. Amer. Soc. Biol. Chemists*, 1907, xii.—xiii., *J. Biol. Chem.*, 3).—Phenolphthalin is readily converted into phenolphthalein by various oxidising agents, including plant oxydases. Animal tissues and blood only produce oxidation in alkaline solution; if the amount of oxidation so produced by blood is taken as 100, the power of spleen is 10, of the lung, 8.2, of the suprarenal, 3, and of the liver, kidney, and testis, 2.5. Drying in air or boiling lessens the oxidising power of the blood. The power is destroyed by chlorine, bromine, or hydrocyanic acid, and by incineration.

W. D. H.

**Nuclein Ferments of Embryos.** WALTER JONES and C. R. AUSTRIAN (*J. Biol. Chem.*, 1907, 3, 227—232. Compare Abstr., 1906, ii, 561).—The distribution of the nuclein ferments (guanase, adenase, and xantho-oxydase) differs in different animals; the livers of the dog, ox, pig, and rabbit are distinguishable by the ferments each exhibits. Not only so, but in the same species, the embryo differs from the adult; thus in small pig embryos the liver contains none of the ferments; as the embryo grows, adenase appears; the adult liver contains both adenase and xantho-oxydase, but no guanase.

W. D. H.

**Proximate Analysis of Yolk of Egg.** N. ALBERTO BARBIERI (*Compt. rend.*, 1907, 145, 133—135).—The author has sought by employment of a single neutral solvent, carbon disulphide, to isolate the proximate components of yolk of egg with the object of comparing these with the substances isolated from nerve tissues (Abstr., 1905, i, 621), and has obtained tristearin, triolein, a nitrogenous substance containing sulphur and phosphorus and in composition approaching Fremy's cerebrie acid, cholesterol, and crystalline sulphur, the source of which remains undetermined.

G. Y.

**Liebig's Extract of Meat.** FRIEDRICH KUTSCHER (*Chem. Zentr.*, 1907, i, 1593; from *Zentr. Physiol.*, 1907, 21, 33—35. Compare Abstr., 1906, ii, 562).—A new compound, *vitiatine*,

$\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ , has been isolated from Liebig's extract of meat. The *aurichloride*,  $\text{C}_5\text{H}_{14}\text{N}_6\cdot\text{HAuCl}_4\cdot\text{HCl}$ , crystallises in broad, lustrous plates.

E. W. W.

**The Passage of Fat in the Food into the Milk.** WILHELM CASPARI and HUGO WINTERNITZ (*Zeitsch. Biol.*, 1907, 49, 558—561).—Winternitz fed animals on iodised fats, and found these again in the milk. Gogitidse (Abstr., 1906, ii, 295) disputed the view that this proved the passage of the food fat into the milk. The present paper is largely polemical, and reasserts Winternitz's original contention.

W. D. H.

**Glomerular Excretion under Certain Conditions.** ARCHIBALD B. MACALLUM (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxx.—xxxi., *J. Biol. Chem.*, 3).—When large quantities of distilled water are

swallowed and the urine examined in ten minute periods,  $\Delta$  progressively diminishes to 0.09, and the percentage of sodium chloride to 0.047. Potassium salts and phosphates are absent or present only in traces. The glomerular epithelium actively removes pure water from the blood, and the small amount of salt is attributed to that washed out from the epithelial cells of tubules, ureters, and bladder. The action of the glomeruli is therefore one of true secretion.

W. D. H.

**Composition of the Hourly Excretion of Urine.** CLARA C. BENSON (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxxi, *J. Biol. Chem.*, 3).—As a result of observations on chlorides, phosphates, nitrogen, specific gravity, conductivity, and depression of freezing point, it was found that whilst the constants of Bugarszky's and Koranyi's formulæ were exemplified in some of the hourly excretions, they were not uniformly or even generally obtained.

W. D. H.

**Acidity of Normal Urine.** WM. OVID MOOR (*Zeitsch. Biol.*, 1907, 49, 562—570).—Normal urine is considered to contain a substance which is neutral in the absence of water, but reacts strongly acid on the addition of water. This new substance is regarded as a specific constituent of urine, and as playing a more important part in rendering the urine acid than acid phosphates. Its chemical constitution is not indicated.

W. D. H.

**The Formation of Creatine and Creatinine in the Organism, Especially in Rabbits.** G. DORNER (*Zeitsch. physiol. Chem.*, 1907, 52, 225—278).—The method of estimation adopted was Folin's colorimetric method; three to four hours' warming with acid is necessary to convert creatine into creatinine; the addition of glyco-cyamine to urine containing creatine has but little influence on the value of creatinine estimation; the small error due to the formation of glyco-cyamidine can be obviated by previous extraction with alcohol. By means of the sodium nitroprusside test, glyco-cyamidine can be detected when diluted 15,000 times. Inanition has no influence on the excretion of creatinine, but creatine appears, presumably owing to the breakdown of tissue protein. The administration of glyco-cyamine increases the formation of creatine; this change, however, is slow and incomplete in frogs. The methylating of the glyco-cyamine into creatine probably occurs in the muscles, for the addition of glyco-cyamine to muscles undergoing autolysis increases the yield of creatine. Experiments with methylguanidine showed no increase in the excretion of either creatine or creatinine. Administration of thymus led to the conclusion that creatine may be formed from nuclein; the administration of meat or fibrin to rabbits caused no increase of creatinine excretion, but in the dog, fibrin caused an increase.

W. D. H.

**The Group of Acids Containing Nitrogen and Sulphur Present in Normal Human Urine.** HANS LIEBERMANN (*Zeitsch. physiol. Chem.*, 1907, 52, 129—145. Compare Thiele, *Abstr.*, 1903, i, 452; Bondzyński, Dombrowski, and Panek, *Abstr.*, 1906, i, 122).—The acids, containing nitrogen and sulphur, which are present in

normal urine and yield insoluble mercuric salts and barium salts soluble in water, but insoluble in alcohol, contain part of their sulphur in the form of alkylsulphuric acids. The so-called alloxypoteic acid is not a homogeneous substance. Its solution when saturated with ammonium sulphate and precipitated with ferric alum yields a product similar to uroferic acid. This product contains alkylsulphuric acid, but no sulphur which can be removed by alkali. Bondzynski's "urochrome" is not a dye and contains only minute traces of a dye. Thiele's determination of alkylsulphuric acid is probably high.

J. J. S.

**Millon's Reaction in the Urine as a Criterion in the Tuberculin Reaction.** C. VOEGTLIN (*Proc. Amer. Soc. Biol. Chemists*, 1907, xvi—xvii, *J. Biol. Chem.*, 3).—Normal urine does not give Millon's reaction, nor does the urine after tuberculin injections on normal people. But if the person suffers from tuberculosis, injection of tuberculin is followed within twenty-four hours by the appearance of a positive Millon's reaction in the urine. The urine is free from protein, and the reaction is attributed to tyrosine. Tyrosine was isolated in one case.

W. D. H.

**Bacterial Production of Scatole and its Occurrence in the Human Intestine.** CHRISTIAN A. HERTER (*Proc. Amer. Soc. Biol. Chemists*, 1907, xiv—xv, *J. Biol. Chem.*, 3).—By the author's method based on the use of sodium  $\beta$ -naphthaquinone-sulphonate and *p*-dimethylaminobenzaldehyde, small quantities of scatole can be detected in the presence of other putrefactive products. The anaërobes, *B. putrificus* and the bacillus of malignant œdema, were found to produce scatole in peptone bouillon, although not uniformly. Scatole is rarely present in the intestinal tract, except in diseased conditions associated with intestinal putrefaction. Indole is usually present also, but in extreme cases this may be absent, or nearly so, and yet scatole be present in relatively larger amounts.

W. D. H.

**The Composition of Liver in Acute Yellow Atrophy.** H. GIDEON WELLS (*Proc. Amer. Soc. Biol. Chemists*, 1907, xv—xvi, *J. Biol. Chem.*, 3).—In the case of acute yellow atrophy, the liver yielded amino-acids, some of which have not previously been found free in human tissues. These were leucine, glycine, tyrosine, alanine, proline, glutamic acid, aspartic acid, lysine, and histidine. Arginine, phenylalanine, and tryptophan were not found. Xanthine and hypoxanthine were also found free, but not adenine or guanine. Seven hundred grams of liver yielded over 8 grams of the amino-acids, and this large amount, which is probably too low owing to loss in preparation, supports the view that they are not all the result of autolysis of the liver cells. Diaminonitrogen (Hausmann's method) was decreased, but not so much so as in Wakeman's cases of phosphorus poisoning in dogs. Sulphur was normal; phosphorus was increased. The amount of fat, both free and combined, was subnormal.

W. D. H.



**The Solubility of Air in Fats and its Relation to Caisson Disease.** HURACE M. VERNON (*Proc. Roy. Soc.*, 1907, 79, B, 366—371).—At the body temperature, the fat of mammals dissolves more than five times as much nitrogen as an equal volume of water or blood plasma.

The special tendency of the fat-containing tissues (such as subcutaneous tissues, spinal cord, and peripheral nerves) of caisson workers and divers to suffer injury from the liberation of gas bubbles after rapid decompression is dependent on this great solubility.

G. S. W.

**Calcium Metabolism in a Case of Myositis Ossificans.** A. E. AUSTIN (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxii—xxiii, *J. Biol. Chem.*, 3).—Calcium equilibrium is maintained in the normal adult on a daily intake of 1 to 1.5 grams of calcium oxide. In a case of *Myositis ossificans*, an ingestion of 1.25 grams daily maintained equilibrium. In diet poor in lime, the excretion of calcium by the urine was increased as it is in healthy people. No evidence of calcium retention in the disease was found.

W. D. H.

**Pancreatic Concrements.** ARTHUR SCHEUNERT and ROBERT BERGHOLZ (*Zeitsch. physiol. Chem.*, 1907, 52, 338—347).—Three cases of concrements in the pancreas are described; the main constituents in all were inorganic. The following analysis of one of these will serve as a sample: CaO, 52.75; CO<sub>2</sub>, 38.98; P<sub>2</sub>O<sub>5</sub>, 2.11; H<sub>2</sub>O, 0.48; fat, 0.48, and protein, 3.49%.

W. D. H.

**Metabolism of Nitrogen and Sulphur in Pneumonia.** ALEXANDER LAMBERT and CHARLES G. L. WOLF (*Proc. Amer. Soc. Biol. Chemists*, 1907, xix—xx, *J. Biol. Chem.*, 3).—On a non-nitrogenous diet of sufficient calorific value, 30 grams of nitrogen were eliminated per diem. The relative excretion of urea was low. The excretion of creatinine was high during the fever, but fell rapidly after the crisis. Creatine also was excreted in considerable amount during the febrile period; this diminished or disappeared after the crisis. The amount of neutral sulphur was 6—8 times greater than the normal.

W. D. H.

**The Diuretic Action of Thymine.** PHÆBUS A. LEVENE (*Biochem. Zeitsch.*, 1907, 4, 316—319).—The diuretic action of purine bases appears to be due to the presence of two oxy-groups (in positions 2:6) and one or more methyl groups. It is shown that the analogous pyrimidine derivative, thymine or 2:6-dioxy-5-methylpyrimidine, also has diuretic properties.

J. J. S.

**Physiological Action of Some Colouring Matters and their Urinary Elimination.** JEAN GAUTRELET and HENRI GRAVELLAT (*Compt. rend.*, 1907, 144, 1467—1468).—Methylene-blue, methyl-violet, and eosin diminish the secretory activity of the kidneys and some functions of the liver. Malachite-green, indigo-carmin, and hæmatoxylin are inactive.

Five c.c. of a saturated solution of methylene-blue sufficed to kill an ordinary rabbit, whilst a similar animal survived with 50 c.c. of nigrosine.  
N. H. J. M.

**The Relation of Toxins to the Cells of the Organism.** G. BELONOWSKI (*Biochem. Zeitsch.*, 1907, 5, 65—98).—The susceptibility of the red corpuscles to the hæmolytic substance in spider poison (arachnolysin) varies greatly even in closely-related animals; thus rabbit's blood is highly susceptible, and guinea-pig's not at all. In some animals, all the corpuscles are attacked equally; in other cases, grades of susceptibility are seen. The stromata of susceptible corpuscles unite with the hæmolsin; those of non-susceptible corpuscles do not. Lecithin has no influence; cholesterol inhibits the action, and is considered to be responsible for the fixation of the poison. There is no relationship between corpuscular susceptibility and the anti-hæmolytic power of the blood-serum. The leucocytes of the guinea-pig possess receptor groups. Extracts of liver, spleen, and muscle neutralise the poison; extracts of brain, kidney, and testis do not; but differences occur in different species of animals. Warming to 60° in cases where the poison is neutralised again sets free the toxin. The serum of immunised rabbits shows no parallelism between its antitoxic and anti-hæmolytic action.  
W. D. H.

**Protein Susceptibility and Immunity.** VICTOR C. VAUGHAN (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxxii—xxxiii, *J. Biol. Chem.*, 3).—By dilute alkali in absolute alcohol, proteins may be split into a poisonous and a non-poisonous portion. The former is soluble in alcohol and is free from carbohydrate groups; the latter contains all the phosphorus and carbohydrate of the original protein. It is held that a similar decomposition occurs in the body, and that susceptibility and immunity can be explained by that circumstance.  
W. D. H.

**Toxicity of Some Aniline Dyes.** GUSTAVE M. MEYER (*J. Amer. Chem. Soc.*, 1907, 29, 892—909).—Curcumine S, tartrazine, naphthol-red S, carmoisine B, naphthol-yellow S, gold-orange, and ponceau 2 R were studied as to their general effects on dogs when administered in varying amounts in food during about two weeks. One fatal result with ponceau 2 R may have been independent of the action of the dye. Otherwise the dyes exhibited no marked degree of toxicity, were excreted in part unchanged with the fæces, and to a smaller extent with the urine, and were found in the bile, but were not secreted in the milk. Peptic digestion experiments have shown that these dyes inhibit peptolysis *in vitro*; the interference may have resulted from the presence of the associated inorganic matter (compare Gudeman, *Abstr.*, 1906, i, 53).  
G. Y.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Comparative Experiments on the Properties of Mercuric Chloride and Sublamin.** FRANCESCO SCORDO (*Centr. Bakt. Par.*, 1907, 44, i, 284—288).—Sublamin (ethylenediamine mercuric sulphate),  $\text{HgSO}_4 \cdot 2\text{C}_2\text{H}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ , does not coagulate albumin even in concentrated aqueous solution; neither does it precipitate soap. Further, its bactericidal and spore-killing capacity is equal to that of mercuric chloride, and a stronger solution than the 0.1% of the latter usually employed does not attack the skin. These qualities indicate it to be superior to the chloride as a disinfectant for the hands in surgical work, &c. Subcutaneously, it is less toxic than mercuric chloride. G. S. W.

**Action of Piperidine and Some Other Amines on Bacteria, and Particularly on the Bacillus of Glanders.** M. NICOLLE and ALBERT FROUIN (*Ann. Inst. Pasteur*, 1907, 21, 443—447).—Piperidine is known to dissolve coagulated egg-albumin. When living glanders bacilli emulsified with distilled water are incubated at 37° for twenty-four hours with piperidine, mono- or di-methylamine, mono- or di-ethylamine, or piperazine, solution takes place. If the emulsion is sealed up with the amine and heated at 100° for ten minutes, the solution is more complete. At the lower temperature, living bacilli are more readily dissolved than those killed previously by heat. The dissolving power of the amine is a function of its dissociation in aqueous solution.

Experiments with a number of bacilli showed that *Bacillus Pestis* and *B. pyocyaneus*, like the bacillus of glanders, dissolve almost completely in piperidine. *B. typhosus* and *B. coli* leave a certain residue. *B. anthracis* and *Staphylococcus* leave still more residue. Tubercle bacilli are to a certain extent soluble. When freed from fat and dried, their solubility is naturally greater. Diethylamine shows similar solution phenomena with emulsions of these micro-organisms.

Intraperitoneal injections of solutions of glanders bacilli in piperidine and diethylamine from which the amine has been removed by precipitation and washing with alcohol-ether are only toxic to guinea-pigs infected with glanders or rendered hypersensitive by previous injections of such a solution. G. S. W.

**New Process for Disinfecting Drinking Waters.** EMANUALE PATERNO and MASANIELLO CINGOLANI (*Gazzetta*, 1907, 37, i, 313—367).—The authors have made an exhaustive study of the disinfection of drinking water, water containing sewage, specific pathogenic organisms, &c., by means of tachyol or silver fluoride. The results of the numerous experiments are given in full in the two memoirs comprising the paper, the principal conclusions being as follows.

The addition of 1 part of tachyol to 500,000 of drinking water

produces a turbidity, owing to the precipitation of silver chloride, but in less than twenty-four hours the water becomes perfectly clear. No taste is imparted to water by as much as 1 part of tachyol per 200,000. Animals drink freely of water containing tachyol, even in relatively great concentration, without harmful results. The drinking of water treated with 1 part of tachyol per 500,000 introduces into the organism never more than 0.001 gram of silver per litre. Compared with chlorine, bromine, or ozone, tachyol is extremely active in destroying all germs with the exception of spore forms of a carbuncle organism and of *B. subtilis*; infection of the former by drinking water is not to be feared, whilst the latter is harmless. Water disinfected with chlorine, bromine, or ozone is liable to become contaminated after a short time, whilst, after treatment with tachyol, water remains sterile for a long period.

Silver fluoride is a far more powerful disinfectant than the nitrate, the use of which has been proposed for this purpose, and this is the case even with water containing 1 gram of sodium chloride per litre.

T. H. P.

**Charentes Brandies.** E. KAYSER and A. DEMOLON (*Compt. rend.*, 1907, 145, 205—208).—On seeding "Folle blanche" musts with a pure yeast, isolated from Charentes lees, and allowing the wine obtained to age for four to eight months, a considerable amount of oxidation occurs, the non-alcohol coefficient of the resulting brandies being double the maximum value for brandies given by Rocques, the increase being principally in the aldehydes and higher alcohols. This active oxidation seems to be effected by the aerobic yeast which develops near the surface of the fermenting must, and forms a ring on the walls of the flask. There appears to be antagonism between the formation of aldehydes and that of esters by yeast, a maximum of the former always corresponding with a minimum of the latter in the same medium; chemical esterification proceeds simultaneously with the formation of esters by the yeast, and is not influenced by it. Light favours the production of higher alcohols, whilst, in absence of light, the proportion of volatile acids is increased. The composition of the nutrient medium is of the greatest importance for the proportion of higher alcohols obtained, no artificial medium examined yielding so much of these alcohols as musts prepared from Charentes grapes.

T. H. P.

**Distribution of Odoriferous Principles in Plants.** EUGÈNE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1907, 145, 201—203).—The essence of verbena flowers contains more citral than the essence of the leaves. Fertilisation is coincident with an increase in the amount of ethers and a decrease in the amount of citral. The reactions of the flower favour the transformation of alcohol into citral, and so contribute to increase the amount of a relatively soluble product. The destruction of odoriferous principles supplies a part of the energy required for fertilisation, and it is chiefly the citral which disappears, being probably oxidised.

N. H. J. M.

**Studies on Apple Juice.** HERBERT C. GORE (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxxvii, *J. Biol. Chem.*, 3).—The juice of apples used in cider making becomes richer in sugar and acid as the season progresses. Acetic acid is found in the juice of decayed apples, and, in view of the tendency of this acid to retard alcoholic fermentation, the use of decayed apples is to be avoided.

W. D. H.

**Complete Analysis of the Fruit of [the Tomato] *Lycopersicum esculentum*.** JACQUES M. ALBAHARY (*Compt. rend.*, 1907, 145, 131—133).—The fresh substance contains: water, 93·5; nitrogenous substances, 0·95; fat, 0·20; carbohydrates, 3·60; ash, 0·74; malic acid, 0·49; citric acid, 0·15, and oxalic acid, 0·001%. Most of the organic acids are in the free state. Traces of tartaric and succinic acids were detected.

N. H. J. M.

**Proteins of the Pea (*Pisum Sativum*).** THOMAS B. OSBORNE and ISAAC F. HARRIS (*J. Biol. Chem.*, 1907, 3, 213—217).—The proteins are three in number, and can be most readily separated by fractional precipitation from a sodium chloride solution by means of ammonium sulphate. (1) Legumin is a globulin which is not coagulated even when heated to boiling point; it contains 17·75% nitrogen and 0·46% sulphur. (2) Vicilin is very similar, but is coagulated at 95°. It contains 17·15% nitrogen and less sulphur than any other protein (0·2% to 0·08%). (3) Legumelin is an albumin, and coagulates below 80°; it closely resembles the leucosin of wheat, and is probably a tissue-protein and not a reserve food-protein.

W. D. H.

**Presence of Raffinose in *Taxus baccata*.** HENRI HÉRISSEY and CH. LEFEBVRE (*J. Pharm. Chim.*, 1907, [vi], 26, 56—62).—The authors have isolated raffinose and sucrose, the latter not quite pure, from the leaves and twigs of *Taxus baccata*.

T. H. P.

**The Rôle of the Oxidising Power of Roots in Soil Fertility.** OSWALD SCHREINER and HOWARD S. REED (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxiv—xxv, *J. Biol. Chem.*, 3).—Growing roots possess well-defined oxidising power, due principally to enzyme activity. This can be demonstrated by the use of such reagents as  $\alpha$ -naphthylamine, benzidine, and vanillin, which form insoluble dyes when oxidised by the roots. Fertilisers promote the oxidising activity of the roots, and the action is greater in fertile soils and their extracts than in unproductive soils and their extracts. Oxidation is also valuable in aiding the decomposition of vegetable matter in the soil.

W. D. H.

**The Products of Germination Affecting Soil Fertility.** OSWALD SCHREINER and M. X. SULLIVAN (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxv—xxvi, *J. Biol. Chem.*, 3).—The water in which seeds have germinated, or in which seedlings have grown, is a bad culture medium for a second crop. The juice expressed from the seeds or seedlings is toxic to growing plants, inhibiting their life activity, the oxidation at their roots, and the amount of leucine and tyrosine produced.

This juice contains a trace of choline, xanthine bases, and soluble organic phosphorus compounds; but whether the toxic action is due to these or other substances, or, in part, to anti-enzymes, has not yet been determined.

W. D. H.

**Secondary Decomposition Products of Proteins in Soils.** OSWALD SCHREINER and EDMUND C. SHOREY (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxxviii—xxxix, *J. Biol. Chem.*, 3).—At present, no accurate knowledge exists in regard to the composition of the organic nitrogenous compounds in soils, which are evidently decomposition products of proteins. In the present research, picoline-carboxylic acid was isolated, and also indications of the presence of pyruvic acid found.

W. D. H.

**Origin of the Deposits of Colouring Matters in Red Wines.** AUGUSTE TRILLAT (*Compt. rend.*, 1907, 144, 1439—1441).—The production of the deposits takes place when aldehyde is formed or when the quantity of aldehyde present is increased. This is brought about by the rapid aëration of the wine and by some diseases, especially that which produces bitterness. The conversion of the alcohol into aldehyde is therefore one of the causes, if not the chief one, of the formation of the deposits.

N. H. J. M.

**Coloration of Brown Bread.** GABRIEL BERTRAND and W. MUTERMILCH (*Compt. rend.*, 1907, 144, 1444—1446).—It was shown previously that the coloration of brown bread is due to a tyrosinase very resistant to heat (*ibid.*, 1285). The process is the result of two different diastatic actions, in the first of which a colourless chromogen, having the essential characteristics of tyrosine, is liberated, whilst the second brings about the combination of the chromogen with atmospheric oxygen, yielding a brown product.

The diastatic substance which produces tyrosine is a protease, *glutenase*. It is inactive in alkaline media and acts better in acid than in neutral media.

N. H. J. N.

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### Analytical Chemistry.

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**Estimation and Recognition of Hydrochloric Acid in the Gastric Contents by a New Reagent.** JOSEPH H. KASTLE and H. L. AMOSS (*Proc. Amer. Soc. Biol. Chemists*, 1907, xi—xii, *J. Biol. Chem.*, 3).—Red cabbage is macerated in water, the solution bleached with sulphur dioxide, boiled to expel excess of acid, and filtered. The normal contents of the stomach cause the solution to become purplish-red, and the amount of hydrochloric acid to which this is due can be determined by a Dubosc-Pellin colorimeter. W. D. H.

**Separation of Tellurium from the Heavy Metals and the Formation of Cupric Acid.** BOHUSLAV BRAUNER and BOHUMIL KUZMA (*Ber.*, 1907, 40, 3362—3371).—The method of reducing and

precipitating tellurium by means of sulphur dioxide does not yield accurate results, as small amounts of other metals are carried down with the tellurium (*Trans.*, 1895, **67**, 549). The amounts of copper precipitated are larger than those of bismuth or antimony, and the amount increases with the amount of copper present in the solution and with the length of time during which the sulphur dioxide is used.

The authors recommend oxidising the tellurium to telluric acid and then precipitating the heavy metals with hydrogen sulphide. The oxidation is most effectively accomplished by means of excess of ammonium persulphate in the presence of potassium hydroxide; the excess of persulphate can be removed subsequently by boiling. The tellurium in the form of telluric acid is most readily estimated by reducing with hydrochloric acid and precipitating with sulphurous acid.

During the oxidation of a solution containing both copper and tellurium with ammonium persulphate, an intense ruby-red coloration is produced, which is, however, destroyed by excess of persulphate. This coloration is attributed to the formation of a derivative of cupric acid (compare Moser, this vol., ii, 549), namely, a tellurocupric acid derivative. By processes of hydrolysis, dark red or violet precipitates have been obtained, which have the composition  $2K_2O, Cu_2O_3, 3TeO_3, xH_2O$  and  $2K_2O, CuO, 2Cu_2O_3, 3TeO_3, xH_2O$ , and are extremely unstable.

A compound,  $2K_2O, CuO, Cu_2O_3, 2TeO_3, xH_2O$ , has been obtained by the electrolytic oxidation of telluric acid in alkaline solution, using a copper anode.

A silver compound,  $5Ag_2O_3, Ag_2O, 9TeO_3$ , has also been obtained.

J. J. S.

**Estimation of Phosphorous Acid.** CHARLES MARIE and A. LUCAS (*Compt. rend.*, 1907, **145**, 60—62).—Phosphorous acid is much more rapidly oxidised by potassium permanganate in alkaline than in acid solution. For the estimation of phosphorous acid or phosphites, the following procedure is recommended. Excess of potassium carbonate is weighed into a flask, and a known volume of standard permanganate solution is added. The flask is warmed on a water-bath at  $80^\circ$ , and the solution of phosphorous acid or phosphite introduced. The solution is digested for fifteen minutes at  $80^\circ$ , then the excess of permanganate is decomposed by addition of a known volume of a strongly acid solution of Mohr's salt (previously titrated against the permanganate solution), and the excess of ferrous salt determined by titration against the standard permanganate solution. The latter is preferably standardised by means of calcium formate, since this can be substituted for the phosphorous acid without alteration of any other condition. The method gives results which agree with those obtained by the gravimetric method by reduction of mercuric chloride.

E. H.

**Chemical Method for the Determination of Available Phosphoric Acid in Soils.** ALEXIUS DE SIGMOND (*J. Amer. Chem. Soc.*, 1907, **29**, 929—936).—The phosphoric acid present in a soil



may be divided into two parts : the more easily soluble part, which dissolves when the soil is treated with nitric acid in such amount that the acidity of the resulting solution is equivalent to not less than 200 mg. or more than 1000 mg. of  $N_2O_5$  per litre, and the less readily soluble part, which dissolves only when the acidity of the solution is greater than 1000 mg. of  $N_2O_5$  per litre (compare Schloesing, *Abstr.*, 1899, ii, 449). The examination of a large number of Hungarian soils shows that, in general, the amount of the easily soluble phosphoric acid increases, but its availability for plant culture decreases, with increasing basicity of the soil. As a rule, soils containing more than 74 mg. of easily soluble phosphoric acid per 100 grams do not require the addition of a phosphate fertiliser ; in the case of soils approaching this limit, the need for phosphoric acid must be decided by cultivation experiments.

G. Y.

**Estimation of Minute Traces of Arsenic. The Insensitivity of Zinc.** ALFRED C. CHAPMAN (*Analyst*, 1907, 32, 247—248).—In rendering zinc sensitive by means of a cadmium salt, the best results appear to be obtained when about 4 grams of cadmium sulphate are used in the evolution flask with from 10 to 15 grams of zinc. Whilst there is usually no great difficulty in depositing the cadmium correctly, samples of zinc are met with occasionally which are very difficult to coat. It is better to reject such samples than to waste time in trying to render them sensitive. Re-granulation sometimes materially alters the sensitiveness of such samples.

W. P. S.

**Application of Palladium as a Catalyst in Elementary Analysis.** ARNOLD JACOBSEN and GEORG LANDESEN (*Ber.*, 1907, 40, 3217—3225).—Palladinised asbestos, prepared by precipitating a solution of palladium dichloride with an alkaline solution of sodium formate in the presence of asbestos, serves as the catalyst ; it contains 17.7% of palladium, and 1.6 grams only are required. For substances containing carbon, hydrogen, and oxygen, a hard glass tube, *ab*, 35 cm. long and 1 cm. in diameter, is required ; 6 cm. from one end the area of the tube is diminished to one-half for a distance of 15 cm., *cd*. In this constricted part of the tube, the catalyst is placed and kept in position by a small bored porcelain stopper at *c*. The porcelain boat is placed in *bd*, the end *b* is attached to the source of the purified air or oxygen, and *a* to the absorption apparatus. The tube, wrapped in asbestos, is placed in an iron trough, which is maintained at a low red heat under the portion *cd*. The combustion is performed with the usual precautions as to heating, and requires from 30 to 40 minutes. When the substance to be analysed contains nitrogen, the part *ac* of the tube is 25 cm. long and contains two small boats filled with lead peroxide, maintained at 200—300°. A similar arrangement is adopted in the case of substances containing sulphur, the percentage of which can be estimated by shaking the lead peroxide for two hours with a 5% solution of sodium carbonate and precipitating an aliquot part of the solution with barium chloride.

C. S.

**Elementary Analysis of Proteids Containing Phosphorus.** MAX DENNSTEDT (*Zeitsch. physiol. Chem.*, 1907, 52, 181—183).—In reply to Erlandsen (*ibid.*, 51, 86), it is pointed out that good results for carbon and hydrogen can be obtained by the author's method if the double oxygen supply is made use of, and if an unglazed porcelain combustion boat is employed. In the latter case, the phosphoric acid produced is absorbed by the boat, and the carbon can be completely burnt. If the compound is rich in phosphorus, it is advisable to take the residue of phosphoric acid and carbon in the boat, to extract it with dilute hydrochloric acid, and then to complete the combustion.

J. J. S.

**Apparatus for the Estimation of Carbon Dioxide in Carbonates.** P. MALHERBE (*Ann. Chim. anal.*, 1907, 12, 261—263).—In the apparatus described, particular attention is paid to the drying of the carbon dioxide, especially during any rapid evolution of the gas. For this purpose, the drying part of the apparatus consists of a cylindrical vessel sealed into the top of the evolution flask, and an inner cylinder forming a stopper and reaching nearly to the bottom of the first. The gas rises through a tube to the top of the inner cylinder, then passes under its lower edge and through the sulphuric acid, finally escaping through a side-tube on the outer cylinder. All the parts are readily taken apart for cleaning.

W. P. S.

**Estimation of Potassium by the Platinic Chloride Method.** HENRI J. F. DE VRIES (*Chem. Weekblad*, 1907, 4, 455—462. Compare this vol., ii, 504).—The author gives further particulars of his work on the estimation of potassium by the platinic chloride method.

A. J. W.

**New Practical Method for Estimating Potassium.** NAZARENO TARUGI (*Gazzetta*, 1907, 37, i, 381—385. Compare Abstr., 1904, ii, 590).—The author replies to the criticisms of Pajetta (Abstr., 1906, ii, 804) and shows that the latter has made errors in the experimental part of his work and possibly also in his calculations. The author has repeatedly tested his method for estimating potassium and has invariably obtained good results.

T. H. P.

**Ignition of Barium Sulphate.** P. TRUCHOT (*Ann. Chim. anal.*, 1907, 12, 267—268).—The author finds that reduction of barium sulphate may take place if the sulphate is moist at the commencement of the ignition. This reduction may be demonstrated by the alkaline reaction of the ignited residue towards phenolphthalein. Prolonged ignition of the residue causes re-oxidation to sulphate to take place.

W. P. S.

**Effect of Sulphuric Acid on the Deposition of Metals when using a Mercury Cathode and Rotating Anode.** LILY G. KOLLOCK and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1907, 29, 797—806).—A series of experiments, illustrated by curves, with zinc, copper, cadmium, iron, cobalt, and nickel salts in the presence of varying

amounts of free sulphuric acid. The volume of the salt solution was 10 c.c., containing about 0.25 gram of metal. The current was maintained at two amperes, while the pressure varied from 2 to 4.5 volts. Separations of cadmium from aluminium, cadmium from magnesium, cadmium from chromium, and copper from aluminium were also studied.

It was found that an increased quantity of free sulphuric acid exerts a retarding influence on the electrolytic deposition of the metals.

L. DE K.

#### Detection of Small Quantities of Thallic Salts in Presence of Thallous Salts. LUIGI MARINO (*Gazzetta*, 1907, 37, i, 55—58).

—Small quantities of thallic salts in presence of thallous salts may be detected as follows. To the very dilute solution, rendered alkaline by means of a few drops of potassium hydroxide solution, are added a little saturated  $\alpha$ -naphthol solution and then a very small quantity of dimethyl-*p*-phenylenediamine hydrochloride. If thallic salts are present, the blue colour of the indophenols is obtained. This reaction is far more sensitive than that with potassium iodide, and, even in presence of thallous salts, admits of the detection of 1 part of thallium, existing as thallic salts, in 30,000 parts of water. The reaction is not diminished in sensibility by the presence of salts of potassium, sodium, or ammonium, but it loses its value when the solution contains other oxidising substances, such as ferric salts or ammonium persulphate.

T. H. P.

**Iodometric Estimation of Copper.** FRANK A. GOOCH and F. H. HEATH (*Amer. J. Sci.*, 1907, [iv], 24, 65—74; *Zeitsch. anorg. Chem.*, 1907, 55, 119—129).—This process has been several times criticised adversely. By carefully following the authors' directions, very accurate results may, however, be obtained.

The solution, which should contain no more than 0.3 gram of copper and at most 3 c.c. of sulphuric, hydrochloric, or nitric acid, or 25 c.c. of 50% acetic acid, is diluted to 100 c.c. Five grams of pure potassium iodide are added, and the iodine liberated is titrated as usual with standard thiosulphate. If the reaction is still incomplete when 25 c.c. of *N*/10 thio sulphate have been used, a few more grams of potassium iodide should be added.

L. DE K.

**Iodometric Estimation of Mercury.** ERWIN RUPF (*Ber.*, 1907, 40, 3276—3277).—Omission to shake vigorously after addition of formaldehyde (*Abstr.*, 1906, ii, 902) occasions low results. It is recommended to work with small quantities and to shake for one to two minutes, mere contact not being sufficient.

W. R.

**Estimation of Manganese in Wine.** A. HUBERT (*Ann. Chim. anal.*, 1907, 12, 264—267).—It is recommended that the hydrochloric acid solution of the ash of the wine be treated with a little ferric chloride, and that the iron and aluminium be then precipitated as basic salts in the usual manner. This precipitate must be dissolved and again precipitated, as it retains traces of manganese.

The calcium is precipitated by the addition of ammonium oxalate to the acid filtrate from the iron precipitate, and the manganese is then separated in alkaline solution by means of an oxidising agent. Most wines contain much less than 0.01 gram of manganese per litre, and any in excess of this quantity must be considered as added. Permanganate is sometimes added to wine for bleaching purposes, and to oxidise the excessive quantity of sulphur dioxide present in certain wines.

W. P. S.

**Use of a Rotating Anode in the Electrolytic Precipitation of Uranium and Molybdenum.** EDGAR T. WHERRY and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1907, 29, 806—808).—Uranium may be completely precipitated electrolytically from the solution containing acetic acid and sodium acetate. Good results are also obtained with sodium carbonate as electrolyte.

Molybdenum is completely precipitated on the cathode as hydrated sesquioxide in the presence of free sulphuric acid and potassium sulphate.

L. DE K.

**Dry Lead Defecation in Raw Sugar Analysis.** WILLIAM D. HORNE (*J. Amer. Chem. Soc.*, 1907, 29, 926—929. Compare Abstr., 1906, ii, 400).—A reply to criticisms by Pellet (*Bull. Assoc. chim. Sucr. Dist.*, 1907, 24, 473). The results of experiments are quoted to show that the precipitate does not occlude sugar, and that the amount of lead dissolved in the filtrate is too small to affect appreciably the polariscopic readings.

G. Y.

**Red Coloration in the Iodoform Test for Acetone in Urine.** WILLIAM H. WELKER (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxvii—xxviii, *J. Biol. Chem.*, 3).—In applying the iodoform test for acetone to urinary distillates, a pink to red coloration is sometimes observed. This, which has long puzzled investigators, is simply due to thymol, which has been added as an antiseptic to the urine. The coloured product is Messinger and Vortmann's di-iodothymol (Abstr., 1889, 1151).

W. D. H.

**Characteristic Reaction of Free Tartaric Acid.** ACHILLE TAGLIAVINI (*Boll. chim. farm.*, 1907, 46, 493—495).—Ganassini (*ibid.*, 1903, 42, 515) has shown that when an aqueous solution of tartaric acid is treated with minium, the supernatant liquid deposits crystalline lead tartrate; after removal of the latter by filtration, the liquid still contains a lead salt, and when boiled with potassium thiocyanate, rapidly becomes black, lead sulphide being precipitated and hydrogen sulphide liberated. The author finds that when formic, acetic, or succinic acid is used instead of tartaric acid, no hydrogen sulphide is evolved, whilst with oxalic or citric acid, hydrogen sulphide is liberated, but no blackening of the solution occurs. The formation of lead sulphide, characteristic of tartaric acid, is found to be due partly to the tartaric acid itself and partly to readily oxidisable substances produced by the action of the minium on the acid.

T. H. P.

**Source of Error in the Use of Light Petroleum as an Extracting Medium.** JOHN MARSHALL (*Amer. J. Pharm.*, 1907, 79, 315—317; *Proc. Amer. Soc. Biol. Chemists*, 1907, xx—xxi, *J. Biol. Chem.*, 3).—Attention is called to the fact that light petroleum from the Pennsylvania oil field, although redistilled, may nevertheless yield a decided residue after being kept for some time in contact with a limited amount of air. L. DE K.

**New Characteristic Constants for Oils.** ÉMILE LOUISE and E. SAUVAGE (*Compt. rend.*, 1907, 145, 183—185).—By determining the temperatures at which 20 c.c. of acetone become completely miscible with quantities of an oil varying from about 15 to 30 grams, a curve is obtained which is characteristic for any one oil, and may be employed for the detection of adulteration. T. H. P.

**Determination of the Iodine Numbers of Oils.** LUIGI MASCARELLI and A. BLASI (*Gazzetta*, 1907, 37, i, 113—124).—The authors have determined the iodine numbers of various oils, and also of several acids occurring in oils, both by Wys' method and by Panchaud's modification of the Hanus method, the duration of the actions being extended, in some cases, to several days. With Wys' method and action, one hour gives concordant numbers, which are generally slightly higher than those obtained by the Hübl method, and are influenced, to some extent, by the temperature of working. The numbers given by the Hanus method are lower than those yielded by the Wys method, and agree well with the Hübl values. Hanus' solution, as modified by Panchaud (*Schweiz. Woch. Pharm.*, 1904, 42, 113—118), is readily prepared and keeps well, whilst the results given by it do not change appreciably even if the reaction is continued for a further two hours. This constancy of results is probably dependent on the fact that the reaction between the iodine and unsaturated compounds in the oil is complete, and is not accompanied by secondary reactions in which hydrogen atoms are substituted in, or halogen hydracid eliminated from, the halogen compounds formed. T. H. P.

**Influence of Oxygen and Nitrogen, Sunlight and Darkness on the Iodine and Saponification Numbers of Olive Oil.** LEON A. RYAN and JOHN MARSHALL (*Amer. J. Pharm.*, 1907, 79, 308—315).—The influence of oxygen on olive oil is to decrease the iodine number, but to increase the saponification number. It also causes the oil to become rancid, and has a bleaching action. Sterilised oil kept in the dark gives a slightly higher iodine number than when exposed to diffused sunlight, but it gives a somewhat lower saponification number.

When kept in an atmosphere of pure nitrogen, there is no change in the iodine number, either with sterilised or non-sterilised oil, but there is an increase in the saponification number. There is not the slightest tendency of the oil to become rancid. L. DE K.

**Detection of Foreign Fats in Lard.** ALEXANDRE LEYS (*Compt. rend.*, 1907, 145, 199—201).—Lard is often adulterated with oil, the lowering of the content of glycerides thus produced being remedied

by the addition of foreign fats. Such addition can be detected by determining the melting point of the olein-free glycerides separated from the lard. These glycerides may be isolated by the following method. Two grams of the fat are weighed in a wide-necked conical flask, mixed with 4 grams of mercuric oxide and 50 c.c. of glacial acetic acid, and boiled for five minutes on an asbestos plate, the flask being fitted with a reflux condenser. After cooling for two hours, during which time mercurous acetate crystallises out and the glycerides separate, the mass is heated at  $50^{\circ}$  on a water-bath, mixed with 50 c.c. of absolute alcohol, and left all night. The separated glycerides are filtered off on a small filter, washed with 100 c.c. of absolute alcohol, allowed to dry in the air, and exhausted with 50 c.c. of benzene, which dissolves the fatty matter and leaves the mercurous acetate. The benzene solution is evaporated on a water-bath and the residue kept for twelve hours in a cool place, after which its m. p. is determined. The following are the m. p.'s. of the glycerides thus isolated from the principal fats: beef fat,  $55.8-56.2^{\circ}$ ; veal fat,  $53-53.4^{\circ}$ ; mutton fat,  $57.4^{\circ}$ ; horse fat,  $53^{\circ}$ ; oleomargarin,  $52.6^{\circ}$ ; pork fat,  $60.4-60.8^{\circ}$ ; fat of cow's milk,  $48-50.6^{\circ}$ ; butter,  $49-52^{\circ}$ ; cacao butter,  $55.8-58.8^{\circ}$ ; cottonseed margarin,  $55.8^{\circ}$ . Any lard yielding glycerides having a m. p. lower than  $60^{\circ}$  should be suspected.

The iodine number of the glycerides is negligible, being only  $0.6-0.7$  per 100 grams. The constitution of the glycerides remains unchanged when the proportion of solvent used is altered, and the m. p. of the deposits is constant for any particular animal fat, no matter from what part of the animal it is obtained. With fats, the production of which depends on intermittent physiological phenomena, such as that of cow's milk, a certain variation in m. p. is observed.

T. H. P.

**Estimation of Fat in Copra.** W. H. BLOEMENDAL (*Pharm. Weekblad*, 1907, 44, 873-880).—The copra is reduced to a fine state of division by the aid of a file, and boiled in a 150 c.c. measuring flask with 125 c.c. of benzene for three hours. When cold, the contents are made up to 150 c.c., thoroughly agitated, and allowed to remain half an hour. 100 c.c. are filtered rapidly into a weighed flask, the solvent distilled, and the residue dried for two hours at  $95^{\circ}$ .

A. J. W.

**Reaction for Distinguishing between  $\alpha$ - and  $\beta$ -Naphthol Camphorides by Means of Piperonaldehyde.** THIÉRY (*J. Pharm. Chim.*, 1907, [vi], 26, 62-63).—On adding to a drop of  $\alpha$ - or  $\beta$ -naphthol camphoride five drops of a 1% solution of piperonaldehyde in 95% alcohol and then 4 c.c. of pure sulphuric acid, a greenish-yellow coloration is obtained with the  $\beta$ -derivative and a red dichroic liquid, appearing violet in thin layers, with the  $\alpha$ -compound. Other similar compounds give the following colorations with the reagent: phenol mono- or semi-camphoride, red; phenol mentholide (1 part of phenol and 3 parts of menthol), orange with violet tint; salol camphoride (3 parts salol, 2 parts camphor), brown; resorcinol dicamphoride,

blood-red; thymol camphoride (1 part thymol, 1 part camphor),  
carmine. T. H. P.

**Modification of Regnard's Ureometer.** M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, 12, 263—264).—The modification consists in the substitution of glass stoppers for the india-rubber stoppers usually employed. The stoppers are hollow; the one closing the outlet end of the apparatus is drawn out to form a short tube, whilst the other stopper is pierced with a small hole, which, on turning the stopper, may be made to coincide with a hole in the side of the tube.

W. P. S.

**Qualitative Separation of Ferrocyanides, Ferricyanides, and Thiocyanates.** PHILIP E. BROWNING and HOWARD E. PALMER (*Amer. J. Sci.*, 1907, [iv], 23, 448—450; *Zeitsch. anorg. Chem.*, 1907, 54, 315—318).—The solution is acidified with acetic or hydrochloric acid and precipitated with thorium nitrate. To make the thorium ferrocyanide settle more readily, a little asbestos is added and the mixture well shaken. To the filtrate is added cadmium chloride, which precipitates the ferricyanide, and the thiocyanate is then tested for with hydrochloric acid and ferric chloride. The ferrocyanide and ferricyanide radicles may be recovered from their respective precipitates by treating these with aqueous potassium hydroxide. The solutions are then acidified with hydrochloric acid and tested with ferric chloride and ferrous sulphate respectively.

L. DE K.

**General Method for Alkaloidal Assay.** M. H. WEBSTER (*Amer. J. Pharm.*, 1907, 79, 301—307).—10 c.c. of the fluid extract (or 2 grams of solid extract dissolved in 10 c.c. of proof spirit) are slowly added to a solution of 1.5 grams of tartaric acid in 85 c.c. of absolute alcohol, and the whole is then made up with alcohol to 100 c.c. 50 c.c. of the filtrate are evaporated to dryness in a flat dish and, when cold, the residue is dissolved in 10 c.c. of *N*/2 sulphuric acid. The solution is filtered through cotton-wool, and the insoluble matter washed twice with 5 c.c. of water. The filtrate and washings are now shaken with a mixture of 16 c.c. of chloroform and 4 c.c. of ether, 4 c.c. of 20% potassium hydroxide solution being also added. The chloroform layer is washed twice with 15 c.c. of water, and then filtered through cotton-wool into a separator of about 150 c.c. capacity. After repeating the extraction with the chloroform mixture a few times, the united extracts are shaken with excess of *N*/50 or *N*/100 sulphuric acid, and, after rejecting the bottom layer, the free acid is titrated with *N*/50 sodium hydroxide, using an ethereal solution of iodoeosin, or cochineal, as indicator.

L. DE K.

## General and Physical Chemistry.

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**Emission Spectra of Phosphorus.** PETER GEUTER (*Chem. Zentr.* 1907, ii, 205—206; from *Zeitsch. wiss. Photograph. Photophys. Photochem.*, 1907, 5, 1—23).—The line spectrum of phosphorus has been produced by means of a Geissler tube, electric sparks, and from potassium phosphate in an electric arc. Whilst the arc spectrum was found to be independent of the conditions of the experiment the other spectra were affected by self-induction in the circuit and by the interposition of a spark gap. The effect of strong self-induction is to render the spark spectrum similar to that of the arc. Experiments with flame, the electric arc and the Geissler tube showed that the character of the band spectrum depends also on the means employed to produce it. The influence of conditions is more complicated in this case and for further information the original paper should be consulted. All the groups of bands of the Geissler tube spectra and the groups with short wave-lengths in the arc and the flame spectra are new.

E. W. W.

**Double Line Spectra of Chemical Elements.** EUGEN GOLDSTEIN (*Ber. deut. physikal. Ges.*, 1907, 5, 321—332).—It has been found that potassium, rubidium, and cesium have two line spectra having no lines in common; one, which coincides with the arc spectrum, is also obtained by the action of a weak electric discharge, the other is obtained by a strong condenser discharge. The new lines do not fit into any ordinary series. The change from one spectrum to another is attended by a change of colour, in the case of rubidium from rose-red to sky-blue, in the case of cesium from bluish-red to greenish-grey. The strength of the discharge required to cause the disappearance of the ordinary spectrum is the greater the smaller the atomic weight, and this probably explains why this point has not been reached with sodium and lithium. It is considered probable that the ordinary spectrum is due to the vibration of aggregates which break up under the influence of powerful electric discharges into individual particles, and the spectrum obtained under these conditions is therefore termed the "fundamental spectrum." Some of the more prominent lines of the fundamental spectra of potassium, rubidium, and cesium are tabulated.

There is some evidence that the phenomenon just mentioned is a general one and that many of the spectra obtained under ordinary conditions are mixed. Under the influence of powerful discharges (sent through the tubes by means of external electrodes) it has been found that many of the ordinary lines of chlorine and bromine disappear, and that many new lines make their appearance, but an entirely different spectrum, as in the case of the alkali metals, has not yet been attained.

The investigation is being continued in various directions.

G. S.



**Fluted Spectrum of Titanium Oxide.** A. FOWLER (*Proc. Roy. Soc.*, 1907, **79**, *A*, 509—518).—In a former paper (*Proc. Roy. Soc.*, 1904, **73**, *A*, 219) it was shown that the fluted spectra of Antarian or third type stars correspond with the spectra obtained from certain titanium compounds, but the question was not settled as to whether the spectra in question were due to metallic titanium or to the oxide. From a comparison of the spectra of titanium salts containing oxygen with those free from that element it is now shown that the spectrum in question is only obtained when oxygen is present.

The wave-lengths of the terrestrial flutings have been carefully redetermined, the titanium oxide for this purpose being volatilised in the electric arc between iron poles. Photographs of the spectra are given and the wave-lengths of the heads of the flutings are tabulated.

Although there can be no doubt as to the identity of many of the stellar bands with those of titanium oxide, it does not seem probable that all the stellar bands can be accounted for in this way.

G. S.

**Absorption and Reflection Spectra of some Rare Earths.** WILHELM MUTHMANN, L. WEISS, and HEINRICH HERAMHOF (*Annalen*, 1907, **355**, 165—174).—The absorption spectra of the chlorides and nitrates of neodymium, praseodymium, and samarium in neutral, acid, and alkaline solutions, and the reflection spectra of neodymium and praseodymium phosphates burnt on porcelain plates (this vol., ii, 774) are tabulated. The reflection spectra exhibit important differences from those of didymium phosphate observed by Wagnier (*Abstr.*, 1905, ii, 35), possibly due to the severe heating to which the plates have been subjected.

C. S.

**Absorption of Ultra-Violet Rays by Adrenaline.** CHARLES DHÉRE (*Bull. Soc. chim.*, 1907, [iv], 1, 834—837).—In view of Friedmann's representation of adrenaline as a catechol derivative (*Abstr.*, 1906, i, 529) the author has examined the ultra-violet absorption spectrum of this substance and compared the data obtained with those recorded by Hartley for catechol. The two absorption spectra are very similar, but in that of adrenaline the single band is displaced towards the less refrangible end. Under the influence of oxidation, the band widens and is displaced further towards the visible spectrum.

T. A. H.

**Chemical Constitution and Rotatory Power. II. Influence of the Chemical Functions of the Substituent Groups.** MARIO BETTI (*Gazzetta*, 1907, **37**, ii, 5—13. Compare this vol., ii, 661).—The author has prepared, and measured the rotatory powers of, the following further aldehydic derivatives of  $\beta$ -naphthylbenzylamine of the type  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHPh}\cdot\text{N}:\text{CHR}$ : with 5-bromosalicylaldehyde, white crystals, m. p. 150—151°,  $[\alpha]_D - 76.37^\circ$ ; 5-bromomethylsalicylaldehyde, white needles, m. p. 119°,  $[\alpha]_D + 39.45^\circ$ ; 5-nitrosalicylaldehyde, straw-yellow, acicular crystals, m. p. 197°,  $[\alpha]_D - 132.37^\circ$ ; 3-nitro-

*salicylaldehyde*, lemon-yellow crystals, m. p.  $193^{\circ}$ ,  $[\alpha]_D + 38.83^{\circ}$ ; *3-bromo-p-hydroxybenzaldehyde*, shining, white crystals, m. p.  $167^{\circ}$ ,  $[\alpha]_D + 150.1^{\circ}$ ; *3:5-dibromo-p-hydroxybenzaldehyde*, shining white crystals, m. p.  $180^{\circ}$ ,  $[\alpha]_D + 92.18^{\circ}$ ; *3-nitroanisaldehyde*, separating from alcohol in shining, white crystals, m. p.  $140^{\circ}$ ,  $[\alpha]_D + 135.83^{\circ}$ ; *o-nitrobenzaldehyde*, shining white needles, m. p.  $138^{\circ}$ ,  $[\alpha]_D - 259.36^{\circ}$ ; *m-nitrobenzaldehyde*, white needles, m. p.  $185^{\circ}$ ,  $[\alpha]_D + 43.88^{\circ}$ ; *p-nitrobenzaldehyde*, straw-yellow needles, m. p.  $196^{\circ}$ ,  $[\alpha]_D + 54.29^{\circ}$ . The values of the rotatory powers refer to benzene solutions at  $14-15^{\circ}$ .

Here, again, are evident the influence of the hydroxyl group in changing the sign of the rotation and the opposite influence of the methoxyl group. The lævo-rotation is increased in magnitude by substituents which render the acid character of the phenyl group more marked, the nitro-group having the greatest influence in this direction. The bromine and nitro-groups have also the effect of lowering the dextro-rotation of the *p*-hydroxy- and *p*-methoxy-benzaldehyde compounds. The values for the rotations of the three nitrobenzaldehyde derivatives show that the influence exerted by the hydroxyl of salicylaldehyde is not a specific property of this group but depends on its acid character.

An apparent exception to the above regularities is found in the case of the 3-nitrosalicylaldehyde compound, but this is explained by the fact that this derivative is intensely yellow and, according to Hantzsch's recent investigations, should contain the *o*-nitrosalicylic residue partly in a pseudo-phenolic form.

T. H. P.

**A New Optical Property (Magnetic Double Refraction) of certain Non-colloidal Organic Liquids.** A. COTTON and HENRI MOUTON (*Compt. rend.*, 1907, 145, 229—230. Compare Abstr., 1906, ii, 146).—The phenomenon of magnetic double refraction not hitherto observed in pure liquids is exhibited by all the liquids of the aromatic series that have been studied. These include benzene, nitro-, iodo-, bromo-, and chloro-benzenes, aniline, toluene, *o*- and *m*-nitrotoluenes, benzoyl chloride, benzyl acetate, xylene, nitro-*m*- and nitro-*p*-xylenes, cumene, ethyl cinnamate, bromonaphthalene, pyridine, and furfuraldehyde. Liquids of the fatty series of which the following have been examined, hexane, octane, light petroleum, amylene, chloroform, carbon tetrachloride, ethylene dibromide, allyl bromide, ethyl, *isobutyl* and amyl alcohols, glycerol, acetone, ethyl ether, sugar syrup, oleic acid, amyl acetate and ethyl tartrate, and the cyclic compounds, *cyclohexane*, *cyclohexanone*, and *terebenthene* are inactive.

Carbon disulphide, however, exhibits a small double refraction which, contrary to those exhibited by all the other liquids, is negative.

E. H.

**Optimum of Phosphorescence.** JOS. DE KOWALSKI and CHARLES GARNIER (*Compt. rend.*, 1907, 145, 391—393).—The contradiction between the results of Bruninghaus (this vol., ii, 520) and those of the present authors (this vol., ii, 418) is only apparent since Bruninghaus observes the cathode-luminescence during excitation, whilst the authors observe the durable phosphorescence at the moment when the excitation

by ultra-violet rays ceases to act. Thus samariferous calcium sulphides containing 0.08% of anhydrous sodium sulphate and 1 atom of samarium to respectively 27,000, 9000, 3000, 1500, 750, 400, and 125 atoms of calcium have been excited both by the ultra-violet rays from a quartz mercury lamp and by cathode rays. In the former case the optimum of phosphorescence is obtained with the 1:3000 sulphide, in the latter with the two sulphides containing most samarium. In the manganiferous calcium sulphides the influence of the mode of excitation is not so pronounced, but the optimum appears to correspond with a greater dilution for the luminous than for the cathodic excitation. The relative intensity of the bands and lines in the photoluminescence spectra of the sulphides also seems to depend on the concentration.

E. H.

**Luminosity of Derivatives of Salicylic Acid.** P. N. VAN ECK (*Chem. Weekblad*, 1907, 4, 539—542).—When rubbed "salophen,"  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , and "salacetolum,"  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\text{Ac}$ , display luminosity. In these, the acetyl group is in contiguity to the carboxyl group of salicylic acid. Acetylsalicylic acid ("aspirin"), with the acetyl group in the phenolic hydroxyl group, does not exhibit the phenomenon.

A. J. W.

**Action of Gravity on the Deposition of Induced Radioactivity.** Madame MARIE CURIE (*Compt. rend.*, 1907, 145, 477—480).—It has been observed that when radium emanation is contained in a vessel the inner wall of which is coated with phosphorescent zinc sulphide, the luminosity of the latter becomes concentrated in regions situated near the bottom of the vessel; if the vessel is inverted, the luminosity gradually disappears from the top and reappears at the bottom. The position of the luminous region seems to be independent of external causes other than the orientation, such as temperature or the proximity of magnets.

The author placed in a bell-jar containing radium emanation pairs of parallel sheets of metal, at a constant distance apart but in some cases horizontal and in others vertical; all the back surfaces were furnished with metallic coatings, so that only the surfaces facing one another could become active. It was found that all the vertical plates and those of the horizontal ones which faced downwards exhibited the same induced activity for a given area, whilst the activity of the horizontal plates facing upwards was 2—5 times as great. It would appear that the induced radioactivity suspended in the gas behaves like a heavy substance. This phenomenon is not observed when the air or other gas in the bell-jar is perfectly dry, but the presence of suspended dust is unnecessary. The intensity of the phenomenon increases with the concentration of the emanation, and, to a certain limiting value, with the distance apart of the plates. When an intense electric field is established between the opposing horizontal plates, the phenomenon is masked, the negatively charged plate, whether above or beneath, always becoming more active than that charged positively.

T. H. P.

**Amount of Radium present in Typical Rocks in the Immediate Neighbourhood of Montreal.** A. S. EVE and DOUGLAS MCINTOSH (*Phil. Mag.*, 1907, [vi], 14, 231—237).—Since the true ratio of radium associated with uranium was not then known (compare Rutherford and Boltwood, *Abstr.*, 1906, ii, 593), it is necessary to revise the values given by Strutt (*Abstr.*, 1906, ii, 411, 716). Applying this correction to his values, it is found that igneous rocks contain on an average  $1.7 \times 10^{-12}$  grams of radium, and sedimentary rocks  $1.1 \times 10^{-12}$  grams of radium per gram of rock. From this it follows that near the earth's surface there is about twenty-eight times as much radium present as will account for the existing temperature gradient within the earth. The authors have therefore examined some representative igneous and sedimentary rocks obtained in the vicinity of Montreal, since Strutt did not test any specimens from the New World. The mean value found is of the same order as that obtained by Strutt, namely,  $1.1 \times 10^{-12}$  grams of radium per gram of rock.

It is further shown that the emanation cannot be completely driven off by simply heating the powdered rock. W. H. G.

**Atomic Weight of Radium.** Madame MARIE CURIE (*Compt. rend.*, 1907, 145, 422—425. Compare *Abstr.*, 1902, ii, 562).—From some decigrams of comparatively pure radium chloride 0.4 gram of a chloride, of which the spark spectrum exhibited only very feebly the most prominent barium line ( $\lambda 4554.4$ ), has been obtained by fractional crystallisation from water containing hydrochloric acid, or by fractional precipitation by alcohol. This chloride, containing certainly not more than 0.1% of barium chloride, has been used to determine the atomic weight of radium. The method was the same as that previously adopted, but it was found necessary to purify the reagents used specially, and as far as possible to use platinum vessels, in order to avoid contamination with sulphuric acid. The results of three experiments gave 226.35, 226.04, 226.15, mean 226.18, as values for the atomic weight of radium ( $Ag = 107.8$ ;  $Cl = 35.4$ ).

The author concludes that radium has the atomic weight  $226.2 \pm 0.5$ , or taking  $Ag = 107.93$  and  $Cl = 35.45$ ,  $Ra = 226.45$ . E. H.

**Evolution of the Emanation from Radium Salts at Different Temperatures.** L. KOLOWRAT (*Compt. rend.*, 1907, 145, 425—428).—Barium-radium chloride, having an activity of 250, is heated in a platinum-tube enclosed in a quartz-tube, by means of an electric furnace.

The quartz-tube is provided with a three-way tap, by which communication with the air or with a previously evacuated condenser can be effected. The quantities of emanation are measured by the usual method with the piezo-electric quartz, the temperature of the furnace by a platinum-iridium couple. By making a sufficient number of extractions of the air in contact with the salt kept fused for fifteen to twenty minutes, it can be momentarily deprived of emanation. The salt so treated when heated at different temperatures for 3.75 hours evolves quantities of emanation which vary with the temperature. The quantity evolved, from ordinary temperatures up to  $350^\circ$ , remains

constant at about 1% of the total production; it then increases rapidly, reaching 90% of the total at 830°. Above 830° the amount falls to 60% at 920°, and then again rises suddenly to 100% at the m. p., about 945°. The anomalous behaviour between 830° and 945° is also observed with the fluoride between 960° and 1130°, fusion occurring at 1212°, the lower limit of evolution being in this case at 600°.

By heating the salt, after removal of the emanation initially present by fusion, at definite temperatures, removing the emanation evolved after intervals of four hours, and plotting the calculated quantities of emanation remaining after each withdrawal against the times, curves are obtained of which the form varies according as the temperature lies within the anomalous interval or not. Below 830° the curves are almost straight lines represented by  $x = C/\mu \cdot (1 - e^{-\mu t})$ , where  $C$  and  $\mu$  are constants,  $C$  varying with the temperature.  $\mu$  cannot be calculated exactly, but is of the same order as  $\lambda$ , the coefficient of the spontaneous destruction of the emanation.

In the anomalous period the curves rise rapidly at first, but soon reach a maximum such that the quantity of emanation remaining absorbed no longer varies with the time. One of the curves so obtained is exactly represented by  $x = 3.89(1 - e^{-0.087t})$ , according to which the curve reaches a maximum after thirty-four hours, and then becomes practically parallel to the time axis. Probably the quantity  $x$  can always be represented by the first expression (which is the integral of  $dx/dt = C - \mu x$ ) if  $x = 0$  when  $t = 0$ .

The conclusion is drawn that it is impossible to estimate the radium present in solid substances by evolution of the emanation unless the solid is fused.

E. H.

**Relation Between Uranium and Radium.** FREDERICK SODDY and THOMAS D. MACKENZIE (*Phil. Mag.*, 1907, [vi], 14, 272—295).—The uranyl nitrate used in this investigation was freed from radium and any intermediate products in the transformation of uranium into radium, by the method of purification employed by Crookes (Abstr., 1900, ii, 586). The increase in the course of 208 days in the amount of radium in a quantity of uranyl nitrate equivalent to 481 grams of uranium which contained originally  $1.3 \times 10^{-11}$  grams of radium was found to be not greater than  $5 \times 10^{-12}$  grams; that is, the amount of radium formed is not greater than 1/10,000 of the uranium disintegrating. It is therefore probable that the growth of radium in Boltwood's experiment (Abstr., 1905, ii, 663) would not have been detected. No appreciable growth of actinium was observed in 278 grams of uranium as uranyl nitrate during a period of 300 days. If actinium is the parent of radium, the actinium emanation should, after the ordinary excited activity has disappeared, leave behind a long-lived, feeble, residual activity, which should either be radium or change into radium. It is found, however, that the residual activity of actinium is not due to radium, neither was any appreciable growth of radium observed, although the activity decayed to a small fraction of its original value. No gaseous intermediate products between uranium and radium were detected.

W. H. G.

**Radioactivity of Thorium Salts.** BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1907, [iv], 24, 93—100; *Physikal. Zeitsch.*, 1907, 8, 556—561. Compare Abstr., 1906, ii, 415).—Observations have been made of the changes in the activity of certain thorium preparations after varying intervals of time, and the results support Hahn's suggestion (this vol., ii, 359) that thorium is not converted directly into radiothorium, but into an intermediate product, mesothorium, which has a slow rate of change and does not emit  $\alpha$ -rays. It is considered probable that thorium can be separated from mesothorium by the precipitation of the former as hydroxide from a solution of the nitrate, and also by its precipitation with sodium thiosulphate. E. G.

**Radioactivity of Uranyl Molybdate.** BELA SZILARD (*Compt. rend.*, 1907, 145, 480—481).—Lancien (this vol., ii, 697) has stated that a preparation of uranyl molybdate made by him exhibited a radioactivity much greater than that of uranyl nitrate and comparable with that of an active barium salt having an activity of 40. The author has prepared two specimens of uranyl molybdate, one in presence of excess of uranyl nitrate, and the other with excess of ammonium molybdate, and finds that the two exhibit equal activities, less than that of uranyl nitrate, and about 0.3 time that of metallic uranium. The photographic activity of uranyl molybdate is also quite normal. T. H. P.

**Action of Cathode Rays on certain Substances.** WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Weekblad*, 1907, 4, 476—479. Compare this vol., ii, 520).—The activity of uranoso-uranic oxide is increased about 45% by exposure to cathode rays, but analysis proves that the change is not due to reduction of the oxide to uranium. With metallic uranium the activity is more than doubled, and with thorium oxide the increase is about 25%. The activity of metallic thorium, lead, and bismuth is not changed appreciably. A. J. W.

**Radioactivity of Lead and other Metals.** J. C. McLENNAN (*Physikal. Zeitsch.*, 1907, 8, 556).—Observations on the natural conductivity of the air enclosed in vessels of different metals have yielded very variable results for different specimens of lead. The higher values are traced to the presence of active impurities in the lead, which itself is inactive. The differences between the values of the natural conductivity of the air are due to differences in the secondary radiation set up in the various metals by incident earth rays. H. M. D.

**Secondary X-Rays and the Atomic Weight of Nickel.** CHARLES G. BARKLA and C. A. SADLER (*Phil. Mag.*, 1907, [vi], 14, 408—422).—Experiments have shown that the penetrating power of the secondary rays emitted by an element under the influence of X-rays is dependent upon the atomic weight of the element. From chromium to selenium the curve expressing the relationship between the absorbability of the ray, and the atomic weight of the radiator is approximately linear, and a small variation in the atomic weight is accompanied by a

considerable variation in the character of the radiation. The radiation of nickel is abnormal and can only be brought into line by assigning to the element an atomic weight considerably greater than that of cobalt, nearly 61.4. Other experiments indicate that the secondary radiation from an element is specially penetrating to that element, and to a less extent to elements of neighbouring atomic weights, the special power being a measure of the proximity. The observations show the proximity of nickel to copper, and of cobalt to iron. The authors consider that the experiments furnish strong evidence in favour of the number 61.4 as representing the true atomic weight of nickel.

H. M. D.

**Radioactivity of Gaseous Products of Etna.** C. BELLIA (*Nuovo Cim.*, 1907, [v], 13, 525—536).—Using an Elster and Geitel bell electroscope, the author has measured the radioactivity of gas emitted, both from fumaroles in the neighbourhood of Etna and from one of the secondary volcanic manifestations of the perimeter of the crater—that at Salinella di Paternà, about 22 kilometres from the central crater. With the three samples of gas examined, the dispersion follows the exponential law,  $I = I_0 e^{-\lambda t}$ , after the first hour or two. For the gas from the fumaroles, the value of  $1/\lambda$  is 543,000 (unit of time, 1 second), whilst for two samples from Salinella di Paternà, it is 484,000 and 471,000. These values all lie between 463,000, found by Rutherford and Soddy (*Abstr.*, 1903, ii, 347), and 497,000, found by Curie (*Abstr.*, 1903, ii, 50), for the emanation of radium. The conclusion that these gases owe their activity to an emanation of the same nature as that of radium is confirmed by a study of the induced radioactivity.

The gases of Salinella are about eleven times as radioactive as those of Etna. Moreover, the radioactivity of mud from Salinella is 8—20 times as great as that of lava. A litre of gas from (1) Salinella, or (2) the fumaroles of Etna contains as much emanation as is developed by 0.001 gram of radium bromide in (1) 1/12, or (2) 1/125 of a second.

T. H. P.

**Production of Images on Photographic Plates by the Action of the Vapours arising from Dissolved Mercuric Chloride. A Case of Reaction Radiation.** K. KOF and HUGO HAEHN (*Zeitsch. physikal. Chem.*, 1907, 60, 367—383).—When a sensitive plate is exposed close to the surface of a solution of mercuric chloride in water, alcohol, benzene, or toluene, then, on developing, a white image is obtained. The author has made a number of experiments bearing on this observation, and shows that the effect in question may be regarded as a negative catalysis, that is, the exposed parts of the plate are developed more slowly than those parts which have been protected. Hydrogen peroxide, on the other hand, the vapours of which also affect a photographic plate, is a positive catalyst. Images obtained by the action of hydrogen peroxide vapour are obliterated by exposure to the vapour arising from a mercuric chloride solution, and vice versa. If the silver nuclei produced on development from the silver sub-bromide of the latent image are regarded as auto-

catalysts, then the production of images by the action of light may be regarded as a special case of such plate effects, and it is pointed out that light images may be obliterated by subsequent exposure to the vapour from mercuric chloride solution. No effect is produced on a plate exposed close to a mercuric chloride solution if the latter is saturated with sodium chloride, probably because in this case the mercuric chloride is present only in the form of a complex. A concentrated aqueous solution of arsenious acid acts like mercuric chloride solution, but the action is much weaker.

When a sensitive plate is laid on the top of a beaker in which the reaction  $2\text{HgCl}_2 + \text{SnCl}_2 = 2\text{Hg} + \text{SnCl}_4$  is taking place, the plate is rapidly affected, and, on developing, a dark image is obtained. This result is reached even when stannous chloride is in excess, and it can be shown that a plate exposed close to the surface of a stannous chloride solution is unaffected. No effect is produced if the vapour above the reaction liquid is continuously removed during the exposure of the plate. The escaping emanation reduces mercuric chloride solution, but experiments show that it cannot be stannous chloride.

J. C. P.

**Ionisation by Spraying.** A. S. EVE (*Phil. Mag.*, 1907, [vi], 14, 382—395. Compare de Broglie, this vol., ii., 664).—The ionisation brought about by spraying different liquids by means of a current of air has been examined. Positive and negative ions are generated in large numbers by spraying, but these can be entirely removed by a cotton wool filter. Water and ether give more negative than positive ions, whilst chloroform, amyl, ethyl, benzyl and methyl alcohols, methyl iodide, acetic acid, acetone, aldehyde, and amyl acetate give equal numbers of the two kinds of ions and from two to four times as many as distilled water. Addition of acids, alkalis, or salts to water reduces the ionisation. Toluene, light petroleum, phenetole, cineole, and turpentine give few ions in comparison with water.

The rate of fall of potential when the ionised air has been passed into the electroscope indicate that the ions present in certain cases are very inert. The slowest ions in the gas produced by spraying benzyl alcohol have a velocity of  $10^{-4}$  cms. per second in a field of 1 volt per centimetre. These ions can be stored for considerable periods; and the author shows that the ionisation is easily detected after the air has been stored for several hours in a closed vessel.

H. M. D.

**The Ionisation Curve of Methane.** WILLIAM H. BRAGG and W. TERNENT COOKE (*Phil. Mag.*, 1907, [vi], 14, 425—427).—The range of the  $\alpha$  particles from radium in methane has been examined in order to ascertain whether the loss of energy experienced by the particles in crossing an atom depends on the speed of the particles. It is found that the more energetic particles travel further in methane than in air, indicating that the stopping power of methane compared with that of air increases somewhat as the speed of the particle diminishes. In consequence of this, the four steps of the ionisation curve are more clearly exhibited in methane than in air. The total ionisation in methane is 1.165 times the ionisation in air.

H. M. D.



**Conductivity of Hydrochloric and Nitric Acids in Aqueous Solution.** PETRU BOGDAN (*Zeitsch. Elektrochem.*, 1907, 13, 596—598).—Measurements of the electrical conductivity of dilute solutions of hydrochloric and nitric acids have been made, from the results of which the author concludes that the usually accepted values of  $\lambda_{\infty}$  are too large. The author gives for hydrochloric acid  $\lambda_{\infty} = 369.6$ , and for nitric acid  $\lambda_{\infty} = 366.8$  at  $18^{\circ}$ . Utilising the experimental data in conjunction with these extrapolated values of  $\lambda_{\infty}$ , it is found that the two acids satisfy the Ostwald dilution formula when the concentration is less than  $N/80$ . The dissociation constants, HCl, 0.85,  $\text{HNO}_3$ , 0.86, are equal.  
H. M. D.

**Organic Solvent and Ionising Media. IX. Electrostriction.** PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1907, 60, 87—100. Compare Abstr., 1904, ii, 227; 1906, ii, 149, 335, 336, 527; this vol., ii, 231, 437, 519).—The molecular solution volume and the degree of electrolytic dissociation have been determined for tetraethylammonium, tetrapropylammonium, and potassium iodides in various organic solvents, such as acetonitrile, propionitrile, methyl thiocyanate, methyl and ethyl alcohols, and nitromethane. In all cases, the molecular solution volume diminishes as the solutions become more dilute, that is, the splitting of the electrolyte into its ions is accompanied by a contraction. It is found for the afore-mentioned salts that a molecule produces by its complete dissociation a contraction in the molecular solution volume (electrostriction) which amounts to about 13—14 c.c. The extent of this contraction is independent of the nature of the binary salt and of the organic solvent. It is noteworthy that the electrostriction for a binary salt in water has been found by Drude and Nernst (*Zeitsch. physikal. Chem.*, 1894, 15, 79) to be about 10 c.c., and by Traube to be about 13.5 c.c. The almost constant contraction which has been found for various electrolytes and various solvents appears therefore to be determined mainly by the process of electrolytic dissociation itself.

In harmony with what Traube found for aqueous solutions, the author finds for non-aqueous solutions of tetraethyl- and tetrapropyl-ammonium iodides (1) that the molecular solution volume is an additive property; (2) that the difference between the molecular solution volumes of two salts is approximately equal to the difference between the molecular volumes of the same salts in the solid state.

J. C. P.

**Electrolysis of Sodium Chloride Solution in a Diaphragm Apparatus.** E. BRINER (*J. Chim. phys.*, 1907, 5, 398—409).—Solutions of sodium chloride containing 187 grams of the salt per litre were subjected to electrolysis at the ordinary temperature in a cell in which the anode and cathode compartments were separated by a Pukall diaphragm. Platinum electrodes were used, and the solutions were stirred during the electrolysis. From the results of similar experiments of varying duration, the yields of the different products have been obtained as a function of the number of coulombs passed through the cell, and the results are represented graphically.

It is shown, in agreement with Förster and Jorre (Abstr., 1900, ii, 343), that the yield of free chlorine is at first less than that of sodium hydroxide, but that they tend to become equal as the electrolysis progresses; this is in accordance with the hypothesis that hypochlorous acid is an important intermediate product.

The yield of sodium hydroxide as a function of the number of coulombs passed through the solution is in satisfactory agreement with that calculated by a formula proposed by Guye (Abstr., 1903, ii, 586).  
G. S.

**Metallic Fogs, Current Efficiency, and Theory of Additions in the Electrolysis of Fused Salts.** RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1907, 13, 582—585).—The addition of an alkali chloride to fused lead chloride improves the yield of lead at the cathode. It is now shown that barium chloride has the same effect in the electrolysis of lead chloride, and that potassium bromide and iodide behave similarly in the electrolysis of lead bromide and iodide. When fused cadmium chloride is electrolysed, no cadmium is obtained, but the addition of potassium or sodium chloride makes it possible to obtain good yields. The effect is due to the prevention of the formation of metallic fogs. The addition of potassium chloride to a fog of lead in lead chloride precipitates the metal and produces a clear, transparent liquid. It is suggested that the precipitation is due to a change in the surface tension of the metal in contact with the fused salt.

T. E.

**The Equilibrium  $\text{Ag} + \text{Ag}' \rightleftharpoons \text{Ag}'_2$ .** EMIL BOSE. (*Zeitsch. Elektrochem.*, 1907, 13, 477—478).—A solution of silver nitrate is caused to circulate through a tube containing metallic silver which is steam-jacketed, and then through a glass tube which is cooled with water. The presence of organic substances is carefully excluded, and the circulation is kept up by the difference of temperature in the two tubes. After about 170 hours' circulation, numerous small crystals of silver were found on the walls of the cold tube. It is therefore probable that the equilibrium  $\text{Ag} + \text{Ag}' \rightleftharpoons \text{Ag}'_2$  is displaced towards the right-hand side at the higher temperature in the same way as the better known equilibrium  $\text{Cu} + \text{Cu}'' \rightleftharpoons 2\text{Cu}'$ .

T. E.

**New Wire Method for the Determination of the Melting Points of Metals and the Calibration of Thermo-elements.** RICHARD LOEBE (*Zeitsch. Elektrochem.*, 1907, 13, 592—593).—The metal to be examined forms a connexion between two platinum wires completing a circuit containing a battery and an electro-magnet. When the metal wire melts, the current through the circuit is broken, and this is indicated by the striking of a gong consequent on the release of the pole-piece of the magnet. The thermo-element is separate, but is so arranged that the junction is in close proximity to the heated metal.  
H. M. D.

**Specific Heats of Solids at Constant Volume, and the Law of Dulong and Petit.** GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1907, 29, 1165—1168; *Zeitsch. anorg. Chem.*, 1907, 55, 200—204).—It is shown from thermo-dynamical considerations that the specific

heats of solids can be calculated from the equation  $C_p - C_v = T\beta^2 v/a$ , where  $C_p$  and  $C_v$  are the specific heats,  $v$  the volume of one gram of the substance at the absolute temperature  $T$ ,  $a$  the coefficient of compressibility, and  $\beta$  the coefficient of thermal expansion. If  $C_p$  and  $C_v$  are required to be expressed in calories per degree, the equation becomes  $C_p - C_v = T\beta^2 V/41.78a$ , where  $V$  is the atomic volume.

By means of this expression, the values at  $20^\circ$  have been calculated for all the solid elements for which  $a$  and  $\beta$  are known, with the exception of the non-metals of atomic weight below 35. The results are tabulated and show that the mean value of  $C_v$  for the nineteen elements considered is 0.3 below the mean value of  $C_p$ . Excluding the results obtained for sodium, magnesium, aluminium, and potassium, the mean value of  $C_p$  is 6.2, and the average deviation from this mean is 0.18. The mean value of  $C_v$  is 5.9, and the average deviation only 0.09. It is suggested therefore that the law of Dulong and Petit may be modified and stated thus: "Within the limits of experimental error, the atomic heat at constant volume, at  $20^\circ$ , is the same for all the solid elements, the atomic weights of which are greater than that of potassium."

In many cases,  $C_p$  increases rapidly with the temperature, but probably  $C_p - C_v$  increases also, and it is therefore not unlikely that  $C_v$  may be nearly independent of the temperature. E. G.

**The Specific Heat of Iron.** P. OBERHOFFER (*Metallurgie*, 1907, 4, 427—443, 447—455, 486—497).—A complete review and criticism of former determinations of the specific heat of iron is given. Preliminary experiments with the Bunsen ice calorimeter showed that it was necessary to work in an exhausted apparatus to prevent oxidation at high temperatures. An elaborate form of vacuum calorimeter is described and illustrated, and the precautions necessary to eliminate various sources of error are detailed. Measurements of the specific heat of iron up to  $1500^\circ$  were made. An iron containing 0.06% of carbon and 0.079% of other impurities was used in masses of 1—6 grams.

The mean specific heat of  $\alpha$ -iron increases almost proportionately with the temperature, rising from 0.1221 at  $250^\circ$  to 0.1463 at  $650^\circ$ . The specific heat of  $\beta$ -iron rises more rapidly with the temperature, and that of  $\gamma$ -iron has a practically constant value of 0.1665 up to  $1500^\circ$ . The course of the curve indicates that the change from  $\beta$ - to  $\alpha$ -iron takes place through a continuous series of mixed crystals, as suggested by Osmond.

A full bibliography of the subject is added.

C. H. D.

**Relationships between Heat Effect and Free Energy.** HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1907, 60, 114—119).—The author has shown (see this vol., ii, 742) that if  $Q$  is the heat effect of a process and  $A$  is the accompanying change of the free energy, then  $Q/A = d(\log_e p)/d(\log_e T)$ . In this paper, the author indicates the significance of this relationship and discusses its application, not only to changes of state, but also to cases of chemical change (compare Nernst, this vol., ii, 153).

J. C. P.

**Silver Nitrate. Calorimetry at High Temperatures.** JOSEPH GUINCHANT (*Compt. rend.*, 1907, 145, 320—322).—Using a calorimetric method previously described (this vol., ii, 667), the author finds for the specific heat of rhombic silver nitrate the value 0.141 (Regnault found 0.143), of the rhombohedral form 0.149, and of the fused nitrate 0.187, for the heat of transformation at 159° of the rhombic into the rhombohedral salt the value 4.9 Cal., and for the heat of fusion at 208° the value 17.6 Cal.

By means of an electrocalorimeter described in the paper, the values 14.3, 9.6, and 17.9 have been found for the heats of fusion of tin, mercuric iodide, and silver nitrate respectively. These agree very well with the numbers 13.6—14.6, 9.8, and 17.6 found by the ordinary calorimeter. E. H.

**Heats of Formation of the Alkali Oxides.** ETIENNE RENGADE (*Compt. rend.*, 1907, 145, 236—238).—The heats of hydration of pure alkali protoxides (this vol., ii, 83, 457) are found to be  $\text{Na}_2\text{O}, \text{aq}$ , 56.5;  $\text{K}_2\text{O}, \text{aq}$ , 75.0;  $\text{Rb}_2\text{O}, \text{aq}$ , 83.0;  $\text{Cs}_2\text{O}, \text{aq}$ , 80.6 Cal. From these and the heats developed in the reaction  $2\text{M} + 2\text{H}_2\text{O} + \text{aq} = 2\text{MOH} + \text{H}_2 + \text{aq}$ , determined by Joannis for sodium and potassium (Abstr., 1888, 1138) and by Beketoff for rubidium and caesium (*ibid.*, 1244), the following values are obtained:  $\text{Na}_2\text{O}$ , 97.7;  $\text{K}_2\text{O}$ , 84.8;  $\text{Rb}_2\text{O}$ , 82.4;  $\text{Cs}_2\text{O}$ , 91.5, for the heats of formation of the anhydrous oxides. Comparison of these figures shows that the heat of the hydration + dilution increases from sodium to rubidium and then diminishes, whilst the heat of formation of the protoxide diminishes from sodium to rubidium and then increases to caesium, in other words, that there is no progressive variation in the heat developed with increase in atomic weight. Contrary to the general rule for binary compounds of sodium and of potassium, the heat of formation of sodium protoxide is greater than that of potassium protoxide. E. H.

**Heat of Formation of the System,  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ .** ROBERT KREMANN and F. KERSCHBAUM (*Monatsh.*, 1907, 28, 911—916).—If the development of heat, which takes place when sulphuric acid and water are mixed, is caused by the formation of hydrates of sulphuric acid, the heat of mixing these substances in molecular proportions should be found the smaller the higher the temperature at which it is determined, since it has been shown (Kremann and Ehrlich, this vol., ii, 748) that the hydrate,  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ , decomposes almost entirely in the temperature interval 0—130°. If this were so, the specific heat of the mixture determined by cooling from 130°, at which temperature the dissociation is still incomplete, would be markedly greater than the specific heat determined by cooling from higher temperatures at which the hydrate is completely decomposed. This is found not to be the case; a series of determinations by cooling from different temperatures between 33.7° and 207.1° gave normal results, the specific heat found increasing slightly with the initial temperature. The average value, 0.430, is slightly smaller than the specific heat, 0.455, calculated by Pfaundler (*Ber.*, 1870, 3, 798), or approximately the same as that, 0.438, calculated by Marignac (*Ann.*,



$\Delta C = -1.0$  Cal., and for solid benzene and solid benzoic acid,  $\Delta F = 92.4$  Cals. and  $\Delta C = 1.5$  Cals. For benzoylecgonine and cocaine (methyl ether of benzoylecgonine),  $\Delta F = 10.5$  Cals. and  $\Delta C = 173.8$  Cals.; for benzoic acid and methyl benzoate,  $\Delta F = 7.4$  Cals. and  $\Delta C = 169$  Cals.; for cinnamic acid and methyl cinnamate,  $\Delta F = 7.5$  Cals. and  $\Delta C = 170.8$  Cals.; and for anisic acid and methyl anisate,  $\Delta F = 10.8$  Cals. and  $\Delta C = 173.9$  Cals. These numbers are in agreement with the values,  $\Delta F = 7-10$  Cals. and  $\Delta C = 169-172$  Cals., given by Berthelot (*Thermochimie*, I, 495, *et seq.*).

The numbers given above confirm the constitutions determined by chemical means for tropine, ecgonine, cocaine, and benzoylecgonine.

T. H. P.

**Thermoelectromotive Forces of Potassium and Sodium with Platinum and Mercury.** HAROLD C. BARKER (*Amer. J. Sci.*, 1907, [iv], 24, 159-166).—An account is given of the determination of the thermoelectromotive forces of potassium-platinum and sodium-platinum couples for varying temperature differences between  $0^\circ$  and  $90^\circ$  and, for comparison, of a mercury-platinum couple through the same range. The measurements were made by means of a Leeds potentiometer used in connexion with a Weston standard cell of 1.0193 volts. The metals were introduced into an apparatus constructed of glass tubing of 4 mm. diam. This apparatus is described with the aid of a diagram, and an account is given of the mode of filling the tubes and carrying out the experiments. The results are given in tabular form and are also plotted as curves. The curves deduced for potassium-mercury and sodium-mercury couples are indicated.

For the potassium-platinum couple, the *E.M.F.*'s vary from 840 microvolts with a temperature difference of  $89.60^\circ$  between the junctions to 70 microvolts with a difference of  $6.82^\circ$ ; the sodium-platinum couple gives from 170 microvolts with a difference of  $84.24^\circ$  to 30 microvolts with a difference of  $12.64^\circ$ ; and the mercury-platinum couple gives from 50 microvolts with a difference of  $84.42^\circ$  to 10 microvolts with a difference of  $10.64^\circ$ .

E. G.

**Formulae of Mercurous Chloride, Bromide, and Iodide, of Cuprous Chloride, and of the Chlorides of Thallium and the Alkali Metals** ERNST BECKMANN (*Zeitsch. anorg. Chem.*, 1907, 55, 175-187).—The molecular weights of the salts mentioned in the title have been determined by cryoscopic measurements in mercuric chloride, bromide, and iodide as solvents.

The molecular freezing-point constant of mercuric chloride, determined with anthraquinone, is 340. In this solvent, mercurous chloride has the formula  $Hg_2Cl_2$ , the molecular weight of cuprous chloride lies between that required for  $CuCl$  and  $Cu_2Cl_2$  and increases with the concentration, whilst thallos, sodium, potassium, rubidium, caesium, and ammonium chlorides have all practically the normal molecular weights. Mercurous bromide has the formula  $Hg_2Br_2$  in fused mercuric bromide (freezing-point constant 367), and mercurous iodide has the formula  $Hg_2I_2$  in mercuric iodide (constant 404).

Mercuric bromide in mercuric chloride and mercuric chloride in the corresponding bromide have higher apparent molecular weights than correspond with their formulæ; this is probably connected with the formation of solid solutions.

In antimony pentachloride (constant 175) the molecular weights of antimony tri-iodide and tin tetraiodide are only about one-third of the normal values, whilst the freezing point of antimony pentachloride is raised by the addition of antimony trichloride; the latter phenomenon is probably due to the formation of solid solutions. G. S.

### Compressibility of Gases at about Atmospheric Pressure.

DANIEL BERTHELOT (*Compt. rend.*, 1907, 145, 317—320. Compare this vol., ii, 668).—Contrary to the assumption of Guye (this vol., ii, 605), the author shows experimentally that at pressures between 0.25 and 2.0 atmospheres the variation of  $pv$  for very compressible gases is not a linear function of the pressure, but is, however, a linear function of the density. The remainder of the paper is devoted to a discussion of the comparative accuracy of the formulæ,  $pv = 1 - \epsilon/v$  (Berthelot),  $(p + a/v^2)(v - b) = 1$  (Van der Waals), and

$$A_1^2 = (a - b)/[1 - 2(a - b)][1 - 3(a - b)], A_1^0 = (a - b)/1 - (a - b)$$

for the determination of coefficients of deviation from Boyle's law. The conclusion drawn is that almost identical results are obtained by all three formulæ. E. H.

### Gas Solubility, Compressibility, and Surface Tension.

ALBERT RITZEL (*Zeitsch. physikal. Chem.*, 1907, 60, 319—358).—The author has determined the compressibility at 25° of various mixtures of the following pairs of organic liquids: chloroform and acetic acid, chloroform and acetone, acetic acid and benzene, acetic acid and toluene, carbon disulphide and acetone, ethyl alcohol and benzene; benzene and nitrobenzene, benzene and aniline; toluene and nitrobenzene, toluene and aniline; also the compressibility at 20° of ethylene dichloride, carbon disulphide, benzene and carbon tetrachloride. The method employed was that used by Richards and Stull (*Abstr.*, 1904, ii, 384). The surface tension of mixtures of (1) benzene and ethyl alcohol, (2) benzene and nitrobenzene, (3) toluene and nitrobenzene, has been determined at 25°. The dilatation which accompanies the absorption of carbon monoxide at 25° by mixtures of (1) chloroform and acetic acid, (2) chloroform and acetone, (3) acetic acid and benzene has been measured.

When Skirrow's measurements of the solubility of carbon monoxide in binary mixtures of organic liquids (*Abstr.*, 1902, ii, 600) are correlated with the author's measurements of the compressibility of the same mixtures, it is seen that the solubility-concentration curve, and the compressibility-concentration curve are very similar in form in each case. Comparison of the solubility-concentration curve, and the capillarity-concentration curve shows that when the former exhibits a maximum, the latter exhibits a minimum. The converse, however, does not hold, for where the solubility-concentration curve exhibits a minimum, the capillarity-concentration curve exhibits one also. That a maximum is not found on the capillarity-concentration curve in the

latter case is probably due to adsorption phenomena involved in the usual statical method of measuring surface tension.

The view is adopted that the power of a liquid to dissolve a sparingly soluble gas is intimately related to its compressibility. Making certain assumptions, the author deduces the formula  $\lambda = P\beta/\delta$ , in which  $\lambda$  is the solubility of the gas,  $\beta$  is the compressibility of the solvent,  $\delta$  is the absorption-dilatation coefficient, and  $P$  is the solubility pressure ('Löslichkeitsdruck') of the gas;  $P$  is simply a measure of the tendency of the gas to dissolve in the liquid. The foregoing formula means that the solubility of a gas is proportional to the solubility pressure and to the compressibility of the solvent, and inversely proportional to the change of volume which accompanies the absorption. This formula is not amenable to quantitative verification by experiment, but the author adduces evidence from various sources which makes its correctness very probable. Thus in addition to his own experiments, he cites the result established by Just (Abstr., 1901, ii, 439), namely, that the ratio of the solubilities of carbon monoxide and nitrogen is independent of the solvent. There is, further, the parallelism between the lowering of compressibility and the lowering of solubility which are produced by adding salts to water. The variation of the solubility of gases with temperature appears also to be in general harmony with the formula already mentioned.

J. C. P.

**Occlusion and Diffusion of Gases in Metals.** ADOLF SIEVERTS (*Zeitsch. physikal. Chem.*, 1907, 60, 129—201).—A comprehensive study of the behaviour of copper, iron, nickel, cobalt, silver and platinum towards hydrogen and nitrogen. The behaviour of silver and platinum also towards oxygen was examined. In all cases the gases were brought into contact with the metals at atmospheric pressure and at various temperatures. The author has studied also the diffusion of hydrogen through copper, iron, nickel, and silver, the diffusion of oxygen through silver, and the diffusion of carbon dioxide through iron. For details of the apparatus employed the original must be consulted.

From 400° upwards, copper wire absorbs small quantities of hydrogen which increase as the temperature rises. On cooling, only 0.05 volume of hydrogen is retained. Copper powder retains after heating and cooling 0.5—0.8 volume of the gas. Many of the data occurring in the literature give too high values for the occlusion of hydrogen by copper: this is probably due to the fact that powdered copper which has been obtained by reduction at a low temperature has a great power of retaining water vapour.

The power of iron to occlude hydrogen varies with the nature of the iron. Soft wire begins to absorb it at about 400°, and the quantity of gas absorbed increases up to 800° at the rate of about 0.04 volume for every 100°. Above 800° the rate of increase is greater, but on cooling all the hydrogen is given up. Refined iron and reduced iron do not absorb appreciable quantities of hydrogen below 800°. At 900° and higher temperatures more hydrogen is absorbed than is released on cooling, even in a vacuum. On cooling from 900° to 800°



both sorts of iron give up 0.16—0.17 volume of hydrogen, and this amount is independent of the quantity which has been absorbed at higher temperatures. Kahlbaum's reduced iron when heated to 900° acquires the ability to absorb nitrogen, which is quantitatively released on cooling below that temperature. The occlusion is possibly exclusively a property of  $\gamma$ -iron.

Absorption of hydrogen by nickel begins below 200°, and increases with the temperature; at 1000° the amount occluded is about 1 volume. In the case of cobalt there is no appreciable absorption below 700°, and at 1000° the amount occluded is about 0.4 volume. In both cases the samples examined retained only traces of hydrogen on cooling. It is probable that the finely divided metals have the power of absorbing larger quantities of hydrogen.

The study of the occlusion of hydrogen and oxygen by silver did not give any very definite results. The amounts of these gases absorbed by silver wire were only fractions of the volume of the wire.

In harmony with the observations of Mond, Ramsay, and Shields (Abstr., 1895, ii, 492; 1898, ii, 599), platinum was found to absorb only traces of hydrogen and oxygen.

The results of the author's experiments on diffusion may be shortly stated as follows. The diffusion of hydrogen through copper becomes appreciable at 640°. In the case of iron the diffusion of hydrogen begins at about 400°. Up to 1000° nitrogen seems to be without the power of diffusing through iron. The diffusion of hydrogen through nickel has been observed down to 450°. With silver no diffusion of either hydrogen or oxygen appears to occur up to 640°. J. C. P.

**Researches on Vapour Pressure. II.** HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1907, 60, 101—113. Compare Abstr., 1906, ii, 522).—The value of  $f$  in the van der Waals equation  $\log \pi = f(1 - 1/\theta)$  has been calculated for hydrogen, oxygen, nitrogen, and ammonia, in addition to the substances already considered (fluorobenzene, mercury, carbon dioxide, water, argon, and xenon). It is now shown that the variation of  $f$  with  $\theta$  is for each substance satisfactorily represented by a formula of the type  $f = f'_0 - a\theta + b/(1 - \theta)$ ; in this formula  $f'_0 = f_0 - b$ ,  $f_0$  being the value which  $f$  assumes for  $\theta = 0$ . At low temperatures the variation of  $f$  with  $\theta$  may be adequately represented by the linear equation  $f = f_0 - a\theta$ .

Combining these equations with the Clapeyron-Clausius equation, the author arrives at the relationship  $\lambda = 4.571(f_0 T_k - aT^2/T_k)$ , whence for  $T = 0$ ,  $\lambda_0 = 4.571f_0 T_k$ . These latter equations are shown to be in harmony with experimental data. That the relationship between  $\lambda$  and  $T$  is expressed by an equation of the general form  $\lambda = \lambda_0 + BT^2$  is in harmony with Nernst's hypothesis regarding the course of the energy curves at the absolute zero.

Further mathematical treatment of the equations leads the author to various relationships. These, stated in words, are: (1) the ratio between the latent heat of a process and the alteration of the free energy is equal to the differential quotient  $d(\log_e p)/d(\log_e T)$ ; (2) the heat of vaporisation is equal to the work done by the liquid in passing from the internal pressure to the pressure of the saturated vapour;

(3) the quantity  $f$  is equal to the logarithm of the ratio between internal pressure and critical pressure. J. C. P.

**Determination of Molecular Weights by Distribution Experiments.** J. LIVINGSTONE R. MORGAN and H. K. BENSON (*J. Amer. Chem. Soc.*, 1907, 29, 1176—1179).—Nernst and Aulich (Abstr., 1891, 1148) and others have shown that the relation between the molecular weights of a substance in two immiscible solvents can be found by determining its distribution between them.

Substances have now been studied which when treated by the freezing point method absorb heat on dissolving and show a variation in the molecular weight with the concentration, together with those necessary to interpret the results. The results of distribution experiments expressed in grams per c.c. are given for acetic acid between water and ethyl ether, acetic acid between fused calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , and ethyl ether, acetic acid between fused lithium nitrate,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , and ethyl ether, ethyl alcohol between water and ethyl ether, ethyl alcohol between fused calcium chloride and ether, ethyl alcohol between fused calcium chloride and benzene, and ethyl alcohol between water and benzene. The values obtained show that ethyl alcohol and acetic acid have practically the same molecular weights in ethyl ether as they have in water (which are nearly independent of the concentration as shown by the freezing point method), and that the molecular weights of these substances in fused calcium chloride and lithium nitrate are also the same as in water, although determinations by the freezing point method lead to abnormal figures at high concentrations (Morgan and Benson, this vol., ii, 747). The molecular weight of alcohol in benzene as derived from the coefficient of distribution does not vary so greatly with the concentration as it does when determined by the freezing point method. E. G.

**Osmotic Pressure of Compressible Solutions of any Degree of Concentration.** ALFRED W. PORTER (*Proc. Roy. Soc.*, 1907, 79, A, 519—528).—By means of a thermodynamical cycle, an exact equation has been obtained connecting the osmotic pressure and vapour pressure for a solution of any given concentration, of any degree of compressibility, and under any hydrostatic pressure. The simplifying assumptions are then made that the solution is incompressible and that the vapour obeys the gas laws, and it is shown that if the osmotic pressure is defined under such conditions that the *solvent* is under the hydrostatic pressure of its own vapour the formula reduces to that proposed by van't Hoff, but if the conditions are such that the *solution* is under the hydrostatic pressure of its own vapour the formula reduces to that recently brought forward by the Earl of Berkeley (see Abstr., 1906, ii, 599; this vol., ii, 440). Exact equations are also given showing how the osmotic pressure and vapour pressure depend on the hydrostatic pressure.

It is further shown that when a solution at any pressure is in osmotic equilibrium with the pure solvent (through a semi-permeable membrane), the vapour pressure of the solution is equal to that of the pure solvent when each is measured for the hydrostatic pressures

to which the solution and solvent are respectively subjected. Moreover, if two solutions, at any hydrostatic pressure the same for both, are isotonic as regards vapour pressure, they are also isotonic as regards osmotic pressure and have the same freezing point.

The question as to what hydrostatic pressure osmotic pressure measurements may be most advantageously referred is discussed.

G. S.

**Impedance of Solutes in Solvents as Manifested by Osmotic "Pressure."** JOHN G. A. RHODIN (*Trans. Faraday Soc.*, 1907, 3, 81—85).—A theoretical paper in which the author explains the phenomenon of osmotic pressure by assuming that a "semi-permeable membrane must have a structure which makes it act approximately as a Bunsen valve" and that "a solute in solution derives its molecular motion only from the motion of the free centres of motion of the solvent."

W. H. G.

**Osmotic Pressure of Sucrose Solutions in the Vicinity of 5°.** HARMON N. MORSE, JOSEPH C. W. FRAZER, and P. B. DUNBAR (*Amer. Chem. J.*, 1907, 38, 175—226).—In previous papers (Abstr., 1906, ii, 601; this vol., ii, 439, 440), it has been shown that at temperatures near 20° both dextrose and sucrose in aqueous solutions exert an osmotic pressure equal to that which a molecular-equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to that of the solvent in the pure state, whereas at temperatures near 0° the osmotic pressure is somewhat in excess of the calculated gas pressure. It is considered desirable to ascertain the point at which these divergences observed at low temperatures disappear and with this object series of measurements are being carried out in the neighbourhood of 5°, 15°, and 20°. In the present paper, the osmotic pressures of sucrose solutions in the vicinity of 5° are recorded. The results afford little evidence of a temperature coefficient for the osmotic pressure of these solutions. The pressures at 0°, 5°, and 20° are approximately the same.

A reply is made to the criticisms of Bancroft (*J. Physical Chem.*, 1906, 10, 320).

E. G.

**Viscosity of some Salt Solutions.** FREDERIC H. GETMAN (*J. Chim. Phys.*, 1907, 5, 344—363).—The viscosity of aqueous solutions of the chlorides, bromides, and nitrates of sodium and potassium, and of potassium iodide, as well as of mixtures of these solutions in varying proportions, has been determined at 18° by Ostwald's method. It is shown (compare Wagner, Abstr., 1890, 441) that whilst the solutions of sodium salts have a higher viscosity than pure water, the solutions of potassium salts have, in certain concentrations, a lower viscosity than the solvent, so that the curves having viscosity as ordinates, concentrations as abscissæ, show distinct minima for certain potassium salts. The latter phenomenon cannot be due to hydration, and it is suggested that the potassium ion lowers the viscosity of water, whilst the respective anions and the un-ionised molecules tend to increase it. The relation between ionisation and viscosity for the

descending branch of the curve is represented by the equation  $\eta = k^a$  ( $\eta$  = viscosity,  $a$  = degree of dissociation,  $k$  = constant).

The solutions of the sodium salts and of sucrose follow very accurately the exponential law of Arrhenius (1887), but this is not the case for the ascending branch of the curves of the potassium salts.

No very definite conclusions have been drawn from the observations on the viscosity of mixed solutions (compare Abstr., 1906, ii, 832).

G. S.

**Measurements of Viscosity at High Temperatures.** KURT ARNDT (*Zeitsch. Elektrochem.*, 1907, 13, 578—582).—In order to measure the viscosity of fused salts, the author measures the time of fall of a weight in the salt. A platinum cylinder is suspended by a fine platinum wire, attached to a silk fibre, passing over a practically frictionless pulley, which also carries a variable counter-balancing weight, and a light pointer. The product of the time required to sink through a given distance in the liquid and the unbalanced weight of the sinker is proportional to the viscosity of the liquid. The factor required to calculate the viscosity is obtained by observations with castor oil of known viscosity. Determinations of the viscosity of boron trioxide, sodium metaphosphate, and mixtures of these substances are made at temperatures between 650° and 1100°. The viscosity of sodium metaphosphate is 80 to 100 times smaller than that of boron trioxide at the same temperature; the viscosities of the mixtures lie between those of the constituents, but are smaller than the mean.

T. E.

**Solubility of Isomeric Organic Compounds.** ALEX. D. BOGOJAWLENSKI, P. BOGOLJUBOFF, and N. WINOGRADOFF (*Chem. Zentr.*, 1907, i, 1738—1739; from *Schrift. Dorpat. Naturforsch.-Ges.*, 1907, 15, 216—229).—The complete curves of solubility of the following compounds in the solvents named have been determined with a view to testing the accuracy of the general rules enunciated by Carnelley and Thomson (Abstr., 1888, 782). The results confirm the conclusion that the more readily fusible isomerides are also more easily soluble in organic solvents, and that the order of solubility is not affected by the nature of the organic solvent. The relationship of the solubilities of two isomerides in various organic solvents does not, however, remain constant. The curves of solubility in benzene of isomerides of which the melting points are not very different are almost parallel.

In benzene, *o*-, *m*-, and *p*-chloro- and bromo-nitrobenzenes, *o*-, *m*-, and *p*-nitrophenols, *o*-, *m*-, and *p*-nitroanilines. In nitrobenzene and in dibromo-acetylene, *o*-, *m*-, and *p*-nitroanilines. In water, *m*- and *p*-nitrophenols.

E. W. W.

**Solubility of Acetanilide, Phenacetin, Caffeine, and Salol in several Solvents.** ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1907, 29, 1088—1091).—The object of this work was to obtain a method for separating the constituents of headache powders.

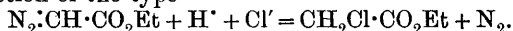
The solubility of acetanilide has been determined in water, alcohol,

and mixtures of these solvents at 25° and 50°, and in methyl alcohol, ethyl alcohol, and chloroform at temperatures ranging from 0° to 60°. The solubilities of acetanilide, phenacetin, caffeine, and salol have been determined in acetone, benzene, benzaldehyde, amyl acetate, and aniline at 30–31°, in amyl alcohol at 25°, in acetic acid at 21.5°, in xylene at 32.5°, and in toluene at 25°. The results are tabulated.

Mixtures of salol, caffeine, and acetanilide can be fairly well separated by digesting first with toluene to remove the salol, and then with amyl alcohol to remove the acetanilide. None of the four compounds is completely insoluble in any of the solvents and therefore no sharp separation can be effected. E. G.

**Chemical Kinetics of Ethyl Diazoacetate.** W. FRAENKEL (*Zeitsch. physikal. Chem.*, 1907, 60, 202–236).—The decomposition of ethyl diazoacetate in dilute aqueous solution takes place with conveniently measurable rapidity at 25° in presence of a small quantity of an acid. The course of the decomposition was followed by measuring the nitrogen evolved, and the apparatus used for this purpose was that described by Walton (Abstr., 1904, ii, 319). As might be expected, the course of the change,  $N_2 \cdot CH \cdot CO_2 Et + H_2O = N_2 + OH \cdot CH_2 \cdot CO_2 Et$ , is that required for a unimolecular reaction. The reaction (which should be carried out preferably in platinum vessels or in vessels of glass coated with paraffin) turns out to be a catalysis by hydrogen ions, and the velocity coefficient is proportional in each case to the  $H^+$  concentration. This result has been established on the basis of experiments with nitric, picric, *m*-nitrobenzoic, fumaric, succinic, and acetic acids. It is noteworthy that the influence of acetic acid in accelerating the decomposition of the ester is diminished by sodium acetate to an extent which can be satisfactorily calculated on the basis of the ionic theory and the law of mass action.

When hydrochloric or sulphuric acid is used as the catalyst the value of the velocity coefficient falls off as the reaction proceeds. A similar result is obtained when a little neutral salt, such as potassium nitrate, sodium sulphate, or sodium chloride is added to the aqueous solution of the ester along with nitric acid. In these cases the evolution of gas begins, but ceases long before the decomposition of the diazoester is complete. This indicates that the hydrogen ions are being removed from the sphere of action, and it may be actually shown that the acidity of the solution diminishes in these cases. This irregularity appears to be due to the simultaneous occurrence of another reaction of the type



When alcohol is added in gradually increasing quantities to the solvent water, the rate of the catalytic decomposition of the ester diminishes very rapidly at first, more slowly afterwards, up to about 90% alcohol. The retarding influence of alcohol is greater when the catalyst is a weak acid than when it is a strong acid. When ethyl diazoacetate is dissolved in absolute alcohol, and a little picric acid added, a decomposition sets in which is markedly retarded by the addition of even very small quantities of water (compare Goldschmidt and Sunde, Abstr., 1906, ii, 219).

The temperature coefficient of the ethyl diazoacetate catalysis is about 2.5 for a rise of  $10^{\circ}$ .

At high temperatures ethyl diazoacetate undergoes decomposition even in pure aqueous solution, and the reaction exhibits the phenomenon of spontaneous acceleration. Incidentally it was found that mercuric and cupric chlorides are very readily reduced by ethyl diazoacetate to mercurous and cuprous chlorides respectively. J. C. P.

**Application of van Laar's Formula to the Determination of the Degree of Dissociation of Compounds which Dissociate in the Liquid Phase.** ROBERT KREMANN (*Monatsh.*, 1907, 28, 919—926. Compare Abstr., 1904, ii, 726; 1906, ii, 267).—The degrees of dissociation of phenol—aniline and phenol—picric acid at their melting points found by the author's method, are shown to be approximately half of the values calculated with the aid of van Laar's general formula for the course of melting point curves of substances which dissociate in the liquid phase (Abstr., 1906, ii, 331). The cause of the discrepancy remains undecided. G. Y.

**Molten Hydrated Salts as Solvents for the Freezing Point Method.** J. LIVINGSTONE R. MORGAN and H. K. BENSON (*J. Amer. Chem. Soc.*, 1907, 29, 1168—1175).—Löwenherz has shown (Abstr., 1896, ii, 149) that fused hydrated sodium sulphate can be used as a solvent for determining molecular weights by the freezing point method, but that it decreases or prevents ionisation if the substance added has an ion in common with it.

These observations have been confirmed by a study of the behaviour of other fused hydrated salts, namely, calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , f. p.  $29.48^{\circ}$ , lithium nitrate,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , f. p.  $29.88^{\circ}$ , and sodium chromate,  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ , f. p.  $19.92^{\circ}$ . The freezing point constants for these salts are 45.0, 26.0, and 38.5 respectively. The depressions of the freezing points of the fused salts produced by various substances have been determined and the results are tabulated. In both calcium chloride and lithium nitrate, acetic acid and ethyl alcohol show increasing molecular weights as the concentration is increased, and it is suggested that this is due to the heat absorbed when the solutions are diluted.

The latent heat of fusion,  $w$ , of lithium nitrate,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , has been calculated by means of the equation  $K = 0.02T^2/w$ , where  $K$  is the freezing point constant and  $T$  the absolute temperature of the freezing point, and has been found to be 70.6 calories per gram.

E. G.

**Continued Existence of Molecular Compounds and Crystalline Hydrates in the Liquid Phase.** ROBERT KREMANN and R. EHRLICH (*Monatsh.*, 1907, 28, 831—892. Compare Abstr., 1905, ii, 76).—A study of the existence of so-called molecular compounds in the liquid state. A compound which dissociates partially when fused must exist above its m. p. in a dissociation equilibrium; this equilibrium must change as the temperature rises, so that the concentration of the undissociated compound gradually diminishes. Little is known as to the degree of this dissociation and the limits of

stability of such compounds in the liquid state (compare Küster and Kremann, *Abstr.*, 1904, ii, 726). With the object of throwing light on these points, the authors have determined the expansion coefficients at different temperature intervals of the systems, phenol—*aniline*, *m*-cresol—*aniline*, sulphuric acid—water, and the changes in volume on mixing the components of these systems, the temperature coefficients of the molecular surface energy of the systems and their components, and the viscosities of the mixtures at different temperatures. The results are tabulated and expressed in curves.

In many cases the formation and dissociation of molecular compounds are accompanied by changes in volume: if the components combine in molecular proportions, the molecular mixture must show the maximum change. At temperature intervals at which the dissociation is complete, the expansion coefficient must be additive, as, apart from any change accompanying the process of solution, is the case with mixtures of substances which do not form compounds. The additive nature of the expansion coefficient of mixtures of such non-combining substances has been confirmed by the study of mixtures of nitrobenzene and *aniline*.

The expansion coefficient of sulphuric acid—water mixtures is found to have a well-defined maximum corresponding with a mixture in molecular proportions. Dilatation, caused by dissociation of the compound  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , is observed throughout the temperature interval,  $0-87.9^\circ$ , and to be greater at the lowest temperatures; hence the hydrate still exists but only to a small extent at  $87.9^\circ$ .

The expansion coefficient for phenol—*aniline* differs only slightly from that for an additive mixture; hence the combination of these substances must be accompanied by only a very slight change in volume. A contraction observed with isothermal mixings throughout the temperature interval,  $34.8-88.1^\circ$ , is ascribed to the process of solution.

The contraction observed with isothermal mixtures of sulphuric acid and water diminishes from 8.41% to 7.24% in the temperature interval,  $0-88.1^\circ$ . Part of the contraction must accompany the formation of the hydrate and the diminution is to be ascribed to the diminished concentration of the hydrate in consequence of its increased dissociation at the higher temperature. A contraction of about 6.70%, which is found by extrapolation to remain at temperatures at which the dissociation of the hydrate approaches completion, must be caused by the solution process. In opposition to this behaviour of sulphuric acid and water is that of nitrobenzene and *aniline*, the solution process in this case being accompanied by a dilatation which remains approximately constant from  $0^\circ$  to  $80.1^\circ$ .

The temperature coefficient of the molecular surface energy,  $\Delta$ , which for unimolecular compounds is 2.1 per  $10^\circ$ , is approximately additive for binary molecular mixtures, such as nitrobenzene and *aniline*. For the system, phenol—*aniline*,  $\Delta = 1.5$  for the temperature interval  $33-46^\circ$ , 1.8 for the interval  $46-60^\circ$ , and 2.3 for the interval  $60-73^\circ$ ; hence the compound exists to the extent of about 50% immediately above its m. p., but is completely decomposed above  $60^\circ$ . Similar results are obtained with *m*-cresol—*aniline*, which has  $\Delta = 1.5$  at  $15-30^\circ$ , but is dissociated almost completely at  $60^\circ$ .

The viscosity curves for the systems, phenol—aniline, *m*-cresol—*aniline*, and  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , belong to Dunstan's second type (Trans, 1907, 91, 83), but approach his first type as the compound reaches the temperature of complete dissociation. The maxima observed correspond with the molecular mixtures. Inspection of the curve for sulphuric acid—water points to the dissociation as almost complete at  $130^\circ$ . The viscosity curve for mixtures of nitrobenzene and aniline belongs to Dunstan's third type; the decomposition of associated molecules, of which this type is characteristic, is connected with the dilatation observed with isothermal mixings. G. Y.

**Heterogeneous Catalytic Reactions. IV. Kinetics of the Sulphuric Acid Contact Process.** MAX BODENSTEIN and COLIN G. FINK (*Zeitsch. physikal. Chem.*, 1907, 60, 1—45. Compare Abstr., 1904, ii, 245, 719; 1905, ii, 692).—Mixtures of oxygen and sulphur dioxide in varying proportions were exposed to temperatures between  $150^\circ$  and  $250^\circ$  in contact with platinum gauze. The progress of the reaction was studied by following the gradual decrease of pressure in the reaction vessel. The rate of combination of the oxygen and sulphur dioxide is independent of the oxygen concentration (except when the latter is very small), directly proportional to the sulphur dioxide concentration, and inversely proportional to the square root of the sulphur trioxide concentration. In harmony with this, the course of the change is found to be accurately represented by the equation:  $dx/dt = k(a - x)/x^{\frac{1}{2}}$ , in which  $a$  is the initial concentration of the sulphur dioxide, and  $x$  is the amount which has undergone change at time  $t$ . If sulphur trioxide is present at the start in the concentration  $s$ , then the formula which represents the experimental data is  $dx/dt = k(a - x)/(s + x)^{\frac{1}{2}}$ . It will be seen from the first formula that the reaction is extremely rapid in its early stages, but is retarded by the sulphur trioxide which is produced.

In offering an explanation of the course of the reaction, the authors suppose that the combination between oxygen and sulphur dioxide takes place with almost infinite rapidity in or at the surface of the platinum, but that in order to reach the platinum the gases have to pass through a layer of adsorbed sulphur trioxide, and that the rate of diffusion of the slower gas, the sulphur dioxide, through this layer, really determines the rate of combination. The oxygen is supposed to pass more rapidly through the trioxide layer, and, provided its original concentration is not too low, it will be always in excess on the platinum surface; hence the rate of combination will be independent of the oxygen concentration. The fact that the course of the change is different in character when the oxygen concentration is very small is probably due to the sulphur dioxide now being in excess on the platinum surface; in this case, it is the velocity of diffusion of oxygen through the trioxide layer which determines the rate of combination. The concentration ratio at which the gases thus interchange their rôles can be calculated in good agreement with the velocity measurements carried out with mixtures on each side of this particular ratio.

From the foregoing equation,  $dx/dt = k(a - x)/(s + x)^{\frac{1}{2}}$ , it may be concluded that when  $s$  is very large, the course of the change should



be that for a unimolecular reaction; this conclusion has been confirmed by experiment.

Nitrogen has no effect, and carbon dioxide has a very small effect, on the rate of combination of oxygen and sulphur dioxide. The temperature coefficient (for an interval of  $10^{\circ}$ ) is 1.36, which, although rather larger than the figure to be expected if the change is determined purely by a diffusion process, is very much smaller than the figure usually obtained for purely chemical processes. J. C. P.

#### Heterogeneous Catalytic Reactions. V. General Remarks.

MAX BODENSTEIN and COLIN G. FINK (*Zeitsch. physikal. Chem.*, 1907, 60, 46—69. Compare Abstr., 1904, ii, 245, 719; 1905, ii, 692; and preceding abstract).—The authors show that the equation which has been found to represent the course of the reaction between oxygen and sulphur dioxide in contact with platinum gauze (see preceding abstract) can be applied also with satisfactory results to other researches on the same reaction; to those, namely, (1) by Bodländer and von Köppen (Abstr., 1903, ii, 639), who also used platinum gauze; (2) by Küster (Abstr., 1905, ii, 82), who used vanadium pentoxide; (3) by Berl (Abstr., 1905, ii, 315), who used arsenic pentoxide. It appears therefore that, whether platinum, vanadium pentoxide, or arsenic pentoxide is the catalytic agent, the rate of combination of oxygen and sulphur dioxide is determined by the rate of diffusion of sulphur dioxide through an adsorbed layer of sulphur trioxide, the chemical union of the components in the catalytic layer taking place with almost infinite rapidity. The rapidity of this union must be due to a common cause in all the cases, and the authors consider that it is to be ultimately referred to adsorption in the catalytic surface, and the consequent increase of concentration. Another reaction which belongs to the same type, and is capable of an explanation similar to that just given, is the combination of hydrogen and oxygen in contact with platinum (Bodenstein, Abstr., 1904, ii, 245). Others probably are the catalytic decomposition of carbon monoxide (Schenck and Zimmermann, Abstr., 1903, ii, 423; Smits and Wolff, Abstr., 1903, ii, 276, 638), and the combination of carbon monoxide and oxygen in glazed porcelain vessels (Kühl, Abstr., 1903, ii, 639).

A second general type of heterogeneous reaction is recognised in which likewise the formation of an adsorption layer must be assumed. In the case of this type, however, the layer consists, not of the product of the reaction, but of the reacting substance or substances, and it is the slow chemical reaction occurring in this layer which determines the velocity of the complete process. Reactions belonging to this type are the decomposition of antimony trihydride (see Stock, Gomolka, and Heynemann, this vol., ii, 180; Stock and Bodenstein, this vol., ii, 181), the decomposition of arsenic and phosphorus trihydrides, the formation and decomposition of hydrogen selenide (Bodenstein, Abstr., 1899, ii, 639). The authors consider it probable that another reaction belonging to this category is the union of hydrogen and oxygen at a hot porcelain surface, and the available experimental work (Bodenstein, Abstr., 1899, ii, 733; Bone and Wheeler, Abstr., 1906, ii, 434; Rowe, this vol., ii, 444) is subjected to a critical review. J. C. P.

**Fatty Esters of the Two Phytosterols of Calabar Fat, and the Analogous Cholesterol Derivatives possessing Three Stable Liquid Phases.** FRANS M. JAEGER (*Rec. trav. chim.*, 1907, 26, 311—356. Compare Abstr., 1906, i, 742).—By boiling cholesterol with the fatty acids and removing the water formed by evacuation, the author has prepared cholesterol heptoate, nonoate, laurate, myristate, palmitate, and stearate, the various phases of which have been examined.

Since the phytosterol extracted from Calabar fat contains about 90% of  $\alpha$ -phytosterol, the properties of the latter, which has been identified with the sitosterol of cheese, are virtually those previously given for the former. Fatty esters of both  $\alpha$ - and  $\beta$ -phytosterol have been prepared and examined with reference to the different phases in which they exist. Several of them melt successively into three different liquids, which are all in stable equilibrium, with reference to the solid phase between fixed limits of temperature. The transition from one of these phases to another may be irreversible in some degree. Most of the fatty esters of cholesterol, *cyclocholesterol*, and the two phytosterols exhibit the phenomenon of anisotropic liquid phases. The rotatory powers of the esters of  $\alpha$ - and  $\beta$ -phytosterols have been measured in benzene, and those of the cholesterol esters in benzene and in chloroform. T. H. P.

**Crystallisation and Melting Points of the Molecular Compounds of Magnesium Bromide and Iodide.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 814—823. Compare this vol., i, 19, 271, 386, 395, 582).—The occurrence of the molecular compounds of magnesium haloid and an organic compound, in a crystalline form, depends largely on the nature of the organic substances; if the latter crystallises well, then its molecular compound does so also, and vice versa, the same being true for the corresponding calcium chloride compounds. It is considered that these compounds are of a similar crystallographic structure to simple crystalline substances, and consequently the crystalline form of the complex should bear some relation to that of the parent substance. Similar regularities are observed regarding the melting points: the higher the melting point of the organic substance the higher that of the complex compound, the difference between the two being the more, the greater the number of organic molecules which enter the complex. In general, in the homologous series of molecular compounds, formed by magnesium iodide and bromide, those containing an even number of carbon atoms have higher melting points than those containing an uneven number. Z. K.

**Velocity of Crystallisation of Isomorphous Mixtures.** ALEX. D. BOGOJAWLENSKI and N. SACHAROFF (*Chem. Zentr.*, 1907, i, 1719—1720; from *Schrift. Dorpat. Naturforsch.-Ges.*, 1907, 15, 197—215. Compare Tammann, Abstr., 1899, ii, 548; Pickardt, Abstr., 1903, ii, 66).—Experiments have been made in order to test the accuracy of Padoa's conclusion (Abstr., 1904, ii, 390) that the

velocity of crystallisation of a substance is either unchanged, or very slightly decreased, by the addition of an isomorphous substance. Mixtures of *m*-bromonitrobenzene and *m*-chloronitrobenzene do not give constant maximum velocities of crystallisation; but the velocity of crystallisation of the mixture was found to lie between those of the components. Mixtures of  $\alpha$ -chlorocinnamaldehyde and  $\alpha$ -bromocinnamaldehyde give a single continuous curve of solidification, corresponding with the formation of a continuous series of mixed crystals of Roozeboom's 1st Type. The curve of maximum crystallisation velocity is also continuous, and has a curvature similar to that of the *m. p.* curves.

Percentage by weight ...	0	10	20	30	40	50	60	70	80	90	100
Max. cryst. velocity at 0°	60	69	83	100	120	139	162	191	217	250	300

The curves of maximum crystallisation velocity, and of solidification of mixtures of azobenzene with dibenzyl, show a distinct minimum.

The curve of solidification of mixtures of azobenzene and benzil has, on the other hand, a eutectic point at 40% of benzil.

The velocity of crystallisation of the pure components is, in this case, considerably decreased by the addition of small quantities of other compounds, and then remain practically constant within rather wide limits of concentration.

The conclusion is drawn therefore (1) that the velocity of crystallisation of isomorphous mixtures changes continuously with regular alteration of composition. (2) The curves of the maximum velocity of crystallisation of isomorphous mixtures are of the same type as the *m. p.* curves. (3) A constant velocity of crystallisation is attained by mixtures of isomorphous substances under the same conditions as in the case of pure substances, that is, when undercooled 20–30° below the *m. p.* (4) Since in the heterogeneous region between the freezing-point and melting-point curves, the velocity of crystallisation is extraordinarily small, the position of the *m. p.* curve can be approximately determined from the effect of temperature on the velocity of crystallisation.

E. W. W.

**Melting-Point Curves of Mixtures of *p*-Azoxyanisole with Benzene, Nitrobenzene, and Dibromoacetylene.** ALEX. D. BOGOWLENSKI and N. WINOGRADOFF (*Chem. Zentr.*, 1907, i, 1741–1742; from *Schrift. Dorpat. Naturforsch.-Ges.*, 1907, 15, 230–238).—Determinations of the solubility of *p*-azoxyanisole in benzene, nitrobenzene, and dibromoacetylene have been made. *p*-Azoxyanisole forms liquid crystals, it melts at 116°, and the liquid crystals became isotropic at 134.8°. The curves of solubility of *p*-azoxyanisole are similar in form to those of other substances. The two first-named pairs show a eutectic point. The addition of crystalline substances to liquid crystals of *p*-azoxyanisole lowers the temperature at which the molten mass becomes clear.

E. W. W.

**Equilibrium in the System Water—Mercuric Chloride—Potassium Chloride.** V. TICHOMIROFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 731–743).—The continual addition of mercuric

chloride to a saturated solution of potassium chloride alters the solubility of the latter, until a double salt of the two compounds separates out, after which no further change in solubility occurs until all the solid potassium chloride has been converted into this double salt. At this point, further addition of mercuric chloride again disturbs the equilibrium and a second double salt commences to separate. Three such double salts have been isolated :  $\text{HgCl}_2 \cdot 2\text{KCl}$ ;  $\text{HgCl}_2 \cdot \text{KCl}$ ;  $2\text{HgCl}_2 \cdot \text{KCl}$ . A curve representing the relative proportions of potassium and mercuric chloride and the various solutions is given.

Z. K.

**Validity of the Law of Mass Action for the Combustion of Nitrogen in the High Tension Flame.** A. GRAU and FRANZ RUSS (*Zeitsch. Elektrochem.*, 1907, 13, 573—578).—The authors' previous experiments (*Sitzungsber. k. Akad. Wiss. Wien.*, 1906, 115, ii, 1) showed an apparent deviation from the law of mass action in flames of constant current. They find, however, that in mixtures containing more oxygen the voltage and therefore the temperature of the flame is higher. Further experiments are made in which the watts consumed in the flames are kept constant. The flame burns in a water-cooled quartz tube between a thick platinum wire and a water-cooled platinum capillary tube through which the gases are drawn off. It is found that for a given mixture of oxygen and nitrogen the quantity of nitric oxide formed in a flame of constant watt consumption diminishes as the rate of flow of the gas increases, owing to the cooling of the flame; by extrapolating for zero rate of flow, a value is obtained which is independent of the watt consumption of the flame. This zero value is different for each mixture; air gives 5.5% NO, and a mixture of equal volumes of oxygen and nitrogen gives 6.6% NO. These numbers give the same value for the ratio  $[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]^{\frac{1}{2}}/[\text{NO}]$ , showing that the law of mass action holds good (compare Nüranen and Le Blanc, this vol., ii, 614).

T. E.

**Reversible Reactions of the First Order.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1907, 13, 494—506).—The author points out that the velocity constants of a reversible reaction of the first order have not yet been determined completely; he has therefore measured the rate of change of *r*-saccharic acid into its lactonic acid and also the rate of the reverse action in aqueous solution. The change is followed by means of the polarimeter. The specific rotation is sensibly independent of the temperature and concentration of the solutions; the values found are: *r*-saccharic acid lactone,  $[\alpha]_D = 40.77^\circ$ , *r*-saccharic acid,  $[\alpha]_D = 9.05^\circ$ .

The rates of change at  $18^\circ$  and at  $25.2^\circ$ , both with and without the addition of hydrochloric acid, are determined. The acid accelerates the change, but the same equilibrium is attained with it and without it. The equilibrium constant at  $18^\circ$  is 1.4417, at  $25.2^\circ$ , 1.3230, from which it is calculated that the conversion of a molecule of the lactone into the acid evolves 2072 cals. A direct determination in the calorimeter gave 2546 cals. The velocity constants of the change of the saccharic acid into its lactone and vice versa do not alter as the change progresses, from which it would follow that the concentration of the hydrogen

ions in the solution is not effected by the reaction. Determinations of the conductivity of the solutions showed that this is the case, the saccharic acid having a slightly lower conductivity than the lactone. The concentrations of the hydrogen ions in the different solutions are calculated and it is found that the rates of change are proportional to them. The final values of the velocity constants, for solutions containing hydrogen ions in normal concentration, are  $k_1$  (rate of change of the lactone) at  $18^\circ = 0.1507$ , at  $25.2^\circ = 0.3204$ , whilst  $k_2$  (rate of the reverse reaction) at  $18^\circ = 0.1045$  and at  $25.2^\circ = 0.2421$ . The rate of formation of the lactone is more accelerated by rise of temperature than the reverse change; hence rise of temperature increases the quantity of lactone.

T. E.

**Velocities of Reaction and their Derivatives with Respect to Time.** ALDO MIELI (*Gazzetta*, 1907, 37, ii, 155—166).—A mathematical paper. By differentiation of the expressions representing the velocity of reaction, the author obtains equations giving the acceleration,  $dv/dt$ , of the reaction, the values given by these equations being discussed. The various cases considered are: (1) Simple reactions. (2) Complex reactions. (3) Catalytic reactions (a) in which the substance undergoing transformation acts catalytically on the reaction and (b) in which the substance which acts catalytically is a product of the reaction. (4) Adiabatic reactions.

T. H. P.

**Catalysis of Hydrogen Peroxide.** NICOLA PAPPADÀ (*Gazzetta*, 1907, 37, ii, 172—178).—The mechanism of the catalysis of hydrogen peroxide by colloidal metal solutions can be readily explained by the author's theory concerning the coagulation of colloidal solutions (Abstr., 1906, ii, 840). Other theories are also discussed.

T. H. P.

**Nature of Colloidal Solutions in Relation to the Properties of Metallic Solutions.** NICOLA PAPPADÀ (*Gazzetta*, 1907, 37, ii, 167—172. Compare Abstr., 1906, ii, 840).—For colloidal solutions of metals as well as of silicic acid, &c., the following rules hold. (1) Organic compounds in non-dissociating solutions have no coagulating action. (2) Electrolytes are the only coagulating agents, and the coagulating action of an electrolyte depends on, and increases with, the velocity of diffusion and electric charge of the cations, the electrolytes being assumed to be in chemically equivalent concentrations.

T. H. P.

**The Unit-Stere Theory: Demonstration of a Natural Relation between the Volumes of the Atoms in Compounds under Corresponding Conditions and that of Combined Hydrogen.** GERVAISE LE BAS (*Phil. Mag.*, 1907, [iv], 14, 324—350. Compare Trans., 1907, 91, 112).—The volume relationships of carbon and hydrogen in the liquid normal paraffins from undecane to pentatriacontane,  $C_{35}H_{72}$ , have been more closely examined, and it is found that the molecular volumes are strictly additive at the melting points of the hydrocarbons and also at temperatures equally removed from the melting points.

The molecular volumes are proportional to the valency numbers of the contained atoms and can be calculated accurately on the assumption that the atomic volumes of combined carbon and hydrogen are as 4 : 1. The densities of the above hydrocarbons at temperatures equally removed from the respective melting points are equal fractions of the densities at the melting points.

The volume relationships of the simpler hydrocarbons of the series have been examined under corresponding conditions. At corresponding pressures, the valency law is satisfied approximately, but the deviations are greater under the condition of equally reduced temperatures, the deviations being in the same direction as, and proportional to, those from the law of corresponding states. The critical coefficients  $T_k/P_k$  and the molecular refractions as calculated from the formula of Lorenz and Lorentz are shown to be subject to the valency law. The relationships indicated favour the view that valency is a volume property and that the laws of additivity and correspondence are closely related.

H. M. D.

**Are the Stoichiometric Laws Intelligible without the Atomic Hypothesis?** F. WALD (*Chem. Zeit.*, 1907, 31, 756—758, 769—770. Compare *Chem. Zeit.*, 1906, 30, 963, 978).—A further contribution to the controversy on this subject (compare Kuhn, this vol. ii, 678).

G. Y.

**Some New Forms of Apparatus.** WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1907, 29, 1052—1065).—On placing a drop of pure mercury in a clean glass tube of diameter less than 3 mm., it assumes a cylindrical form and is capable of acting as an air-tight piston of very easy mobility. It has been found that such a drop of mercury is sensitive to a difference of pressure of less than 0.1 mm.

Several forms of apparatus have been devised which involve the use of this mercury drop. A small flask (20—50 c.c.), the capacity of which has been accurately determined, is fitted with a stopcock and a horizontal side-tube. The latter is graduated to 0.01 c.c. and has an internal diameter of less than 3 mm. To the stopcock is attached a vertical graduated tube of 2 c.c. capacity carrying a funnel at its upper end. This apparatus can be used as a hygrometer. The flask, after being carefully cleaned and dried, is filled with the air to be tested. The drop of mercury is placed in the side-tube and caused to move along to the zero point which is situated near the flask. The stopcock is closed and the position of the mercury noted. Concentrated sulphuric acid is placed in the vertical graduated tube, its height is read, and a small quantity is then carefully admitted through the stopcock into the flask until the mercury drop takes up a position near the middle of the side-tube. The moisture in the confined air is absorbed and the volume of the air is consequently diminished. After a minute or two, the final position of the mercury drop and the height of the sulphuric acid are noted. The method of calculating the relative humidity from the data thus obtained is given. Another method of making the determination is to admit water into the flask instead of sulphuric acid; the water vapour quickly saturates the

air and thus causes an increase in volume. The method of calculation is described.

The same apparatus can be used as a tensimeter and modifications are described for determining the vapour pressure of solids or small quantities of liquids. Closed forms of tensimeters are described for determining vapour pressures at high temperatures. These instruments have also been applied to the determination of molecular weights, the dissociation of vapours, and boiling points. For details, the description and diagrams in the original must be consulted.

E. G.

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## Inorganic Chemistry.

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**Preparation of Hydrogen by means of Iron and Carbon Dioxide in the Cold and at Ordinary Pressure.** ALBERT BRUNO (*Bull. Soc. chim.*, 1907, [iv], 1, 661—662).—Vigorous shaking for thirty-six to forty hours of a steel bottle containing water and iron filings in an atmosphere of carbon dioxide causes the whole of the carbon dioxide to be replaced by hydrogen according to the equation:  $\text{CO}_2 + \text{H}_2\text{O} + \text{Fe} = \text{FeCO}_3 + \text{H}_2$ . If a glass vessel is used, this reaction is accompanied by the absorption of part of the carbon dioxide by the alkali of the glass. The above process offers an easy and perhaps economical means of preparing a powerful combustible from a product of combustion.

Further, a mixture of iron filings, water, and nitrobenzene yields aniline just as if a strong acid were employed. T. H. P.

**Preparation of Hydrochloric Acid by Synthesis from its Elements.** MARIO G. LEVI and E. MIGLIORINI (*Gazzetta*, 1907, 37, ii, 122—134).—The authors describe an apparatus adapted to the combustion of chlorine in hydrogen and propose to apply the method to the commercial manufacture of hydrochloric acid.

T. H. P.

**Dibasicity of Hydrogen Fluoride.** ROBERT KREMANN and W. DECOLLE (*Monatsh.*, 1907, 28, 917—918).—Mallet (*Abstr.*, 1881, 973; compare, however, Thorpe and Hambly, *Trans.*, 1889, 55, 163) found hydrogen fluoride at the laboratory temperature to have the molecular formula  $\text{H}_2\text{F}_2$ , which agrees with the results of freezing point determinations with not too dilute aqueous solutions of hydrogen fluoride by Paternò and Peratoner (*Chem. Centr.*, 1891, 306). Hence fluorine must be a bivalent element and hydrogen fluoride a dibasic acid. This is now confirmed.

According to Ostwald's rule, the equivalent conductivity of sodium salts of monobasic acids increases on dilution from  $N/32$  to  $N/1024$ , by about 10 units, and that of sodium salts of dibasic acids by 20 units, or if  $\Delta$  is the increase in the equivalent conductivity and  $n$  is



the basicity of the acid,  $n = \Delta/10$ . The conductivities of sodium fluoride at these dilutions, as now determined, give  $n = 2.08$ .

G. Y.

**Action of Certain Substances on Potassium Iodide.** BELÁ SZILÁRD (*Compt. rend.*, 1907, 145, 433—435).—When certain solid substances insoluble in water, such as the oxides of uranium, thorium, iron, cobalt, manganese, copper, and nickel, prepared by heating any of their salts, and the minerals tourmaline, pyromorphite, samarskite, fergusonite, cleveite, and pitchblende, are added to a concentrated solution of potassium iodide containing a little starch, a blue coloration is developed in a shorter or longer time. The reaction occurs also in an atmosphere of carbon dioxide. The intensity of the decomposition varies greatly and does not appear to be related to the composition of the mineral; thus the dark tourmalines produce a visible effect in one day, whilst the clear tourmalines require five days. The most intense action is produced by some uranium minerals (pitchblende, fergusonite), whilst others (thorianite, carnotite, orangite) are inactive. The most active mineral is the pitchblende from Joachimsthal. A very active pitchblende acts on potassium iodide solution containing no starch, liberating iodine, which dissolves some of the metals of the mineral. Similarly, uranium oxide forms uranium iodide. Pitchblende is not rendered inactive by washing with cold or hot water or sulphuric acid, but the wash-waters acquire the property. The activity of pitchblende is reduced by heating to redness, but when powdered very finely the mineral becomes almost or quite inactive. The activity towards potassium iodide bears no relation to the radioactivity.

E. H.

**Precipitated Sulphur.** R. H. BROWNLEE (*J. Amer. Chem. Soc.*, 1907, 29, 1032—1052. Compare Smith, *Abstr.*, 1903, ii, 139, 284; 1905, ii, 382; Smith, Holmes, and Hall, *Abstr.*, 1905, ii, 580; Smith and Holmes, *Abstr.*, 1906, ii, 157).—Berthelot prepared amorphous sulphur by various methods of precipitation and stated that the variety obtained (soluble or insoluble in carbon disulphide) does not depend on the reagent used for precipitating, but solely on the state of the sulphur in the original compound. Cloez, on the other hand, was of opinion that the sulphur obtained was soluble or insoluble according as the solution from which it was precipitated was acid or alkaline. The present investigation was undertaken with the view of studying the relation between the proportion of amorphous sulphur ( $S_\mu$ ) in samples of precipitated sulphur and the conditions under which the precipitation and hardening of the samples have taken place.

By the interaction of sulphurous acid and hydrogen sulphide, a precipitate is obtained containing from 79% to 82.6% of  $S_\mu$ . When a solution of calcium or sodium polysulphide is treated with concentrated hydrochloric acid, the precipitate contains a small proportion of  $S_\mu$ , but with acetic or dilute hydrochloric acid,  $S_\mu$  is not produced. It is found that the so-called "soluble" or "soft, amorphous sulphur" precipitated from polysulphides is not amorphous, but crystalline.

A quantitative study has been made of the proportions of  $S_\mu$  pro-

duced by the action of bromine and iodine on the sulphides and polysulphides. Bromine gives much larger proportions of  $S_\mu$  than does iodine, and the quantity formed increases in each case as the amount of the halogen is increased.

The amounts of  $S_\mu$  produced by the addition of hydrochloric acid to a solution of sodium thiosulphate of given concentration are directly proportional to the concentration of the acid after mixing. Curves which have been constructed by plotting the concentrations of the hydrogen ion after mixing as abscissæ and the percentages of  $S_\mu$  as ordinates show that the percentages of  $S_\mu$  increase more rapidly than the concentrations of the hydrogen ion. There are, however, other factors concerned in determining the proportion of  $S_\mu$  which have not yet been investigated. On comparing corresponding results at different temperatures, it is shown that the proportions of  $S_\mu$  are, in general, smaller the higher the temperature. This observation accords with the fact that  $S_\mu$ , when once hardened, is more permanent at lower temperatures.

The experiments lead to the conclusion that freshly precipitated sulphur consists entirely of  $S_\mu$  and that the reversion to  $S_\lambda$  is retarded during the hardening by the contact action of the acid or halogen in the liquid. The proportion of  $S_\mu$  which overcomes this tendency to revert depends on the concentration of the acid or halogen employed. E. G.

**A Mixed Anhydride of Sulphuric and Nitric Acids.** AMÉ PICTET and GEORGES KARL (*Compt. rend.*, 1907, 145, 238—240).—Nitric anhydride dissolves in freshly distilled melted sulphur trioxide with development of heat and production of a liquid which distils almost entirely at 218—220°. The distillate, which is a thick liquid, solidifies to a very hard, white, crystalline mass, m. p. 124—125°. The same substance is obtained as a crystalline precipitate by mixing solutions of the two anhydrides in carbon tetrachloride; it is very hygroscopic and fumes in the air. Its composition corresponds with the formula  $(SO_3)_4N_2O_5$ , and the authors propose for it the constitution represented by  $O < \begin{matrix} SO_2 \cdot O \cdot SO_2 \cdot O \cdot NO_2 \\ SO_2 \cdot O \cdot SO_2 \cdot O \cdot NO_2 \end{matrix}$ . When the powdered anhydride is added to cold benzene, nitrobenzene and benzenesulphonic acid are formed, but on pouring benzene on to excess of the anhydride the product is *m*-dinitrobenzene, which is also formed by the action of the anhydride on cold nitrobenzene. Naphthalene, anthracene, and phenanthrene give tarry products, whilst pyridine appears to form an additive compound. E. H.

**Kinetics of the Formation of Sodium Thiosulphate from Sodium Sulphite and Sulphur.** ROBERT KREMANN and K. HÜTTINGER (*Monatsh.*, 1907, 28, 901—909).—It is well known that the oxidation of sodium sulphite by atmospheric oxygen is retarded by the presence of traces of alcohol or similar substances, such as glycerol or dextrose. Considerable interest being attached to the question whether the catalyst diminishes the reactivity of the sulphite or the oxygen, the authors have studied the influence of glycerol and dextrose on an analogous reaction: the formation of sodium thiosulphate from

sodium sulphite and sulphur. It is found that the velocity of the thio-sulphate formation in aqueous solution at  $51^{\circ}$  remains unchanged on addition of 1/500 mol. of dextrose or 1/10 mol. of glycerol. Hence, in the oxidation of sodium sulphite, it must be the reactivity of the oxygen which is diminished by the catalyst. G. Y.

**Hydrazine Chlorate and Perchlorate.** ROBERTO SALVADORI (*Gazzetta*, 1907, 37, ii, 32—40).—*Hydrazine chlorate*,  $\text{N}_2\text{H}_4\cdot\text{HClO}_3$ , prepared by neutralising hydrazine hydrate solution with chloric acid, evaporating in a vacuum over sulphuric acid, and washing the yellow oil thus obtained with absolute alcohol, crystallises in white, hygroscopic plates, m. p. about  $80^{\circ}$ , and dissolves readily in water and sparingly in alcohol. In dilute solution, it gives a precipitate of hydrazine sulphate with sulphuric acid, but gives no precipitate with silver nitrate, although it reduces ammoniacal silver nitrate solution on heating. When treated with hydrochloric acid, the solid salt liberates chlorine, whilst with sulphuric acid, it explodes. Explosion of the salt is also caused by heating to its melting point, by percussion, or by detonation, the violence of the explosion being about three times as great as that obtained with mercury fulminate. On exploding or on decomposing slowly over sulphuric acid, the salt is resolved, thus:  $2\text{N}_2\text{H}_4\cdot\text{HClO}_3 = 2\text{HCl} + 4\text{H}_2\text{O} + \text{NO}_2 + 3\text{N}$  and  $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3$ . The chlorate is a powerful oxidising agent, alcohol being converted into aldehyde or even ethyl acetate at the ordinary temperature.

*Hydrazine perchlorate*,  $\text{N}_2\text{H}_4\cdot\text{HClO}_4$ , prepared by evaporation of a neutral solution of the base and acid on a water-bath, separates from absolute alcohol in acicular prisms, m. p.  $131\text{--}132^{\circ}$ , and at  $13^{\circ}$  is soluble in 1.48 times its weight of water or 34 times its weight of alcohol. When heated beyond its melting point, it does not explode, but burns rapidly like gun-cotton. Explosion occurs on percussion and is as violent as with the chlorate. From water, the salt separates in prisms, m. p.  $85^{\circ}$ , having the composition  $2\text{N}_2\text{H}_5\text{ClO}_4\cdot\text{H}_2\text{O}$ . Cryoscopic measurements show that in alcoholic solution (1.37—4.43%) the salt is only slightly dissociated, whilst in aqueous solution (0.885—7.938%) dissociation is almost complete. Hydrazine perchlorate is valuable as an explosive, owing to its stability and to the fact that it leaves no residue. T. H. P.

**Action of the Electric Spark on a Mixture of Nitrogen and Oxygen at Low Temperatures.** E. BRINER and E. DURAND (*Compt. rend.*, 1907, 145, 248—250. Compare this vol., ii, 342).—The action of the electric spark on mixtures of nitrogen and oxygen at low temperatures has been studied in the manner previously described for nitrogen and hydrogen. The mixtures used consisted of (1)  $4\text{N}_2 + \text{O}_2$  (air); (2)  $\text{N}_2 + \text{O}_2$ , and (3)  $\text{N}_2 + 2\text{O}_2$ , the last two being prepared by adding oxygen to air. For air, the limiting concentrations of the nitrogen peroxide,  $\text{NO}_2$ , formed at ordinary temperature, at the temperature of a mixture of solid carbon dioxide and ether ( $-80^{\circ}$ ), and at the temperature of liquid air ( $-190^{\circ}$ ), are 5—6%, 12—15%, and 20% respectively, the last concentration corresponding with an almost complete fixation of oxygen. With all three mixtures at the temperature of liquid air,

the product of sparking is almost entirely nitrogen peroxide, but on the region of the tube nearest the electrodes a deep blue spot is observed which at the ordinary temperature melts to a small, blue drop, most probably of nitrogen trioxide,  $N_2O_3$ .

The amounts of  $NO_2$  per kilowatt hour obtained by sparking the mixtures (1), (2), and (3) at the temperature of liquid air are 0.55, 0.77, and 0.50 gram respectively. For the third mixture at pressures from 460—217 mm., the yield of nitrogen peroxide varies from 0.8—0.6 gram per kilowatt hour, whilst at pressures between 145 mm. and 4 mm. it reaches a mean value of 1.43 grams. Comparison with the results obtained by sparking a mixture of nitrogen and hydrogen shows that more nitrogen is fixed as oxide than as ammonia.

The authors consider that both gases are formed by dissociation of nitrogen, oxygen, and hydrogen molecules, followed by recombination to nitric oxide or ammonia, the former undergoing subsequent oxidation and condensation in the cooler regions of the tube. E. H.

**Synthesis of Nitrogen Trioxide by Helbig's Method.** OSCARRE SCARPA (*Gazzetta*, 1907, 37, ii, 185—190).—For synthesising nitrous anhydride by Helbig's method (Abstr., 1903, ii, 361), the author has devised an arrangement which dispenses with fusion of a platinum wire electrode into the base of the Dewar vessel containing the liquid air, and hence lessens the danger of fracture of the vessel. The synthesis takes place in two stages: (1) In the region of the arc small amounts of the oxygen and nitrogen, formed by the evaporation of the liquid air, combine to form nitric oxide. (2) In the boiling air the reaction  $2NO + O = N_2O_3$  occurs; since the nitrous anhydride is solid, and at a temperature lower than its critical dissociation temperature, this reaction may, under favourable conditions, be practically complete. T. H. P.

**Solidifying Point and Density of White Phosphorus.** JACOB BÖSEKEN (*Rec. trav. chim.*, 1907, 26, 289—292).—When phosphorus solidifies under water, it always retains several per cent. of the latter even after being kept for some days in an evacuated desiccator. When purified by heating with chromic acid, drying in a vacuum first at 40—42°, and afterwards at 80°, and distilling, phosphorus is perfectly white and remains so if kept in evacuated tubes in the dark; in diffused light, it becomes pale yellow in a few minutes. Such purified phosphorus has m. p. 44.77°/8 mm. and  $D_{18}^{20}$  1.831; whilst, if liquefied under water, it has the solidifying point 44.14° and  $D_{18}^{20}$  1.824. The values previously obtained by different investigators for the density and melting point of phosphorus refer to the moist element. T. H. P.

**Heat of Combustion and Formation of Gaseous Hydrogen Phosphide.** PAUL LEMOULT (*Compt. rend.*, 1907, 145, 374—376).—Using a calorimetric bomb, the author has determined the heat of combustion of two samples of hydrogen phosphide containing respectively 96.7%  $PH_3$ , 0.25% hydrogen, 3.25% air, and 98.07%  $PH_3$ , 1.93% air. The amount of gas burnt was determined both by its volume and by the quantities of ortho- and pyro-phosphoric acids formed. As the mean of three concordant results, the heat of com-

bustion of pure hydrogen phosphide is found to be 310 Cal. at constant volume, 311.2 Cal. at constant pressure, and from thence the heat of formation from solid, yellow phosphorus and gaseous hydrogen to be -5.8 Cal. (compare Ogier, *Abstr.*, 1879, 5; Giran, *Abstr.*, 1904, ii, 166).

It is observed that hydrogen phosphide is spontaneously inflamed by bringing into it suddenly a jet of oxygen at about 20 atmospheres pressure, the products being hydrogen, a little yellow phosphorus, and a brick-red substance. E. H.

**Direct Oxidation of Phosphorus.** ÉMILE JUNGFLISCH (*Compt. rend.*, 1907, 145, 325—327).—The oxidation of pure dry phosphorus at low temperatures in pure oxygen at atmospheric pressure gives exclusively phosphoric oxide, but at pressures of 18—20 mm. the immediate products of oxidation are phosphorous oxide and a bright yellow compound which on dissolution in alcoholic potassium hydroxide solution and precipitation with hydrochloric acid gives the sub-oxide  $P_4O$ . When oxidised in oxygen at low pressure, the phosphorus becomes very luminous, partially fuses, and soon ignites with a large pale glaucous flame which is extinguished in a few moments, all the oxygen being absorbed. After cooling, the unchanged phosphorus is left surrounded by phosphoric oxide (formed before the reduction in pressure), by the yellow compound (a little farther away), and lastly by a white aureole of phosphorous oxide. On admission of a very small quantity of air, the vapour of the latter burns with a phosphorescent glow, whilst a larger quantity of air causes the ignition first of the solid  $P_2O_3$ , and then of the remaining phosphorus. Introduction of water instead of air into the combustion vessel produces bright flashes of light, as the dissolved oxygen oxidises small quantities of  $P_2O_3$  vapour. The resulting solution contains phosphoric and phosphorous acids with the yellow compound in suspension, the phosphorous acid amounting to 57.9% of the total phosphorus. The oxidation in this manner can be effected continuously in a tube, and the  $P_2O_3$  obtained in well-defined crystals. Whether air, pure oxygen, or oxygen mixed with an inert gas is used at low pressure, the products of oxidation are the same.

Partial oxidation of phosphorus in this manner renders it spontaneously inflammable, owing to the inflammability of the phosphorous oxide formed. E. H.

**Ortho- and Pyro-arsenic Acids.** E. BAUD (*Compt. rend.*, 1907, 145, 322—324).—Besides the two hydrates of arsenic oxide,  $As_2O_5 \cdot 4H_2O$  and  $As_2O_5 \cdot 1\frac{1}{2}H_2O$ , described by Auger (*Abstr.*, 1902, ii, 393) as the only ones existing, the author has obtained pyroarsenic acid. The hydrate,  $As_2O_5 \cdot 4H_2O$ , when placed in a desiccator containing sulphuric acid, is stable below  $10^\circ$ , but at  $15$ — $20^\circ$  it effloresces, losing  $2H_2O$ , giving  $As_2O_5 \cdot 2H_2O$  or  $H_4As_2O_7$ . The heat of solution of the product in water at  $10^\circ$  is +2.766 Cal. From this value and the heat of solution of tetrasodium pyroarsenate, on the one hand, and the heat of neutralisation of orthoarsenic acid, on the other, the value +51.87 Cal. is calculated for the mean acidity of pyroarsenic acid. Since the corresponding value for orthoarsenic acid is +47.92 Cal. (Baud and

Astruc, this vol., ii, 605), the heats of solution of the two acids differ in a like degree to those of pyro- and ortho-phosphoric acids, which are +54.15 Cal. and +49.38 Cal. (Forcrand, *Abstr.*, 1893, ii, 60) respectively. The substance  $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  is thus a hydrate of pyroarsenic acid. The very slight elevation of temperature required to transform the former into the latter indicates that both are probably of the same molecular complexity.

The heat of solution of the hydrate  $\text{As}_2\text{O}_5 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  at  $10^\circ$  is +2.306 Cal., and the values calculated for the heats of formation of  $\text{As}_2\text{O}_5 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , and  $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  from solid arsenic anhydride and liquid water are +3.694, +3.234, and +8.514 Cal. respectively. The excess of the value for the hydrate  $\text{As}_2\text{O}_5 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  over that for  $\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  indicates that the former has a greater molecular complexity.

The conclusion is drawn that orthoarsenic acid exists only in solution which deposits a hydrate of pyroarsenic acid on crystallisation.

E. H.

[Behaviour of] Carbon at High Temperatures and Pressures. HON. CHARLES A. PARSONS (*Proc. Roy. Soc.*, 1907, 79, A, 532—535).—The paper gives an account of attempts made to melt carbon by electrical resistance heating under pressure.

In one series of experiments, a thick-walled steel tube, lined with asbestos and closed with insulated steel poles, was employed; the material to be melted, carbon rods or graphite, was placed as a core between the poles. The contents were subjected to a pressure of about 30 tons per sq. inch, while currents of 6000—50,000 amperes were passed through. The heating was limited by short-circuiting, caused by the melting of the steel poles, but it was found that in some cases the carbon rods were partially converted into graphite, and when graphite was used a nucleus of very soft graphite was found in the centre. In another series of experiments, a barrier of insulating material, with a hole in it between the poles, was used; the hole was filled with graphite and a powerful current passed through while the materials were under a pressure of 100 tons per sq. inch. When fused magnesium oxide was used as insulating material, magnesium carbide was formed, and the rest of the graphite was changed to a soft, flaky form. Silica was also used as insulating material.

In a third series of experiments, the tube, lined with marble, was filled with liquid carbon dioxide, subjected to a pressure of 30 tons to the sq. inch, and a powerful current passed through the central carbon rod. The resulting carbon monoxide was allowed to escape, and it was found that part of the carbon had been changed into graphite and part was found in the amorphous form. The stable form of carbon, after heating at very high temperatures, is probably soft graphite. In none of the experiments did the residue contain "more than a suspicion" of black or transparent diamond.

Cores of iron and carbon were subjected to intense heat under a pressure of 30—75 tons per sq. inch, but the cooled residue contained little or no carbon in the form of diamond, and as these pressures are probably greater than those produced in cast-iron when suddenly

cooled, it appears that mechanical pressure is not the cause of the production of diamond in rapidly-cooled iron containing carbon. G. S.

**Preparation of Certain Silicates.** GERH. STEIN (*Zeitsch. anorg. Chem.*, 1907, 55, 159—174).—The experiments described in the paper were mainly carried out in specially-prepared carbon crucibles which could be used up to  $2100^{\circ}$ ; the temperatures were determined by means of an optical pyrometer.

Quartz fuses at  $1600^{\circ}$  to a viscous liquid, which is mobile at  $1750^{\circ}$ ; at the latter temperature, it is somewhat volatile and condenses partially as crystals of tridymite, D 2.4; the fused mass in the crucible could not be brought to crystallise, even on cooling very slowly.

Quartz sand has a reversible transition point at  $552^{\circ}$ ; chalcedony one at  $173^{\circ}$ .

The *metasilicates* of the alkaline earths and of zinc, manganese, and iron were prepared by fusing together calculated amounts of the respective oxides and silicon dioxide at  $1600^{\circ}$ . The melting points and densities (in crystalline, and in some cases also in amorphous, form) of the compounds in question are as follows:  $\text{GHSiO}_3$ , m. p. above  $2000^{\circ}$ , D 2.35 (crystals);  $\text{MgSiO}_3$ , m. p.  $1565^{\circ}$ , D 3.06 (crystals);  $\text{CaSiO}_3$ , m. p.  $1512^{\circ}$ , D 2.92 (crystals), 2.90 (glass);  $\text{FeSiO}_3$ , m. p.  $1500$ — $1550^{\circ}$ , D 3.44;  $\text{MnSiO}_3$ , m. p.  $1470$ — $1500^{\circ}$ , D 3.58 (crystals), 3.36 (glass);  $\text{ZnSiO}_3$ , m. p.  $1479^{\circ}$ , D 3.42 (crystals), 3.86 (glass);  $\text{SrSiO}_3$ , m. p.  $1287^{\circ}$ , D 3.91 (crystals);  $\text{BaSiO}_3$ , m. p.  $1368.5^{\circ}$ , D 3.77 (crystals), 3.74 (glass).

Some *orthosilicates* were prepared by fusing 2 mols. of the oxide with 1 mol. of silicon dioxide in carbon or porcelain crucibles. Orthosilicates of calcium, strontium, and barium could not be obtained in this way, as at the high temperatures employed the oxides attacked the carbon crucible with formation of calcium carbide. The data for the orthosilicates are as follows:  $\text{GHSiO}_4$ , m. p. above  $2000^{\circ}$ , D 2.46 (crystals);  $\text{Mg}_2\text{SiO}_4$ , m. p. below  $1900^{\circ}$ , D 3.2 (crystals), 3.19—3.24 (natural mineral);  $\text{Zn}_2\text{SiO}_4$ , m. p.  $1484^{\circ}$ , D 3.7 (crystals), 3.4—3.7 (mineral);  $\text{Sr}_2\text{SiO}_4$ , m. p.  $1593^{\circ}$ , D 3.84 (crystals).

The formation of calcium carbide, referred to above, was further investigated. Two mols. each of charcoal (lamp-black) and of an alkaline earth oxide were fused for a considerable time with 1 mol. of silicon dioxide, and it was then found that both silicate and carbide were formed, but a large proportion of the metallic oxide remained uncombined. When metasilicates of the alkaline earths are heated with carbon at  $2000^{\circ}$ , a considerable proportion of metallic carbide is formed. Calcium carbide and silicon dioxide were heated at  $1950$ — $2000^{\circ}$  for some time, and it was found that the fused residue contained no carbide, but a large proportion of free carbon.

A number of double silicates containing aluminium were prepared by fusing the components in the requisite proportions for some time at  $1600^{\circ}$ . Some were obtained as crystals, one in the amorphous form only, whilst two were prepared in both forms. The crystals of natural and artificial potassium nepheline,  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , have both D 2.6, whilst artificial spodumene,  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ , has D 2.42 and the mineral D 3.4—3.7.

Aluminium oxide as well as cerium oxide was fused with silicon dioxide in varying proportions at 1700—1900°. From an examination of sections of the solidified crystalline products, it has not been found possible to determine definitely what silicates of aluminium are produced, but evidence has been obtained that two cerium silicates,  $\text{Ce}_2\text{O}_3\cdot\text{SiO}_2$  and  $\text{Ce}_2\text{O}_3\cdot 2\text{SiO}_2$ , are formed.

Silicates of the rare earths, yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, and erbium, of the type  $\text{M}_2\text{O}_3\cdot\text{SiO}_2$  have been obtained by fusing the respective oxides with silicon dioxide at 1700° for some time. The cooled conglomerates were all crystalline, stable towards water; they are attacked slowly by boiling concentrated sodium hydroxide, but rapidly by dilute acids. The compound,  $\text{Nd}_2\text{O}_3\cdot\text{SiO}_2$ , is violet,  $\text{Pr}_2\text{O}_3\cdot\text{SiO}_2$  green, and  $\text{Er}_2\text{O}_3\cdot\text{SiO}_2$  rose-coloured. Several of these silicates break down to a powder on being kept.

Silicon dioxide was also heated with equivalent amounts of the anhydrous oxides,  $\text{ZrO}_2$ ,  $\text{ThO}_2$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ , and  $\text{TiO}_2$ . The mixture containing the first two oxides could not be properly fused even at 2000°; the oxides,  $\text{MoO}_3$  and  $\text{WO}_3$ , were partially reduced by the carbon of the crucible, whilst the mixture containing titanium oxide fused completely at 1750°; the solidified mass contained some small blue crystals, but also combined carbon. G. S.

**Production and Alteration of Glass containing Water.** FRANZ MYLIUS and ERICH GROSCHUFF (*Zeitsch. anorg. Chem.*, 1907, 55, 101—118. Compare Foerster, *Abstr.*, 1894, ii, 541).—Resistant glass is only slightly affected by prolonged contact with dilute sulphuric acid and very little water is absorbed, but ordinary glass at room temperature loses up to 12% of alkali and absorbs about 12% of water without losing its characteristic properties. When glass containing absorbed water is heated slowly, the altered surface layers peel off, but when the temperature is suddenly raised to at least 400° the glass loses its ordinary (colloidal) properties, and either a solid compound is precipitated in the interior or a "frothy" appearance is produced. The latter phenomenon is due to the sudden production of bubbles of steam in the interior and only occurs in plastic glasses, not in difficultly fusible glasses rich in silica. On the other hand, the separation of a solid phase takes place most readily in glasses rich in silica, and the substance in question is probably silica. Glass does not lose its characteristic properties at the ordinary temperature, even although kept for fifteen years in dilute sulphuric acid, and the separation of a new phase may not take place even at 400° if the rise of temperature is very gradual. G. S.

**Polymorphism of Rubidium Dichromate.** WILLEM STORTENBEKER (*Rec. trav. chim.*, 1907, 26, 240—247. Compare Wyruboff, *Bull. Soc. chim.*, 1901, [iii], 25, 105; *Abstr.*, 1901, ii, 149).—The author has measured the solubilities of monoclinic and triclinic crystals of rubidium dichromate, as well as of the crystals obtained at the ordinary temperature. The last are slightly more soluble than the monoclinic, and these appreciably more soluble than the triclinic crystals. The triclinic form is hence the most stable. The conclusion is drawn



that the monoclinic and triclinic modifications of rubidium dichromate are monotropic, but that the small difference in stability between them retards the transformation of one into the other. If the time is great, the triclinic form is obtained, but a rapid crystallisation gives sometimes the monoclinic, sometimes the triclinic, and sometimes a mixture of the two. This is probably the explanation of Wyruboff's statement (*loc. cit.*) to the effect that, if crystals of one form are placed in contact with a saturated solution of the other, they remain indefinitely without showing the slightest indication of transformation, no matter what the temperature.

T. H. P.

**Lithium Orthophosphate.** ANTONIO QUARTAROLI (*Gazzetta*, 1907, 37, i, 598—611).—In aqueous solution, monocalcium or monobarium phosphate is partially decomposed by heat, by alcohol or other solvents into phosphoric acid and dicalcium or dibarium phosphate; the corresponding magnesium compound is slightly decomposed in a similar way by alcohol, but is unaffected by heating, whilst the lithium salt is not changed either by heat or by alcohol. These changes, produced by alcohol or heat, also take place, although extremely slowly, in the cold. Dilithium orthophosphate dissolves in water to an appreciable extent, being much more soluble than the analogous magnesium salt, but, like the latter and like also the corresponding calcium and barium salts, it undergoes partial decomposition into trilithium and monolithium phosphates when the solution is heated. On addition of three or more equivalents to 1 mol. of phosphoric acid in solution, phosphates are formed containing more than 3 and sometimes as much as 3.5 equivalents of lithia, the base being unequally distributed between the precipitate formed and the solution.

On heating 1 mol. of phosphoric acid with 1 equivalent of lithia and 2 equivalents of potash or with 2 of the former and 1 of the latter base, a phosphate is precipitated having a basicity of about 3.5, whilst with 1 mol. of phosphoric acid, 1 equiv. of lithia, and 1 equiv. of potash the precipitate is practically tribasic lithium phosphate. With 1 mol. of phosphoric acid, 1 equiv. of lime, and 2 equivs. of lithia, one-third of the acid is precipitated as tricalcium phosphate and the remaining two-thirds remains in solution as trilithium phosphate; and with 1 mol. of phosphoric acid, 1 equiv. of baryta, and 2 equivs. of lithia, an insoluble double phosphate is formed, but to a less extent than when soda or potash is used in place of the lithia (see Abstr., 1905, ii, 821).

When precipitating salts of lithium by disodium phosphate, it is generally recommended to add alkali to render complete the precipitation according to the equation:  $3\text{LiCl} + \text{Na}_2\text{HPO}_4 = \text{Li}_3\text{PO}_4 + 2\text{NaCl} + \text{HCl}$ . The author finds that, if the solution is kept just sufficiently alkaline to give a scarcely perceptible reaction with phenolphthalein, the precipitate obtained contains 59.9—60.5%  $\text{P}_2\text{O}_5$ , instead of 61.2%, the error amounting to 0.87—0.47%. If, however, precipitation occurs in presence of excess of alkali, the precipitate always contains about 55.6%  $\text{P}_2\text{O}_5$ , the error of the estimation being hence 3.8%.

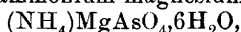
T. H. P.

**The Ammonia Soda Process from the Standpoint of the Phase Rule.** ERNST JÄNECKE (*Zeitsch. angew. Chem.*, 1907, 20, 1559—1564).—An application of the author's graphical method of representing reciprocal pairs of salts (Abstr., 1906, ii, 833) to the discussion of the ammonia soda process from the standpoint of the phase rule (compare Fedotéeff, Abstr., 1904, ii, 730). The theoretical consideration of the problem points to the possibility of increasing the yield of ammonia by maintaining the temperature at 32° and adding solid sodium chloride to the saturated salt solution. G. Y.

**Decomposition of Hydrated Ammonium Salts.** WILLIAM M. DEHN and EDWARD O. HEUSE (*J. Amer. Chem. Soc.*, 1907, 29, 1137—1165).—When ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , is heated, it loses  $1\text{H}_2\text{O}$  below 100°; between this temperature and 150°, it suffers a further loss of water and is partially converted into oxamide. Above 150°, ammonia is evolved, and above 280° the oxamide undergoes decomposition into cyanogen and water. These observations have been confirmed by determining the vapour pressures of ammonium oxalate between 71° and 141°, and of oxamide between 265° and 292°. Ammonium hydrogen oxalate,  $(\text{NH}_4)\text{HC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , is stable up to 75°, loses  $1\text{H}_2\text{O}$  below 170°, and suffers decomposition at 183° with further loss of water and probable formation of oximide. In this case also, the changes have been confirmed by vapour pressure determinations.

These results indicate that the initial and predominating reaction of such decompositions involves the expulsion of water, and that, simultaneously and especially at higher temperatures, secondary reactions occur involving the dissociation of the ammonium salt. A study of the decomposition of inorganic hydrated ammonium salts has been carried out with the object of elucidating the structure of hydrated salts.

The effect of heat on ammonium magnesium arsenate,



ammonium calcium arsenate,  $(\text{NH}_4)\text{CaAsO}_4 \cdot 6\text{H}_2\text{O}$ , strontium and barium hydrogen arsenates,  $\text{SrHAsO}_4 \cdot \text{H}_2\text{O}$  and  $\text{BaHAsO}_4 \cdot \text{H}_2\text{O}$ , ammonium magnesium phosphate,  $(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ , and sodium ammonium hydrogen phosphate,  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot \text{H}_2\text{O}$ , has been investigated. The results are tabulated and the vapour pressures are plotted as curves. The data thus obtained have led to the following conclusions.

When ammonium salts are partially dehydrated, products of indefinite composition are formed, owing to the fact that both water and ammonia are evolved simultaneously at most temperatures above the initial temperature of decomposition, and for this reason homogeneous products cannot be obtained by drying such salts on the water-bath. Consequently, many of the empirical formulæ which have been assigned to these compounds are incorrect. The water of composition and the ammonia in these salts do not differ much from one another in their affinity and mode of union. Water of crystallisation is held in definite molecular structures in accordance with the laws of valency. The quadrivalent oxygen involved in these structures

is loosened at temperatures above  $100^{\circ}$ , and it is usual therefore for water of crystallisation to be expelled below  $100^{\circ}$  and water of composition above this temperature. The discovery of dissimilar molecules of water in hydrated salts gives a clue to their structure, and constitutional formulæ have been suggested for all the salts investigated. For example, the structure of ammonium magnesium arsenate is regarded as  $\text{H}_2\text{O} \xrightarrow{\text{H}} \text{OMg} \cdot \text{O} \cdot \text{As} \left( \text{O} \xleftarrow{\text{H}} \text{OH}_2 \right)_3$ . This formula is supported by the following facts. When the salt is heated,  $4\text{H}_2\text{O}$  are given off below  $80^{\circ}$ ,  $2\text{H}_2\text{O}$  between  $80^{\circ}$  and  $100^{\circ}$ , and the last  $\frac{1}{2}\text{H}_2\text{O}$ , derived from the  $\cdot\text{O}(\text{NH}_4)$  group, is slowly expelled at  $150\text{--}225^{\circ}$ , magnesium pyroarsenate being produced.

E. G.

**Silver.** ÉMILE VIGOUROUX (*Bull. Soc. chim.*, 1907, [iv], 1, 792—796).—Silver chloride is readily reduced by aluminium in presence of hydrochloric acid or ammonia solution. With water alone, the reduction proceeds slowly even on warming, and similarly in presence of benzene, ether, or chloroform the action is slow, but is accelerated by the addition of powdered silver.

Details are given of a process for the preparation of pulverulent silver, containing 99.8 per cent. of the metal, from jewellers' or demonetised silver, depending on the reduction of the chloride by aluminium in presence of hydrochloric acid.

T. A. H.

**Bivalent Silver.** GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 72—79. Compare Abstr., 1906, ii, 612).—In the oxidation of silver pyrophosphate by means of potassium persulphate, the ratio Ag : active oxygen in the compound formed is found to be 13.12—14.89, the value required by a compound corresponding with the oxide AgO being 13.5.

The oxide AgO, in concentrated nitric acid solution, does not reduce lead dioxide, manganese dioxide, or potassium permanganate (compare Piccini, Abstr., 1897, ii, 99), nor does it give rise to hydrogen peroxide; it cannot therefore be regarded as a true peroxide. Confirmation of this view is found in the observation that silver oxide, when treated with permanganate in alkaline solution, undergoes partial oxidation to  $\text{AgO} : \text{Ag}_2\text{O} + 2\text{KMnO}_4 + 2\text{NaOH} = 2\text{AgO} + \text{K}_2\text{MnO}_4 + \text{Na}_2\text{MnO}_4 + \text{H}_2\text{O}$ , an action which is reversible.

The oxide AgO is a weaker base than  $\text{Ag}_2\text{O}$  and its solution in concentrated nitric acid contains the readily hydrolysable salt  $\text{Ag}(\text{NO}_3)_2$ . The ion  $\text{Ag}^{++}$  is moderately stable only in presence of a large excess of the anions  $\text{NO}_3$ , with which it probably forms complex anions; in the free state, it decomposes water like the ions  $\text{Co}^{+++}$ ,  $\text{Ce}^{++++}$ , &c. When dissolved in concentrated nitric acid, silver nitrate acts as a reducing agent towards  $\text{PbO}_2$  or  $\text{Bi}_2\text{O}_3$ , and in some cases as much as 90% of the silver nitrate undergoes oxidation to  $\text{Ag}(\text{NO}_3)_2$ . It is to this oxidisability in nitric acid that silver salts owe the accelerating influence they exert on certain oxidations.

T. H. P.

**Metallic Calcium.** WILHELM MUTHMANN, L. WEISS, and JOSEF METZGER (*Annalen*, 1907, 355, 137—143).—Commercial calcium con-

tains calcium chloride, which can be removed to a large extent by treatment with absolute alcohol. A further purification is effected by fusing calcium with calcium chlorofluoride in an iron bomb at a temperature not exceeding bright redness, whereby the metal is obtained free from chlorine and iron; it has D 1.4153. The heat of combustion of Bitterfeld calcium is 80.097 Cal., or 81.32 Cal. assuming the presence of 1% of chlorine. A perfectly clear molten oxide is obtained when calcium, containing more than 1% of chlorine, is burnt in compressed oxygen; with less than this amount of chlorine, the oxide does not fuse.

By the action of calcium on molten salts in an iron bomb, the following results are obtained. Sodium chloride at 950° is reduced to the metal, which, however, cannot be obtained free from calcium; potassium chloride at 1200—1600° behaves in a similar manner, but, in addition, the surface of the metallic regulus is covered with fine steel-blue crystals, which decompose rapidly in air; their composition approximates to that of the *chloride*,  $K_2Cl$ . Barium chloride or strontium chloride yields an alloy. Cryolite yields aluminium (99.82%) free from calcium. Calcium borate yields a brown substance,  $CaB_7$ , which is probably a mixture of amorphous boron and Moissan's boride,  $CaB_6$ . When equal quantities of calcium and sodium are fused in the bomb, the regulus obtained consists of two layers, the upper rich in sodium and the lower in calcium; these alloys appear to disintegrate into their constituents when cold. The tendency of potassium to dissolve calcium is very much less than that of sodium. C. S.

**Dissociation of Calcium Carbonate.** D. ZAVRIEFF (*Compt. rend.*, 1907, 145, 428—429).—By heating quantities of 5 grams of white marble or calcite, in some cases previously treated with a fused mixture of alkali and alkali-earth double carbonates, taking precautions to obtain a uniform temperature, the author obtains the following dissociation pressures at the temperatures indicated:

Temperature	926°	910°	892°	870°	840°	815°	725°
Pressure in mm.	1022	755	626	500	342	230	67.

910°, which corresponds with a dissociation pressure of 1 atmosphere, is the temperature observed by Le Chatelier (*Abstr.*, 1886, 760) for the rapid decomposition of calcium carbonate. E. H.

**Potassium Ammoniozincate.** EDWARD C. FRANKLIN (*Zeitsch. anorg. Chem.*, 1907, 55, 195—199).—A *potassium ammoniozincate*,  $Zn(NHK)_2 \cdot 2NH_3$ , previously prepared according to two different methods by Fitzgerald (this vol., ii, 545), but not fully investigated, has now been obtained in well-formed crystals by the action of excess of potassamide, dissolved in liquid ammonia, on ammoniacal zinc iodide, the reaction being represented by the equation:  $ZnI_2 \cdot 4NH_3 + 4KNH_2 = Zn(NHK)_2 \cdot 2NH_3 + 2KI + 2NH_3$ . The compound is only slightly soluble in liquid ammonia, but dissolves in that solvent in the presence of ammonium salts. It is rapidly decomposed by water and is readily soluble in dilute aqueous solutions of acids. It is not explosive. It is stable when heated at 160° in a vacuum, but at 250° it loses a considerable proportion of ammonia, and at higher temperatures suffers more complete decomposition. As the products of decomposition

attack glass and platinum, the formulæ of the compounds obtained on heating the salt could not be definitely established, but there is some evidence that at  $250^{\circ}$  a compound,  $\text{Zn}(\text{NHK})_{2, \frac{1}{2}}\text{NH}_3$ , is produced.

G. S.

**Ternary Alloys of Lead, Magnesium, and Tin.** A von VEGESACK (*Zeitsch. anorg. Chem.*, 1907, 54, 367—416).—In the theoretical part of the paper, the application of thermal analysis to systems of three components, *A*, *B*, and *C* (compare Sahmen and Vegesack, this vol., ii, 532), is extended to cases in which two binary compounds,  $\text{Am}_1\text{Bn}_1$  and  $\text{Am}_2\text{Cn}_2$ , occur, but no ternary compounds or ternary mixed crystals. The cases (*a*) in which no binary mixed crystals occur, (*b*) in which the binary compounds are wholly or partially miscible in the solid state, are considered separately.

The experimental investigation of the system lead—magnesium—tin has shown that the only solid phases are the three components, the binary compounds  $\text{SnMg}_2$  and  $\text{PbMg}_2$ , and two series of mixed crystals rich in  $\text{SnMg}_2$  ( $\alpha$ -crystals) and  $\text{PbMg}_2$  ( $\beta$ -crystals) respectively. The equilibrium temperatures have been determined in several series of investigations and the results are represented on a projected space diagram, the temperature being represented on the vertical axis in the usual way. The more important points on the diagram and the composition of the alloy at these points are as follows: Saturated  $\alpha$ - and  $\beta$ -crystals are in equilibrium at  $570^{\circ}$  with a fused alloy of the composition 66.7 atom % magnesium, 0.9 tin, and 32.4 lead. Lead and  $\alpha$ -crystals are in equilibrium at  $300^{\circ}$  with a fused alloy of the composition 7.8 atom % magnesium, 4 of tin, and 88.2 of lead.  $\alpha$ - and  $\beta$ -Crystals are in equilibrium with magnesium and with a fused alloy of the composition 80.7 atom % magnesium and 19.3 of lead at  $467^{\circ}$ . The binary mixed crystals are in equilibrium with lead and with a fused alloy of the composition 20.8 atom % magnesium and 79.2 lead at  $248^{\circ}$ . From a fused alloy of the composition 7.9 atom % magnesium, 73.6 atom % tin, and 18.5 lead, the latter metal, tin, and  $\alpha$ -crystals separate simultaneously at a temperature of  $166^{\circ}$ , which represents a temperature minimum. The highest point of the figure represents the melting point of  $\text{SnMg}_2$  at  $783^{\circ}$ .

The results deduced from the freezing-point observations have been confirmed by microscopic observations. The alloys, consisting mainly of the compounds  $\text{PbMg}_2$  and  $\text{SnMg}_2$ , are very porous and brittle, and oxidise rapidly in the air; with increase in the amount of magnesium, the brittleness decreases.

The paper is illustrated by photomicrographs.

G. S.

**Oxides of Thallium. III.** OTTO RABE (*Zeitsch. anorg. Chem.*, 1907, 55, 130—146).—Even after drying in a vacuum over sulphuric acid to constant weight, the brown and black thallic oxides already described (Abstr., 1906, ii, 285, 672) contain traces of moisture (much less than one equivalent) which can only be removed completely by heating for several hours at  $500^{\circ}$ . When heated in a current of dry air at  $110$ — $500^{\circ}$ , there appears to be an equilibrium in which the brown oxide retains gradually diminishing amounts of moisture; the equilibrium at any one temperature is reached in one to two hours,

and is not altered after twenty-four hours. When completely dried at  $500^{\circ}$ , the oxides are not hygroscopic.

Contrary to the general opinion, black thallic oxide can be heated at  $600^{\circ}$  for hours without decomposing, although under these conditions it volatilises slightly; it melts at  $725 \pm 10^{\circ}$ , and at  $800\text{--}1000^{\circ}$  rapidly loses oxygen and changes to thalious oxide.

On heating at  $100^{\circ}$ , the brown oxide changes slowly to the black modification, and this change proceeds more rapidly the higher the temperature; at  $520^{\circ}$ , it is complete within twenty-four hours. G. S.

**Chemistry of Thallium.** II. L. F. HAWLEY (*J. Amer. Chem. Soc.*, 1907, 29, 1011—1019. Compare this vol., ii, 460).—Thallium can be easily and accurately estimated by precipitation with sodium thioannate, since thallium thioannate,  $\text{Tl}_4\text{SnS}_4$  (Abstr., 1906, ii, 854), is practically insoluble in water and can be dried at  $105^{\circ}$  without decomposition. Excess of sodium thioannate is added to a hot and very slightly acid solution of the thalious or thallic salt. A solution of sodium sulphide is added drop by drop until the liquid is neutral and then in larger quantity. The mixture is boiled gently for five minutes, then diluted with water, and left for two or three hours. The precipitate is collected in a Gooch crucible, dried, and weighed.

A study has been made of the composition of the precipitates produced when mixtures of thalious salts and arsenic salts are treated with hydrogen sulphide in alkaline or acid solution. The products formed by the simultaneous precipitation of antimony sulphides and thalious sulphide, and of stannous sulphide and thalious sulphide, have also been investigated. With arsenic trisulphide, no definite compound is produced, but a series of solid solutions,  $x\text{Tl}_2\text{S}_3.y\text{As}_2\text{S}_3$ , are formed extending from pure arsenic trisulphide to about 62 mol. % arsenic trisulphide. With arsenic pentasulphide, a compound,  $\text{Tl}_3\text{AsS}_4$ , is produced, but solid solutions are not formed. Antimony trisulphide and pentasulphide yield complete series of solid solutions extending from pure thalious sulphide to pure antimony tri- or penta-sulphide. Stannous sulphide yields similarly a complete series of solid solutions.

The compounds of thallium and sulphur have also been studied. By treating thalious sulphide with sodium sulphide solutions in which varying amounts of sulphur have been dissolved and afterwards saturating with hydrogen sulphide, products are obtained containing from 90.49% of thallium (corresponding with  $\text{Tl}_2\text{S}$ ) to about 70% of thallium. By adding an acid solution of a thallium salt to a slight excess of sodium polysulphide, precipitates can be obtained containing from 25% to nearly 100% of sulphur. It is found that between pure thalious sulphide and the product containing about 81% of thallium, the solid is homogeneous; from 81% to 76% of thallium, phases are distinguishable, whilst from 76% of thallium to pure sulphur the solid is again homogeneous. The conclusion is drawn that the end concentration is 80.93% of thallium (equivalent to  $\text{Tl}_2\text{S}_3$ ), and that the salts  $\text{Tl}_2\text{S}$  and  $\text{Tl}_2\text{S}_3$  form a complete series of solid solutions. E. G.

**Thalious Salts.** WILLEM STORTENBEKER (*Rec. trav. chim.*, 1907, 26, 248—252).—With reference to the dimorphism of thalious hydrogen

sulphate, the author finds that the rhombic needles obtained previously by him (Abstr., 1902, ii, 397) really have the composition  $\text{TiHSO}_4$ .

The preparation of thallous dithionate from thallous sulphate and barium dithionate is complicated by the facts that barium and thallium dithionates form anhydrous mixed crystals and that thallous sulphate and dithionate form a double salt. Either the calculated amounts of the two salts may be taken or else the thallous sulphate may be added in such slight excess that a fresh addition to the filtered solution causes no further precipitation. The salt is then fractionally crystallised until free from sulphate.

Thallium may be separated from most other metals in the form of chloride or iodide. The solution is precipitated by hydrochloric acid and the thallous chloride filtered and washed with water. The small amount of thallium remaining in the filtrate is precipitated by the addition of potassium iodide, the thallous iodide being washed first with dilute potassium iodide solution and afterwards with 75% alcohol. The mixture of thallous chloride and iodide is dried and weighed, and then decomposed by an equal weight of sulphuric acid mixed with a little water in a porcelain capsule on a sand-bath. Prolonged heating removes the volatile substances, fused thallous hydrogen sulphate remaining. This is dissolved in boiling water, from which, after any lead or silver present is precipitated by hydrogen sulphide, thallous sulphate,  $\text{Ti}_2\text{SO}_4$ , crystallises. T. H. P.

**Copper Peroxide and the Catalytic Decomposition of Hypohalogenite Solutions by Copper.** ERICH MÜLLER (*Zeitsch. anorg. Chem.*, 1907, 54, 417—422).—Krüger (1844) found that by the action of chlorine gas on cupric hydroxide, suspended in potassium hydroxide solution, a red solution was obtained, which rapidly decomposed with liberation of oxygen and precipitation of black cupric oxide. Moser (this vol., ii, 549) could not confirm this observation, but the author now shows that an unstable red solution, and, under different conditions, an unstable, yellow copper peroxide may be obtained by the action of bromine or chlorine on cupric hydroxide in alkaline solution.

The formation of the yellow peroxide in solution or (in more concentrated alkali) as a precipitate is best shown by the action of chlorine or bromine on a solution of cupric hydroxide in concentrated sodium hydroxide solution; on being kept, the yellow solution gradually regains its blue colour, oxygen being evolved simultaneously. When, on the other hand, a strongly alkaline hypochlorite or hypobromite solution is added drop by drop to cupric hydroxide rubbed up in a mortar, the hydroxide thus being in excess, the mass is at first carmine-red, then violet-blue, and finally brownish-black.

The intermediate formation of the yellow peroxide in the solid form can also be observed when a strongly alkaline hypochlorite solution is brought into contact with copper foil. G. S.

**Reduction of Cupric to Cuprous Sulphide.** RUDOLF F. WEINLAND and L. STORZ (*Ber. deut. pharm. Ges.*, 1907, 17, 272—274).—Gutmann (Abstr., 1905, ii, 384, 813) has shown that sodium arsenite reduces sodium tetrathionate and trithionate to sulphate. It is now

found that cupric sulphide is rapidly reduced to cuprous sulphide by an alkaline solution of trisodium arsenite, which becomes monothioarsenate.  
E. F. A.

**Mercuric Bromide.** A. VICARIO (*J. Pharm. Chim.*, 1907, [vi], 26, 145—152).—To the solubility of mercuric bromide have been ascribed values varying from 0.4 to 1.25 per 100 parts of cold water and from 4 to 20 parts per 100 of boiling water. The differences in the numbers given by various investigators are due to the fact that mercuric bromide is attacked by boiling water with formation of hydrobromic acid and yellow oxybromides which crystallise on cooling. The author finds that mercuric bromide is soluble in cold water, with which it has not been heated, to the extent of 0.4%, whilst its solubility in water just beginning to boil is about 2.5%. Mercuric bromide forms, with sodium bromide and chloride, the compounds  $\text{HgBr}_2 \cdot 2\text{NaBr}$  and  $\text{HgBr}_2 \cdot 2\text{NaCl}$ , which are extremely soluble in water and are very suitable for hypodermic injection. These solutions should be prepared in the cold, owing to the facility with which the mercuric bromide decomposes. When thus prepared, they can, however, be boiled or sterilised at  $120^\circ$  without undergoing decomposition. The compound  $\text{HgBr}_2 \cdot 2\text{NaBr}$  is preferable to  $\text{HgBr}_2 \cdot 2\text{NaCl}$ , owing to its absolute neutrality and to the fact that it has no action on protein. Both these compounds can be obtained in a crystalline condition.  
T. H. P.

**New Method of Preparing Mercurous Iodide.** PANCHANAN NEOGI (*J. Asiatic Soc. Bengal*, 1907, 3, 133—134. Compare Strohman, *Abstr.*, 1888, 111; Rây, *Proc.*, 1899, 239).—Mercurous iodide is formed when mercury is allowed to remain in contact with either methyl, ethyl, or isopropyl iodide; the product so obtained yields on sublimation, and subsequent treatment with alcohol to remove mercuric iodide, yellow crystals of pure mercurous iodide.  
W. H. G.

**A Triple Salt of Mercury.** CAMILLO BRÜCKNER (*Monatsh.*, 1907, 28, 961—963).—The reaction mixture obtained when mercuric sulphate is treated with iodine and water (*Abstr.*, 1906, ii, 613) consists of a liquid and a solid phase. The liquid phase contains free sulphuric acid together with traces of mercuric iodide and the double salt of mercuric iodate and basic sulphate. The solid phase contains mercuric iodide and a triple salt,  $6(3\text{HgO} \cdot 2\text{SO}_3) \cdot 6\text{HgI}_2 \cdot \text{HgI}_2\text{O}_6$ , which is formed also by adding alcoholic iodine to the aqueous solution obtained on shaking neutral mercuric sulphate with water. It forms doubly refracting, white, microscopic needles, is decomposed by water forming basic mercuric sulphate, mercuric iodide, and mercuric iodate, or by dilute sulphuric acid forming the iodide and iodate, whilst the sulphate remains in solution and on treatment with hydrochloric acid yields free iodine.  
G. Y.

**Preparation of the Metals of the Rare Earths by Electrolysis of the Fluorides.** WILHELM MUTHMANN, L. WEISS, and JULIUS SCHEIDEMANDEL (*Annalen*, 1907, 355, 116—136).—A detailed account of experiments carried out with the object of ascertaining the most satisfactory conditions for the electrolytic preparation of the rare



metals. It is found, for example, that a yield of metal, corresponding with 57% of the current used, is readily obtained by the electrolysis of cerium oxide dissolved in cerium fluoride, with a current density at the cathode of 9—10 amperes, and at the anode of 3 amperes per sq. cm. With the furnace employed, a current of 750 amperes and 7.5 volts was used during the electrolysis. It is important that the materials used should be free from silica, otherwise the metal obtained is contaminated with this impurity. Potassium fluoride, calcium fluoride, and cryolite cannot be employed with success in place of the fluoride of the rare metal.

W. H. G.

**A General Method of Preparing Anhydrous Metallic Bromides from the Oxides.** FRANÇOIS BOURION (*Compt. rend.*, 1907, 145, 243—246).—The simultaneous action of sulphur chloride and hydrogen bromide on oxides heated never above redness and often at a lower temperature affords a convenient method of preparing anhydrous bromides.

Thus by distilling sulphur chloride at 135° in a current of hydrogen bromide on to heated thoria, a white, crystalline mass of thorium tetrabromide,  $\text{ThBr}_4$ , is formed, whilst if the temperature of the sulphur chloride vapour is reduced (by reducing the pressure) to 125° a white, amorphous, friable mass of thorium oxybromide,  $\text{ThOBr}_2$ , which completely dissolves in water with a slight hissing, is produced. Chromium sesquioxide with sulphur chloride at 135° gives the bromide,  $\text{CrBr}_3$ , in black, crystalline scales. Nickel and cobalt oxides give the salmon-yellow nickel bromide,  $\text{NiBr}_2$ , and the green cobalt bromide,  $\text{CoBr}_2$ , both well crystallised. The oxides of the rare earths, whatever their degree of oxidation, give bromides of the type  $\text{MBr}_3$ . The violet neodymium oxide,  $\text{Nd}_2\text{O}_3$ , gives the violet bromide,  $\text{NdBr}_3$ ; black praseodymium oxide,  $\text{Pr}_4\text{O}_7$ , the green bromide,  $\text{PrBr}_3$ ; yellowish-white samarium oxide,  $\text{Sm}_2\text{O}_3$ , the yellow bromide,  $\text{SmBr}_3$ ; yellowish-white cerium oxide,  $\text{Ce}_2\text{O}_3$ , the bromide,  $\text{CeBr}_3$ , and the oxides of lanthanum, dysprosium, gadolinium, ytterbium, and terbium give white bromides.

The first four of these bromides are obtained in a fused state and dissolve slowly in water, the others dissolve with hissing. All give solutions which change litmus to a wine-red colour, but have no action on methyl-orange.

In the case of the more easily reduced oxides, for instance, those of nickel and cobalt, the method can be simplified by omitting the use of sulphur chloride. In order to obtain bromides entirely free from chlorides, it is necessary to vaporise the sulphur chloride between 60° and 90°.

E. H.

**Electrolysis of Thorium Nitrate.** OTTORINO ANGELUCCI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 196—198).—When thorium nitrate solutions of various concentrations are electrolysed, an extremely thin layer of material having an extraordinarily high radio-activity is deposited on the negative electrode, whilst if the current density is sufficiently great, thorium oxide is deposited on the positive electrode. The deposit on the negative electrode consists of lead

oxide, and electroscopic examination shows that its activity is due exclusively to thorium *A*; hence the latter, even in solution, is deposited on negatively charged bodies. Electroscopic examination of the thorium oxide from the positive electrode indicates that it contains thorium *X*. When a 60—70% solution of thorium nitrate is electrolysed and the operation is interrupted, the solution continues for some months to emit considerable quantities of nitrogen, the formation of which is probably due to the oxidising properties exhibited by the rare earths.

T. H. P.

**Porcelain Colours.** WILHELM MUTHMANN, L. WEISS, and HEINRICH HERAMHOF (*Annalen*, 1907, 355, 144—164).—The limited number of materials adapted for the production of under-glaze colours on porcelain led the authors to investigate the suitability of the oxides and salts of neodymium, praseodymium, cerium, and other metals. The oxides and silicates are too infusible, but the phosphates answer admirably, being stable at high temperatures (1400—1450°), unchanged by oxidising or reducing flames, yielding fine colours, and being unattacked by the fusing glaze. Neodymium phosphate produces a rose-red colour; praseodymium phosphate, a green colour; didymium phosphate yields practically the same colour as neodymium phosphate. Ferric phosphate forms a yellow colour, and cobalt phosphate a fine blue, deeper than that of smalt. Chromium phosphate yields various shades of green according to its method of preparation. Iron titanate gives an orange-red; cerium titanate a yellow; manganese titanate a reddish-yellow or orange; cerium tungstate a bluish-green; neodymium tungstate a bluish-red, and cerium molybdate a fine blue.

It has been long known that phosphoric acid is expelled from its salts by silicic acid at high temperatures. The authors have heated equal weights of finely powdered quartz and cobalt phosphate for two hours at definite temperatures between 300° and 1400°; the percentage of phosphoric oxide decreases continuously, and evidence of the formation of a cobalt silicophosphate is obtained above 1000°. On the other hand, a mixture of quartz and magnesium pyrophosphate does not decrease in weight at 900°.

C. S.

**Potential and Nature of Alloys.** NICOLAI A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 528—566. Compare this vol., ii, 325, 618).—Aluminium forms with copper, silver, and gold alloys similar in many respects to bronze, and in the type of compounds also to brass. The aluminium alloys are exceedingly difficult to investigate, owing to their instability in air and in acids; the most suitable medium was found to be a weak solution of calcium hydroxide. The potential curves indicate the existence of  $AlM$  (where  $M$  is  $Cu$ ,  $Ag$ ,  $Au$ ), but the gold alloys were not investigated. The following series of alloys most probably exists:  $AlM$ ,  $AlM_2$ ,  $AlM_3$ ,  $Al_2M$ , and possibly  $AlM_4$ . Antimony and bismuth, as was to be expected, do not form compounds, but yield isomorphous mixtures, and the potential curve corresponds completely with the one deducible from the properties and relation of the two metals. Contrary to the statement of Laurie, tin and lead

have been found to form, not only mechanical mixtures, but also solid solutions of tin in lead of considerable concentration, the electrolyte used being potassium hydroxide. Antimony and arsenic form compounds with silver, zinc, tin, and nickel which can be regarded as derivatives of the compounds,  $\text{PH}_3$ ,  $\text{PH}_2$ , in which the phosphorus is replaced by antimony or arsenic and the hydrogen by the other metal. The same is true for many compounds, such as  $\text{Na}_3\text{Sb}$ ,  $\text{Ag}_3\text{Sb}$ ,  $\text{Ag}_2\text{Sb}$ , and  $\text{Zn}_3\text{P}_2$ , &c. Zinc and antimony form the compounds  $\text{Zn}_3\text{Sb}_2$  and  $\text{ZnSb}$ , as has also been indicated by other methods, but Herschkowitch's  $\text{ZnSb}_2$  and May's  $\text{Zn}_2\text{Sb}_3$  do not exist. Contrary to Laurie's statement, antimony and tin certainly form the compound  $\text{SnSb}$  and possibly also  $\text{Sn}_3\text{Sb}_2$ , which, however, only appears on the curve when sulphuric acid is used. The most suitable electrolyte for antimony-silver, antimony tartrate, gave potential differences far too low; potassium hydroxide was therefore employed; the curve indicates the compounds  $\text{Ag}_2\text{Sb}$  and  $\text{Ag}_3\text{Sb}$  as well as the formation of solid solutions of  $\text{Ag}_3\text{Sb}$  in  $\text{Ag}_2\text{Sb}$ , and of  $\text{Ag}$  in  $\text{Ag}_3\text{Sb}$ .

The alloys of antimony and nickel are very hard and brittle, only those containing a high proportion of nickel are not brittle, although still very hard. Contrary to Lassen (Abstr., 1906, ii, 361), it is considered that the nickel antimony alloys, like those of tin, zinc, &c., correspond with the types  $\text{PH}_3$  and  $\text{PH}_2$ , and not with the oxides  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$ . The compounds indicated by the potential curve are  $\text{NiSb}$  and  $\text{Ni}_3\text{Sb}$ . Tin and arsenic form the compounds  $\text{Sn}_3\text{As}_2$  and  $\text{SnAs}$ , the latter only being indicated when sulphuric acid is employed as electrolyte. When the alloys of arsenic and tin contain about 40–50% of arsenic, splendid crystals, with a bright metallic lustre, are formed.

Z. K.

**Action of Carbonyl Chloride on Aluminium Haloid Compounds.** I. AUREL VON BARTAL (*Zeitsch. anorg. Chem.*, 1907, 55, 152–158).—The action of carbonyl chloride on aluminium bromide has been investigated, and it is shown that under varying conditions the compounds  $\text{AlCl}_2\text{Br}$ ,  $\text{AlCl}_2\text{Br}\cdot 6\text{H}_2\text{O}$ ,  $\text{COClBr}$ , and  $\text{COBr}_2$  are obtained.

Carbonyl chloride was passed into aluminium bromide in a flask heated in a water-bath and connected with a second flask placed in a freezing mixture until the contents of the first flask became solid. The distillate in the second flask consisted mainly of bromine with some carbonyl bromide (compare Abstr., 1906, i, 731). From part of the solid residue in the first flask, anhydrous *aluminium chlorobromide* was obtained by sublimation in a vacuum as small, brick-red leaflets which fume and deliquesce in the air. The compound sublimes practically unchanged at  $110\text{--}120^\circ/15\text{--}20$  mm., and melts when heated at  $142\text{--}143^\circ$  in a sealed tube. Another portion of the solid residue was dissolved in ice-cold water, and on careful evaporation *aluminium chlorobromide hexahydrate*,  $\text{AlCl}_2\text{Br}\cdot 6\text{H}_2\text{O}$ , was obtained in small, light red to yellow crystals. The hydrate does not fume in the air, but is deliquescent and easily soluble in water; it does not melt even when heated in a sealed tube, but at higher temperatures loses water and decomposes.

When carbonyl chloride was used in excess, different products were obtained. To this compound, cooled in a freezing mixture, an equal weight of aluminium bromide was gradually added, the resulting liquid was fractionated, the fraction boiling at 20—45° shaken with mercury to remove excess of bromine, and finally *carbonyl chlorobromide*,  $\text{COClBr}$ , was obtained. The yield is better if the reaction mixture is heated seven to eight hours in a sealed tube at 140—145° before fractionation.

Carbonyl chlorobromide is a colourless or slightly yellow, mobile liquid with a disagreeable odour, b. p. 25°,  $D_{15}^{15}$  1.82. It is stable at 100° and attacks antimony, but not mercury; it reacts vigorously with dimethylaniline to form crystal-violet.

The carbonyl chlorobromide described by Besson (*Abstr.*, 1895, i, 317) as boiling at 36—38° must have been a mixture. G. S.

**Mode of Combination of Trihydroxy-bases with Dibasic Acids in General and of Some Aluminium Silicates in Particular.** FRITZ ULFFERS (*J. pr. Chem.*, 1907, [ii], 76, 143—165).—The results obtained by Jordis (*Zeitsch. angew. Chem.*, 1906, 19, 1697) in his study of the formation of silicates in aqueous solution are shown to be characteristic of the combinations of weak, polyhydroxy-, and especially of trihydroxy-, bases with polybasic and more especially dibasic acids. The formation of acid salts by these, when present in equivalent proportions, results, on the one hand, from the hydrolysis of the normal salt by water, and, on the other, from the differences in the acidities of the individual acid groupings of a polybasic acid. The acid salts so formed may undergo change into complex acids, the components of which are not precipitated by the ordinary reagents. The discussion is illustrated by reference to the combinations of sulphuric, oxalic, and silicic acids with aluminium, chromium and ferric hydroxides. G. Y.

**Reaction between Potassium Aluminium Sulphate and a Bromide-Bromate Mixture.** FRANK A. GOOCH and R. W. OSBORNE (*Amer. J. Sci.*, 1907, [iv], 24, 167—172; *Zeitsch. anorg. Chem.*, 1907, 55, 188—194).—In Stock's method for estimating aluminium (*Abstr.*, 1900, ii, 247, 315), aluminium sulphate is boiled with a mixture of potassium iodide and iodate; aluminium hydroxide is precipitated, and iodine is liberated. Moody (*Abstr.*, 1905, ii, 765) has shown that the first insoluble product formed is a basic aluminium sulphate, but that this, on prolonged boiling, is completely hydrolysed and the theoretical amount of iodine is set free.

A study has now been made of the action of a mixture of potassium bromide and bromate on potassium aluminium sulphate under varying conditions, and the results are tabulated. It is found that the reaction progresses much more slowly than in the case of the iodide and iodate mixture. When a moderate excess of the bromide and bromate is used, the hydrolysis of the aluminium sulphate proceeds to a point corresponding with the removal of five-sixths of the acidic ion in approximately the same time that, under similar conditions, the iodide and iodate mixture would remove the whole of it.

Experiments with potassium chloride and chlorate indicate that the hydrolysis of aluminium sulphate in this case is very slight.

E. G.

**Compounds of Phosphorus and Manganese.** S. F. SCHEM-TSCHUSCHNY and N. N. EFREMOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 777—787).—The addition of phosphorus considerably lowers the melting point of manganese, the atomic lowering being  $30-31.5^{\circ}$ ; from this, the latent heat of fusion of manganese can be calculated to be 27.5 Cal. per gram. At  $960^{\circ}$  when the alloy contains 9.5 atom. % phosphorus, a eutectic point occurs, after which further addition of phosphorus raises the melting point until at a composition 28.57 atom. % phosphorus and m. p.  $139^{\circ}$  the compound  $Mn_3P_2$  (analogous to  $Ni_3As_2$ ) separates. This compound is fairly stable even at high temperatures and does not form solid solutions with manganese. Further addition of phosphorus again lowers the melting point until at  $1095^{\circ}$  and 40.5 atom. % P another eutectic point is reached. The compound  $MnP$  probably also exists and forms solid solutions with manganese.

Z. K.

**Alloys of Manganese with Copper and Nickel.** S. F. SCHEM-TSCHUSCHNY, G. URAZOFF, and A. RYKOVKOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 787—802).—The alloys of both series form continuous solid solutions. The freezing-point curve of copper and manganese is continuous with a minimum at  $868^{\circ}$  at the composition 35.5% manganese. At compositions between 10 and 15% manganese, the interval between the commencement and end of solidification is a maximum, whilst the two curves coincide at the minimum. Photographs of the microstructure show that crystallisation occurs in different directions in neighbouring parts of the alloy containing 87.5% copper. Contrary to Wologdine (*Revue de Metallurgie*, 1907, **4**, 25), it is considered that no definite compound of the metals exists and that the supposed compound was really a carbide of manganese.

The curve for manganese and nickel is similar to that for the copper alloys, but the minimum occurs at  $1030^{\circ}$  at the composition 56% manganese. At the composition 36—51% manganese, the solution of the two metals is partially decomposed at  $790-816^{\circ}$  with the possible formation of a definite compound.

Z. K.

**Behaviour of Iron towards Lead, Bismuth, Thallium, and Cadmium.** EDUARD ISAAC and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, **55**, 58—62).—Iron is not miscible with lead or bismuth, either in the solid or fused state, and does not form chemical compounds with them.

Iron and thallium do not form mixed crystals, but it was not found possible to determine whether these metals are miscible in the fused state, as the boiling point of thallium lies below the melting point of iron. The boiling point of thallium under atmospheric pressure is  $1515 \pm 2^{\circ}$ .

Cadmium appears to be insoluble in fused iron, and when iron is

brought into contact with fused cadmium it is either insoluble or forms a compound insoluble in fused cadmium. G. S.

**Methods for the Study of Alloys.** LÉON GUILLET (*Bull. Soc. chim.*, 1907, [iv], 1, 775—781. Compare this vol., ii, 608).—Of the three principal methods available for the investigation of alloys, the study of cooling curves, due regard being paid both to the *solidus* and *liquidus*, and micrographical examination are believed to furnish the most trustworthy results. Apart from these two methods, attempts to isolate and characterise constituents of alloys by chemical methods are likely to give misleading results, and in this connexion the author states that the results of some preliminary experiments he has made indicate that several of the compounds asserted by Vigouroux to occur in manganese-iron and molybdenum-iron alloys (*Abstr.*, 1906, ii, 364) do not exist. T. A. H.

**Colloidal Ferric Hydroxide and Carbamide.** A. V. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 743—751. Compare this vol., ii, 175).—When a solution of carbamide is added to a colloidal solution of ferric hydroxide, the time of coagulation is observed to increase as the concentration of the carbamide is diminished, but the concentration of the colloid has no effect on the process. Experiment shows that until the occurrence of coagulation the concentration of the coagulating substance is less than its calculated value, but after coagulation the colloid retains hardly any of the coagulating substance. The process of coagulation is therefore explained thus: carbamide passes readily through the walls of the bubbles of the colloid suspended in the water, consequently no coagulation appears at first, but the carbamide solution is concentrated within the cells of the colloid until the strain causes them to burst and coagulation takes place. Under certain conditions, the bubbles of the colloid do not burst, but they stretch, thus occupying a larger volume and finally causing the formation of a jelly. Z. K.

**Limits of Existence of the Hydrates of Ferrous Sulphate.** F. FRAENCKEL (*Zeitsch. anorg. Chem.*, 1907, 55, 223—232).—It is shown by solubility determinations that between 0° and 100° only three hydrates of ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ,

exist in stable equilibrium with the aqueous solution. The heptahydrate is stable from  $-1.82^\circ$  (the eutectic point) to  $56.6^\circ$ , the tetrahydrate from  $56.6^\circ$  to  $64.4^\circ$ , and the monohydrate above the latter temperature; the position of the last two points has been confirmed by dilatometer experiments.

Experiments on the rate of dehydration of solutions of ferrous sulphate at different temperatures afford evidence of the existence of the same three hydrates, as Scharizer also found (see *Abstr.*, 1899, ii, 30).

Several other hydrates of ferrous sulphate mentioned in the literature may possibly be formed under certain conditions, but cannot exist in stable equilibrium with water. G. S.

**Compounds of Nickel and Cobalt with Boron.** ARMAND BINET DU JASSONNEIX (*Compt. rend.*, 1907, 145, 240—241. Compare this vol., ii, 691, 692).—By heating mixtures of cobalt or nickel with boron in porcelain tubes at 1100—1200° in a current of hydrogen, borides are obtained similar to those of iron. The product from cobalt and boron, containing about 5% of the latter, consists of an agglomeration of small, elongated, prismatic crystals; it is only very slowly attacked by hot hydrochloric acid, leaving a residue which is still less easily attacked. This consists of the boride  $\text{Co}_2\text{B}$  in the form of small, brilliant, steel-grey needles,  $D^{20} 7.9$ , which are violently attacked by nitric acid and slowly oxidised by moist air. The nickel mass, containing 5% of boron, has a microcrystalline structure, and is very slowly attacked by hot hydrochloric acid, but leaves no residue, and the compound  $\text{Ni}_3\text{B}$  is isolated by dissolving the excess of nickel electrolytically in nickel chloride solution. The boride forms small, very slender, yellow, acicular crystals,  $D^{20} 8.0$ , which are violently attacked by nitric acid and are slightly oxidised by long exposure to moist air. Borides of cobalt and nickel, containing more than 20% of boron, are more easily prepared in the electric furnace. It is impossible to prepare products containing more than 21% of boron, and the borides  $\text{CoB}_2$  and  $\text{NiB}_2$  containing respectively 27.1% and 27.2% of boron constitute under the conditions employed the superior limit of the combination of boron with cobalt and nickel. E. H.

**Alloys of Cobalt and Copper.** N. C. KONSTANTINOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 771—777. Compare Reichardt, *Abstr.*, 1902, i, 118).—As cobalt is added to copper, the freezing point is raised, the freezing-point curve consisting of four branches and indicating the existence of solid solutions. The breaks in the curve occur at 6.5%, 30%, and 70% of cobalt respectively, the first representing a saturated solution of cobalt in copper. The latter metal forms a solid solution with the former up to a concentration of 15% of copper. The alloys containing 30—70% of cobalt form two layers in the liquid state. Photographs of the microstructure of various alloys are given and confirm the results obtained by the freezing-point method. Z. K.

**Alloys of Cobalt and Tin.** F. DUCELLIEZ (*Compt. rend.*, 1907, 145, 431—433. Compare this vol., ii, 693).—When alloys of cobalt and tin containing from 8.76% to 57.25% of the latter metal are treated with 15% nitric acid followed by potassium hydroxide solution, a residue is obtained containing approximately 57.65% of tin which corresponds with the formula  $\text{Co}_3\text{Sn}_2$ . The alloys behave like mixtures of cobalt and the compound  $\text{Co}_3\text{Sn}_2$ , their fragility and the proportion of the latter substance increasing with the percentage of tin. The alloy containing 40% of tin shows no characteristic property, so that the existence of a compound corresponding with the  $\text{Ni}_3\text{Sn}$  isolated by Vigouroux (this vol., ii, 622) is improbable. The substance  $\text{Co}_3\text{Sn}_2$  forms a brilliant powder,  $D 8.86$ , having no well-characterised, crystalline form; it, like all alloys containing it, is magnetic, whilst its chemical properties resemble those of the substance  $\text{CoSn}$ , but it is less easily attacked by hydrochloric, and more easily by nitric, acid than the latter compound. E. H.

**Alloys of Nickel and Tin.** ÉMILE VIGOUROUX (*Compt. rend.*, 1907, 145, 246—248; 429—431. Compare this vol., ii, 354, 622).—Alloys of nickel and tin containing from 45% to 57% of the latter metal, on repeated treatment with hydrochloric acid, leave a residue approximately corresponding with the formula  $\text{Ni}_3\text{Sn}_2$ . The action of hydrochloric acid on the alloys containing 59—66% of tin tends to diminish the proportion of this metal towards the limit 57.47%, which corresponds with the compound  $\text{Ni}_3\text{Sn}_2$ , whilst nitric acid tends to raise the proportion towards a maximum of 66.97%, corresponding with the substance  $\text{NiSn}$ .

The magnetic alloys are those containing 0—40.22% of tin, the sonorous ones those containing 66.76—85%, whilst their fragility increases with the proportion of tin up to 66.76% and then diminishes, the alloys containing 85—100% of this metal being somewhat malleable.  
E. H.

**Discontinuities Observed in the Molecular Conductivities of the Dissolved Chromic Sulphates.** ALBERT COLSON (*Compt. rend.*, 1907, 145, 250—252. Compare this vol., ii, 267).—The conductivities at increasing dilutions of solutions of chromic sulphate, prepared and diluted with water at 0°, have been measured at 0°, and compared with those of the same solutions at 0° after several days' heating at 20°.

According to the theory of electrolytic dissociation, the increase in molecular conductivity of a solution arises from (1) increase in ionisation, or (2) decomposition of the ions first liberated. With the solutions at 0°, the second phenomenon only occurs after very considerable dilution, thus causing a break in the continuity of the series of measurements, but with solutions previously heated the two phenomena are superposed, and thus the variation in conductivity appears more continuous. Similar results were obtained with the green salt prepared by the action of sulphur dioxide on a cold solution of chromic anhydride.

The existence of these phenomena does not depend on the ionic hypothesis, but, since sulphuric acid is a better conductor than the metallic sulphates, can be explained by such a hydrolysis as that represented by  $2\text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Cr}_4\text{O}(\text{SO}_4)_5$ . In fact, the acidity of *N*/1000 solution of chromic sulphate corresponds with such a reaction, and as it increases with the dilution other hydrolyses, such as  $\text{Cr}_4\text{O}(\text{SO}_4)_5 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{Cr}_2(\text{SO}_4)_2(\text{OH})_2$ , may succeed the first or be superposed on it.  
E. H.

**New Double Phosphates of Chromium.** LOUIS J. COHEN (*J. Amer. Chem. Soc.*, 1907, 29, 1194—1198).—In attempting to prepare an ammonium chromic phosphate in a strongly acid solution, such as was used in the preparation of the iron and aluminium salts (this vol., ii, 552), no precipitate was produced. On reducing the acidity, however, a green precipitate was obtained of the double salt  $(\text{NH}_4)_2\text{HPO}_4 \cdot 2\text{CrPO}_4 \cdot 3\text{H}_2\text{O}$ . When no hydrochloric acid or only a



very small quantity was present, the product had the composition  $5(\text{NH}_4)\text{H}_2\text{PO}_4, 2\text{CrPO}_4, 4\text{Cr}(\text{OH})_3$ .

Bloxam (Abstr., 1886, 17), on boiling solutions of chromium salts with sodium phosphate and acetic acid, obtained a precipitate which he regarded as consisting of normal chromic phosphate mixed with a slight excess of chromic oxide,  $\text{Cr}_2\text{O}_3$ , and containing  $5\text{H}_2\text{O}$ . It is now found that under certain conditions, *sodium chromic phosphate*,  $\text{Na}_2\text{HPO}_4, 2\text{CrPO}_4, 5\text{H}_2\text{O}$ , can be obtained, but on repeatedly washing the precipitate with water it is converted into a basic salt. E. G.

**Preparation of Metallic Molybdenum.** WILHELM MUTHMANN, L. WEISS, and ALFRED MAI (*Annalen*, 1907, 355, 100—115).—An account of attempts to prepare pure metallic molybdenum on a large scale from molybdenite. The metal obtained by heating mixtures of the mineral and ferric oxide or molybdic acid in an electric furnace always contains iron and sulphur (5—6%). If, however, molybdenum dioxide is heated with the mineral, the metal contains only 0.72% of sulphur. Molybdenum free from sulphur and containing only small quantities of iron is obtained by heating the mineral with lime in an electric furnace; the yield of massive metal is, however, small, and is not increased by the addition of carbon. A mixture of molybdenite, lime, and fluorspar, heated in an electric furnace with a current of 600—800 amperes and 110 volts, does not give metallic molybdenum in large masses, but instead bluish-black crystals of molybdenum sesquisulphide,  $\text{Mo}_2\text{S}_3$  (Guichard, Abstr., 1900, ii, 211), are obtained. If, however, a current of 70—100 amperes and 30—40 volts is employed, a good yield of the metal in a homogeneous mass is obtained. If the mineral employed is previously treated with concentrated hydrochloric acid, this metal contains 98.95% of molybdenum and only 0.67% of iron; such a metal is tough, malleable when hot, and shows a granular, crystalline fracture. The presence of more iron (1.8%) renders the metal harder and somewhat brittle; it then shows a smooth, homogeneous fracture. The formation of the metal in the electric furnace is shown to be due to the high temperature and not to electrolysis. W. H. G.

**Metallic Vanadium, Columbium, and Tantalum.** WILHELM MUTHMANN, L. WEISS, and RUDOLF RIEDELBAUCH (*Annalen*, 1907, 355, 58—99).—These metals have been obtained in a pure state and in fairly large masses by the method previously described (Weiss and Aichel, Abstr., 1905, ii, 164), and their physical and chemical properties investigated.

Vanadium is similar in appearance to cast-iron, with a high carbon content, has hardness 7.5,  $D_{15}^{15}$  6.025, specific heat 0.124, and is as brittle as glass. The finely-divided metal combines with oxygen at a bright red heat, but is not converted completely into the pentoxide. The heat of combustion was found to be 31.303 Cal. per equivalent. The finely-divided metal combines at  $1300^\circ$  with 16.1% of its weight of hydrogen forming a stable *hydride*, a black powder, which is not affected by water or boiling hydrochloric acid, but is oxidised by

nitric acid. The metal also combines with nitrogen at a bright red heat, forming the *nitride*  $V_2N$ , a black powder, stable towards boiling water, hydrochloric acid, and potassium hydroxide solution, but soluble in concentrated nitric and sulphuric acids; when fused with potassium hydroxide, ammonia is evolved.

Columbium is white with a yellow tinge; it is as brittle as cast-iron, has hardness 6.5,  $D_{15}^{25}$  8.400,  $D_{19.8}^{19.8}$  8.431, and specific heat 0.0617. The metal is converted by oxygen at a red heat into the pentoxide, the heat of combustion being 44.133 Cal. per equivalent. The finely-divided metal combines with 7.5% of its weight of hydrogen at a red heat, forming a *hydride*, and is converted by nitrogen into the *nitride*,  $Cb_3N_5$ . This nitride is not decomposed by concentrated nitric and sulphuric acids, but is attacked when fused with potassium hydroxide; it burns when heated in air with the formation of the pentoxide.

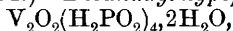
Tantalum is pure white, is malleable in small pieces, has hardness 6.0—6.5,  $D_{16}^{16}$  14.491, and specific heat 0.0346. It is converted by oxygen at a fairly low temperature into the pentoxide, the heat of combustion being 30.80 Cal. per equivalent. The metal when heated in hydrogen absorbs this gas in the proportion of 1 equivalent of metal to 12.5 equivalents of hydrogen; from this, it follows that either tantalum is capable of absorbing hydrogen or else that a hydride is formed which is capable of occluding hydrogen. The product evolves hydrogen when heated. The metal absorbs nitrogen at 1000° in the proportion  $Ta : N = 1 : 2.2$ , forming a *nitride* similar in properties to the columbium nitride,  $Cb_3N_5$ .  
W. H. G.

**Reduction of Vanadium Pentoxide.** B. MDIVANI (*Ann. Chim. anal.*, 1907, 12, 305—307).—Vanadium pentoxide is most conveniently reduced to the trioxide by ignition in a current of pure carbon monoxide. When heated in a current of hydrogen cyanide, a black substance is obtained which the author believes to be the dioxide.

On account of the fusibility of the pentoxide, the heat at first should be moderate, but towards the end a higher temperature should be employed.

When the pentoxide is made by heating ammonium metavanadate in a platinum crucible, the latter is liable to become porous, and a loss of material is noticed.  
L. DE K.

**Divanadyl Hypophosphite.** FRANZ MAWROW (*Zeitsch. anorg. Chem.*, 1907, 55, 147—151).—*Divanadyl hypophosphite*,



was obtained in small, bluish-green crystals by heating together 3—5 grams vanadic acid, 20—30 c.c. water, and 40—60 c.c. of hypophosphorous acid until the vanadic acid was completely dissolved, the blue solution being then evaporated over sulphuric acid. The compound is insoluble in cold, but slightly soluble in hot, water; it is insoluble in acetic acid, but soluble when heated in hydrochloric, sulphuric, nitric, and oxalic acids. By the direct action of alkalis on divanadyl hypophosphite, *dihypovanadates* are produced; the ammonium compound,  $(NH_4)_2V_4O_9 \cdot 3H_2O$ , is brown in colour and soluble in water.

A modified method for the complete separation of vanadium from phosphorus is described.  
G. S.

**Alloys of Antimony with Manganese, Chromium, Silicon, and Tin, of Bismuth with Chromium and Silicon, and of Manganese with Tin and Lead.** ROBERT S. WILLIAMS (*Zeitsch. anorg. Chem.*, 1907, 55, 1—33).—From an investigation of the alloys mentioned in the title, by thermal analysis controlled by microscopic observations, evidence has been obtained of the existence of the following compounds:  $\text{Sb}_2\text{Mn}_3$ ;  $\text{SbMn}_2$ ;  $\text{Sb}_2\text{Cr}$ ;  $\text{SbCr}$ ;  $\text{SbSn}(\text{?})$ ;  $\text{SnMn}_4$ ;  $\text{SnMn}_2$ ;  $\text{SnMn}(\text{?})$ . In the systems antimony—silicon, bismuth—chromium, bismuth—silicon, and manganese—lead, chemical compounds do not occur.

Antimony and manganese alloys form two compounds of the respective formulæ,  $\text{SbMn}_2$ , m. p.  $919^\circ$ , and  $\text{Sb}_2\text{Mn}_3$ , which decomposes below its melting point and is only stable below  $852^\circ$ . There are two series of mixed crystals, one, of which the components are  $\text{Sb}_2\text{Mn}_3$  and antimony, extends from 50—60 atom. % of manganese, whilst  $\text{SbMn}_2$  is miscible with both antimony and manganese, forming a series extending from 65—69 atom. % of the latter metal.

The compounds  $\text{SbMn}_2$  and  $\text{Sb}_2\text{Mn}_3$  are silver-grey in colour, and the former is less brittle than its components. Both are magnetic (compare Heusler, *Zeitsch. angew. Chem.*, 1904, 17, 260);  $\text{SbMn}_2$  loses its magnetic permeability on heating to  $250\text{--}260^\circ$ ,  $\text{Sb}_2\text{Mn}_3$  at  $320\text{--}330^\circ$ .

Antimony and chromium form two compounds,  $\text{SbCr}$ , m. p. about  $1125^\circ$ , and  $\text{Sb}_2\text{Cr}$ , which decomposes below its melting point, and is only stable below  $675^\circ$ . There are two series of mixed crystals, one, of which the components are  $\text{SbCr}$  and chromium, extends from 50—52.5 atom. % of the latter metal, the other, composed of chromium and antimony, extends from 95—100 atom. % of the former metal.

The compound  $\text{SbCr}$  is dark grey in colour, exceedingly brittle, and readily attacked by dilute acids;  $\text{Sb}_2\text{Cr}$  is silvery white in colour, very brittle, and only slightly acted on by dilute acids.

Antimony-tin alloys (compare Reinders, *Abstr.*, 1900, ii, 731; Gallagher, *Abstr.*, 1906, ii, 367) give freezing-point curves which show two breaks at  $420^\circ$  and  $243^\circ$  respectively; there was no evidence of the break at  $310\text{--}319^\circ$  referred to by Reinders and by Gallagher. The alloys were kept at a high temperature for some hours in order to attain equilibrium, and it was then found by microscopic observation that three series of mixed crystals are formed extending from 0—8, 49.8—52.8, and 90—100 atom. % of antimony. The end member of the middle series may perhaps be regarded as a compound  $\text{SbSn}$ . The results of Reinders and of Gallagher (*loc. cit.*) are criticised.

Antimony and silicon are completely miscible in the fused state, and form two series of mixed crystals extending from 0—0.3% and 99—100% by weight of silicon respectively. There is no evidence of chemical combination.

Bismuth is insoluble in fused silicon, but the latter element is soluble to the extent of about 2% in fused bismuth at  $1414^\circ$ . These elements appear to form one series of mixed crystals from 0—0.8% by weight of silicon.

Bismuth and chromium are not miscible in the fused state.

The freezing-point curve of tin-manganese alloys shows three breaks at  $989^{\circ}$ ,  $898^{\circ}$ , and  $541^{\circ}$  respectively, corresponding with the compounds  $\text{SnMn}_4$ ,  $\text{SnMn}_2$ , and probably  $\text{SnMn}$ , all of which decompose below their respective melting points. A series of mixed crystals extends from 95—100 atom. % of manganese.

The compound  $\text{SnMn}_4$  not only shows considerable magnetic permeability, but is permanently magnetic; the remaining two compounds show very slight magnetic permeability.

The compound  $\text{SnMn}_4$  is fairly hard, not so brittle as manganese, and takes a good polish.  $\text{SnMn}_2$  is softer than  $\text{SnMn}_4$ , and less readily attacked by dilute acids. The compound  $\text{SnMn}$  is silvery-white.

Fused manganese dissolves 10% by weight of lead, and its melting point is lowered from  $1228^{\circ}$  to  $1197^{\circ}$ . At the same temperature, lead dissolves 12% of manganese, but the latter metal crystallises out completely as the temperature falls to the melting point of lead.

G. S.

**Properties and Constitution of the Tantalum Steels.** LÉON GUILLET (*Compt. rend.*, 1907, 145, 327—329).—Four tantalum steels, containing 0.12—0.16% carbon, 0.09—1.05% tantalum, 0.19—0.23% manganese, 0.12—0.16% silicon respectively, together with traces of sulphur and phosphorus, have been examined. The normal steels are all pearlitic in character; the quantity of pearlite is in proportion to the carbon content, but is better distributed as the percentage of tantalum increases. Examination of the mechanical properties shows that the tantalum produces a slight increase in the breaking load, the limit of elasticity, and the resistance to shock, and a slight decrease in the elongation. The effect produced by 1% of tantalum can, however, be obtained by addition of other substances, particularly nickel.

The transformation points between  $600^{\circ}$  and  $675^{\circ}$  are scarcely visible on the curve, but those between  $770^{\circ}$  and  $790^{\circ}$  on heating, and between  $730^{\circ}$  and  $750^{\circ}$  on cooling, are very clear; the last transformation, at about  $900^{\circ}$ , is rather slow.

The quenched steels have the same structure as the ordinary steels. The influence of the tantalum on the mechanical properties is somewhat more evident with the quenched than with the ordinary steels. The conclusion drawn is that the tantalum steels, at least when containing little carbon, do not call for any special attention. E. H.

**A New Silicide of Platinum.** PAUL LEBEAU and A. NOVITZKY (*Compt. rend.*, 1907, 145, 241—243. Compare Winkler, *J. pr. Chem.*, 1864, 91, 203; Guyard, *Abstr.*, 1876, ii, 550; Colson, *Abstr.*, 1882, 357; Vigouroux, *Abstr.*, 1899, ii, 211).—When pastilles composed of a mixture of very finely-divided silicon and platinum sponge, contained in a carbon crucible enclosed in one of porcelain, are heated for half an hour in a Forquignon and Leclerc furnace, a fused ingot is obtained with the appearance of silicon. Examination of a polished surface of the ingot reveals the presence of two substances, one of which is silicon, and can be dissolved by means of dilute potassium hydroxide solution. The residue, which is soluble in aqua regia, has a composition corresponding with the formula  $\text{SiPt}$ . The same silicide is obtained by heating a mixture of equal parts of platinum

and silicon for five minutes in an electric furnace, using a current of 250 amperes. The silicide can be crystallised from fused silver silicide, the latter being afterwards dissolved by successive treatment with sodium hydroxide and nitric acid, and is then obtained in very fine prismatic crystals,  $D^{15}$  11.63, m. p. about  $1100^{\circ}$ . It is not attacked by hydrochloric, sulphuric, nitric, or hydrofluoric acid, but is attacked by hydrochloric acid and bromine, and is completely dissolved by aqua regia. When heated with tin, the product contains a mixture of free silicon with prismatic crystals and lamellæ. After washing with potassium hydroxide, this leaves a residue of  $\text{SiPt}_2$ . E. H.

**Platinum Silicide,  $\text{PtSi}$ , and a Double Silicide of Platinum and Copper.** ÉMILE VIGOUROUX (*Compt. rend.*, 1907, 145, 376—378. Compare preceding abstract).—The author claims priority in the discovery of the platinum silicide,  $\text{PtSi}$ . This silicide, when heated with excess of aluminium, gives an ingot which, after treatment with 10% hydrochloric acid, leaves a residue containing 91.2% of the silicon from the silicide in a free state. Removal of the free silicon by alkali and treatment of the residue with aqua regia leaves a substance containing only 1.5% of combined silicon. Similarly, when heated with copper (10 grams), the silicide (1 gram) gives an ingot which is vigorously attacked by nitric acid (10%), leaving a residue consisting of platinum containing traces of combined silicon. By heating the copper silicide,  $\text{SiCu}_4$  (12 grams), with  $\text{SiPt}$  (3 grams), a very brittle, grey ingot is formed, containing 20.6% of platinum, 67.2% of copper, and 12.20% of silicon. This is attacked with difficulty by nitric acid and by aqua regia, but is dissolved by aqua regia + hydrofluoric acid. Finally, by heating the silicide,  $\text{SiCu}_4$  (30 grams), with platinum (10 grams), a hard, greyish-white ingot is obtained, which is attacked by 5% nitric acid, leaving a black residue, from which a dense, grey substance soluble in aqua regia, and having the composition represented by  $\text{SiCu}_2\text{Pt}$ , is isolated by levigation. E. H.

**Platinum Alloys.** FRIEDRICH DOERINCKEL (*Zeitsch. anorg. Chem.*, 1907, 54, 333—366).—The alloys which platinum forms with copper, silver, gold, tin, and lead have been investigated by Tammann's method of thermal analysis. The three first-mentioned metals do not enter into chemical combination with platinum, whilst lead forms three compounds, one of which has the formula  $\text{PtPb}$ , and tin forms four compounds the formulæ of two of which have been established as  $\text{Pt}_3\text{Sn}$  and  $\text{PtSn}$ . Owing to the high melting point of platinum, the freezing-point curve of alloys very rich in that metal could not be conveniently determined.

**Platinum-Copper Alloys.**—The freezing-point curve of these alloys (30—100% of copper) falls continuously to the melting point of copper, so that the metals form a continuous series of mixed crystals. The alloys are exceedingly tenacious, and rather harder than their components; those containing over 40% of platinum are white.

**Platinum-Silver Alloys** (compare Thompson and Miller, *Abstr.*, 1906, ii, 764).—When heated at  $1184^{\circ}$  until equilibrium is attained, these metals form a series of mixed crystals from 0—48% of the

former metal. The composition of the end member of the series is approximately  $\text{PtAg}_2$ , but it does not appear to be a chemical compound; above  $1184^\circ$ , it decomposes into crystals rich in platinum, and a fused mass containing about 32% of the same metal. Up to 30% of platinum, the alloys are scarcely harder than their components, but beyond that point the hardness increases; the alloy containing 70% of platinum is rather harder than calcite.

*Platinum-Gold Alloys.*—These metals, at least up to 60% of platinum, form a continuous series of mixed crystals; there is a considerable interval of temperature between the commencement and end of crystallisation. The alloys containing 30–60% of platinum are harder than that metal; those containing over 40% of platinum are white.

*Platinum-Tin Alloys.*—The freezing-point curve of this system shows four breaks, one maximum at  $1280^\circ$  and 62.5% of platinum corresponding with the compound  $\text{PtSn}$ , and one eutectic point at  $1080^\circ$ , the components of the eutectic mixture being the compounds  $\text{PtSn}$  and  $\text{Pt}_3\text{Sn}$ . The latter compound is only stable below  $1370^\circ$ , decomposing above that temperature into crystals of platinum and a fused mass containing about 80% of the same metal. A break at  $846^\circ$  indicates the interaction of  $\text{PtSn}$  and the fused alloy to form a new compound, probably  $\text{Pt}_2\text{Sn}_3$ ; at  $537^\circ$ , the latter reacts with the fused alloy to form a fourth compound, the probable formula of which is  $\text{Pt}_3\text{Sn}_8$ . The fourth break at  $738^\circ$  appears to indicate a polymorphous transition of the compound  $\text{Pt}_2\text{Sn}_3$ .

The alloys containing up to 30% of platinum are scarcely harder than their components, but beyond this point the hardness rapidly increases, and attains a maximum at 80% of platinum.

*Platinum-Lead Alloys* (compare Heycock and Neville, *Trans.*, 1892, 61, 888).—The freezing-point curve of this system contains three breaks and a eutectic point, so that none of the three compounds which these metals form are stable at their respective melting points. The one richest in platinum, the formula of which could not be determined by thermal analysis, is stable below  $910^\circ$ ; at  $787^\circ$ , it reacts with the fused mass to form a compound  $\text{PtPb}$ . At  $356^\circ$ , the latter reacts with the fused alloy to form a third compound of unknown composition. The eutectic mixture of the latter compound and lead contains about 5% of platinum, and solidifies about  $290^\circ$ .

The hardness of these alloys increases gradually from 0–45% of platinum; from 45–85% of that metal they are rather harder than fluorite. Those containing 5–30% of platinum are readily fractured by pressure, and the fresh surfaces oxidise very rapidly in air.

G. S.

**Alloys of Iron and Platinum.** EDUARD ISAAC and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, 55, 63–71).—At high temperatures, iron and platinum form a continuous series of mixed crystals, but as the temperature falls this decomposes into two other series of mixed crystals extending from 0–50% and from 60–100% of platinum respectively.

There are further breaks in the cooling curve of the solid alloys

from 0—40% and from 70—90% of platinum respectively. The latter are probably connected with a change in modification of the mixed crystals rich in platinum, the former with transitions of the iron. Up to 10% of platinum, there are two breaks indicating the changes from  $\gamma$ - to  $\beta$ -iron and from  $\beta$ - to  $\alpha$ -iron respectively; with from 10—40% of platinum  $\gamma$  changes directly to  $\alpha$ -iron.

All the alloys from 0—90% of platinum are magnetic, and this property appears to diminish in the same ratio as the iron from 80—20% of that metal. The alloys from 10—50% of platinum lose their magnetic power on heating at temperatures varying from 800° to 650°, and this property returns on cooling at much lower temperatures; the curve of temperature at which the magnetic power reappears practically coincides with that representing the transformation of  $\gamma$ - to  $\alpha$ -iron referred to above. On the other hand, the temperatures at which the alloys containing 60—90% of platinum regain their magnetic power are much lower than the breaks in the cooling curve in this region.

The hardness of the alloys decreases up to 5% of platinum, rises gradually up to a composition of 40%, and beyond that point to 90% of platinum remains constant. The brittleness of the alloys reaches a maximum at 50% of platinum.

G. S.

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## Mineralogical Chemistry.

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**Differences in the Rate of Solution on Different Crystal-faces.** A. KÖRBS (*Zeitsch. Kryst. Min.*, 1907, 43, 433—450).—The crystals examined were of substances readily soluble in water, and plates were cut parallel to various faces of the crystals. The plates, with their edges protected by a coating of paraffin wax, were immersed in a beaker of water, maintained at a fixed temperature, and the liquid kept in agitation; after a certain time, the loss in weight of each plate was determined. The substances examined fall into two groups; in one (which includes sodium chloride, potassium chloride, alum, potassium sodium tartrate, and potassium nitrate), there is very little difference between the rate of solution on different faces, the difference not amounting to more than a few per cent. In the other group, there are wide differences: in copper sulphate, amounting to 37% on different faces; in tartaric acid, 76%; and in potassium ferrocyanide 86%.  
L. J. S.

**Variation of Crystal-habit in Sodium Chloride.** A. KÖRBS (*Zeitsch. Kryst. Min.*, 1907, 43, 451—460).—Haüy long ago observed that sodium chloride crystallises from urine as octahedra instead of cubes, and many other cases of the influence of substances in solution have since been recorded: a summary of these is given. Experiments were made with the following substances in solutions of sodium



chloride: carbamide, formamide, chromium chloride, cadmium chloride, a mixture of calcium chloride and magnesium sulphate, alcohol, pyridine, acetic acid, ammonium acetate, and glycine. Octahedra are deposited from solutions containing carbamide, formamide, or acetic acid; cubo-octahedra in the presence of alcohol or pyridine, and tetrakis-hexahedra in the presence of glycine. L. J. S.

**Mercury Minerals from Terlingua, Texas: Kleinite, Terlinguaite, &c.** WILLIAM F. HILLEBRAND and WALDEMAR T. SCHALLER (*J. Amer. Chem. Soc.*, 1907, 29, 1180—1194; *Amer. J. Sci.*, 1907, [iv], 24, 259—274).—A description is given of the several mercury minerals, from the mercury mines at Terlingua, in Texas, first described by Moses (Abstr., 1904, ii, 46), one of which was afterwards described by Sachs under the name kleinite (Abstr., 1906, ii, 176, 369).

*Kleinite*.—Crystals are hexagonal with  $a:c=1:1.6642$ ; they are canary-yellow, changing on exposure to light to orange-yellow; D 7.98. The peculiar chemical reactions of the mineral are described in detail; the mean of several analyses made on orange-yellow crystals is:

Hg.	Cl.	SO <sub>4</sub> .	N.	H <sub>2</sub> O.	Total.
85.86	7.30	3.10	2.57	1.03	99.86

No formula can be deduced from these results, but the mineral appears to be a mixture of a mercury-ammonium chloride,  $\text{NH}_2\text{Cl} \cdot \frac{1}{3}\text{H}_2\text{O}$ , with a smaller amount of mercury sulphate or oxysulphate.

*Montroydite*.—A direct estimation of the oxygen (O, 7.49%; Hg, 92.74%) agrees with the formula  $\text{HgO}$  deduced by Moses.

*Terlinguaite*.—New analyses of this also confirm the formula given by Moses: Hg, 88.61; Cl, 7.83; O, 3.75 = 100.19%. It is a mercuric-mercurous oxychloride,  $\text{HgO} \cdot \text{HgCl}$ .

*Eglestonite*.—The mean of three new analyses is: Hg, 89.00; Cl, 8.22; O, 1.79%, proving the mineral to be a mercurous oxychloride with the formula  $\text{Hg}_4\text{Cl}_2\text{O}$  or  $\text{Hg}_2\text{O} \cdot 2\text{HgCl}$ , which differs from that proposed by Moses.

The crystals of calomel and the native mercury from this locality are also described. L. J. S.

**Spectral Photography of Minerals in Different Regions of the Spectrum: Galena and Argentite.** ANTOINE DE GRAMONT (*Compt. rend.*, 1907, 145, 231—234).—The author has photographed the ultra-violet and the visible regions of the spark spectra of galena and argentite. A description of the method employed and reproductions of the photographs obtained are given.

Their ultimate rays (compare this vol., ii, 517) reveal the presence in galena and argentite of copper, tin, iron, calcium, and magnesium; in galena, of antimony and bismuth also, and of lead and zinc in argentite. E. H.

**Vanadium Sulphide (Patronite) and Associated Minerals from Peru.** WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1907, [iv], 24, 141—151).—A thick vein occurring with eruptive dykes in cretaceous

shales, sandstones, and limestones at Minasragra, near Cerro de Pasco, in Peru, consists of three kinds of vanadiferous material, each of which forms a distinct band in the vein.

One of these, to which the name *quisqueite* is given, is a lustrous, black, brittle substance resembling asphalt, but differing from this in containing much sulphur and very little hydrogen (anal. I). The hardness is  $1\frac{3}{4}$ ; D 2.5. It is infusible, and when heated burns with a blue flame. The ash contains much vanadium.

The central band of the vein consists of a coke-like material, the cavities of which are lined or filled with a brittle, pitchy material. Analysis gave results under II; the ash is highly vanadiferous:

S (sol. in CS <sub>2</sub> ).	S (combined).	C.	II.	N.	O (by diff.).	Moisture (at 105°).	Ash.
I. 15.44	31.17	42.81	0.91	0.47	5.39	3.01	0.80
II. 0.64	5.36	86.63	0.25	0.51	4.64	nil	1.97

The third band of the vein consists of a rich vanadium ore, black in colour, with perhaps a suggestion of green, and breaking with an uneven fracture. When heated, it gives off sulphur and afterwards hydrogen sulphide, but it does not fuse. Bulk analyses (III, by Hillebrand) of this material show that it consists largely of a vanadium sulphide, for which the name *patronite* is proposed by F. Hewett (*Ann. Rep.*, 3, 310), mixed with variable amounts of sulphur, carbonaceous matter, silica, &c. After dissolving out sulphur with carbon disulphide, hot water extracts some vanadium sulphate, and warm sodium hydroxide solution extracts vanadium and sulphur. Owing to the partial oxidation of the sulphur during the experiments, the determinations of the ratio of vanadium to sulphur vary somewhat, but they suggest the formula  $VS_4$  or  $V_2S_9$ .

	S.*	V.	Mo.	Fe.	Ni.	C.	SiO <sub>2</sub> .	TiO <sub>2</sub> .
III.	58.79	19.53	0.18	2.92	1.87	3.47	6.88	1.53

Al <sub>2</sub> O <sub>3</sub> (P <sub>2</sub> O <sub>5</sub> ).	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	Cr.	Alkalis.	H <sub>2</sub> O.	O (from sulphate).	Total.
2.00	0.20	trace	trace (?)	0.10 (?)	1.90	0.38	99.75

\* Including 4.5% free sulphur.

Disseminated through the vanadium ore are pyritous grains with a colour rather whiter than pyrites and tarnishing with a red shade; D about 4.33. Analysis IV agrees with the formula (Fe,Ni)S<sub>2</sub>, with Fe:Ni=5:3, indicating that the mineral is a highly nickeliferous pyrites and related to gunnarite (3FeS<sub>2</sub>,2NiS; G. Landström, 1887); for it the name *bravoite* is proposed. The vanadium shown in analysis IV is not a constituent of the metallic sulphide, being extracted by hydrofluoric acid with silica, alumina, and titanium dioxide.

	S.	Fe.	Ni.	Co.	V.	Mo.	C.	H <sub>2</sub> O.	TiO <sub>2</sub> .	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> (P <sub>2</sub> O <sub>5</sub> ).	Total.
IV.	45.06	25.38	15.70	trace	4.31	0.09	0.47	1.38	0.93	1.93	2.45	97.70

The oxidation product of the vanadium ore at the outcrop of the vein resembles porous limonite, and contains: V<sub>2</sub>O<sub>5</sub>, 45; Fe<sub>2</sub>O<sub>3</sub>, 14—15; H<sub>2</sub>O, 15; siliceous gangue, 20%.

An occurrence of vanadium with carbonaceous matter, similar to that here described from Peru, is noted from eastern Utah.

L. J. S.

**Manganspinel in a Furnace Slag.** JOSEF KRENNER (*Zeitsch. Kryst. Min.*, 1907, 43, 473—475).—Brown octahedral crystals were found embedded in a white, enamel-like slag from the blast furnaces at Menyháza, in Hungary, where iron ores rich in manganese are smelted. The crystals are very hard and their resistance to hydrofluoric acid enabled them to be isolated from the slag: Analysis by J. Loczka gave:

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	MgO.	CaO.	SiO <sub>2</sub> .	Total.	Sp. gr.
49.52	1.83	42.19	4.63	0.22	1.29	99.68	4.05

To bring this analysis into agreement with the spinel formula, (Mn,Mg)(Al,Mn)<sub>2</sub>O<sub>4</sub>, the manganese is recalculated as: MnO, 32.14; Mn<sub>2</sub>O<sub>3</sub>, 11.18. The silica shown in the analysis was probably abraded from the agate mortar by the very hard crystals. This spinel contains more manganese than any artificial or natural member of the spinel group hitherto analysed. The white, enamel-like slag was found to contain much silica and manganese, considerable calcium and magnesium, and only traces of iron and sodium.

JOSEF LOCZKA (*ibid.*, 1907, 43, 571—574) gives further details respecting the analysis quoted above.

L. J. S.

**Mineralogical Notes [Purpurite, &c.].** WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1907, [iv], 24, 152—158).—*Purpurite* (Abstr., 1905, ii, 724) is recorded from two new localities, namely, Hill City, in South Dakota (anal. I), and Branchville, in Connecticut (anal. II). It occurs as purple films on a black iron-manganese phosphate, and has the same optical characters as in the original mineral (extinction parallel to two cleavages and pleochroism rose-red to bluish-purple). The analyses agree with the formula (Fe,Mn)<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.H<sub>2</sub>O, previously given, but the iron and manganese are present in different proportions. For the end members of the isomorphous series, the names *ferripurpurite* and *manganipurpurite* are suggested:

	P <sub>2</sub> O <sub>5</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Mn <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Insol.	MgO,Na <sub>2</sub> O,Li <sub>2</sub> O.	Total.	Sp. gr.
I. 43.45	38.36	12.08	1.37	4.82	0.19	traces		100.27	3.40
II. [44]	27	23	—	6	—	—		100.00	—

*Manganotantalite*, from the lithium-bearing pegmatites of Mt. Apatite, in Maine, gave on partial analysis: Ta<sub>2</sub>O<sub>5</sub> + Cb<sub>2</sub>O<sub>5</sub>, 85.35; FeO, 0.16; MnO, by difference, 14.49%. The D 7.14 indicates that tantalic acid largely predominates over columbic acid, and the very small amount of iron shows the mineral to be manganotantalite. Goniometric measurements of the small crystals are given, and a new form recorded.

*Evansite* is recorded from two new localities. Near Goldburg, in Idaho, it occurs in seams, and is amorphous and very brittle, with a conchoidal fracture. It varies from colourless to brown; analysis of brown material gave anal. III.

Dark red material had D 2.00 and contained 6.60%  $\text{Fe}_2\text{O}_3$ , whilst yellow material had D 1.94 and 2.15%  $\text{Fe}_2\text{O}_3$ . The D of pure evansite is about 1.90. Light yellow, transparent evansite from a coal seam near Columbiana, in Alabama, gave anal. IV:

	$\text{H}_2\text{O}$ .	$\text{P}_2\text{O}_5$ .	$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{FeO}$ .	Total.	Sp. gr.
III.	36.96	19.14	5.49	34.48	4.32	trace	nil	100.39	1.98
IV.	38.19	[21.70]	—	38.33	1.02	0.75	—	100.00	—

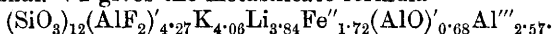
*Tourmaline*: pale pink crystals from the island of Elba gave anal. V. The ratios  $\text{SiO}_2 : \text{B}_2\text{O}_3$ : total H = 4.00 : 0.93 : 20.08, agree with those proposed by Penfield (Abstr., 1899, ii, 304):

	$\text{SiO}_2$ .	$\text{B}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{Ti}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{Na}_2\text{O}$ .
V.	37.89	10.28	43.85	0.04	0.11	0.11	0.07	2.43
VI.*	46.80	—	24.50	—	6.35	1.38	0.24	1.73

	$\text{Li}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	F.	Total less O for F.	Sp. gr.
V.	1.66	nil	3.47	0.10	99.97	3.04—3.05
VI.*	3.73	9.20	0.88	8.63	100.31	—

\* Also  $\text{Fe}_2\text{O}_3$ , 0.50.

*Zinnwaldite* occurs with cassiterite and topaz in the York region, Alaska; anal. VI gives the metasilicate formula



L. J. S.

**Tschermigite from Brůx, Bohemia.** ARTHUR SACHS (*Centr. Min.*, 1907, 465—467).—Tschermigite (ammonia-alum) occurs as a thin, crystalline crust on the surfaces of lignite (which contains streaks of pyrites) in the Nieder-Georgenthal, near Brůx. The alum crystals are water-clear and brilliant, and show the forms of the octahedron and the cube. They are optically isotropic, thus confirming R. Brauns's suggestion that the optical anomalies of the alums are due to isomorphous mixing. Analysis gave:

$\text{SO}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{NH}_3$ .	$\text{H}_2\text{O}$ .	$\text{K}_2\text{O} + \text{Na}_2\text{O}$ .	$\text{Fe}_2\text{O}_3$ .	$\text{C} + \text{SiO}_2$ .	Total.
35.14	11.39	3.67	49.54	0.17	0.007	0.083	100.00

L. J. S.

**Analysis of the Water of the Dead Sea.** ALBERT STUTZER and ALFRED REICH (*Chem. Zeit.*, 1907, 31, 845).—A comparison of the authors' recent analysis (I), and one by Genth made in 1857 (II). The results are given in percentage by weight:

	KCl.	NaCl.	$\text{CaCl}_2$ .	$\text{MgCl}_2$ .	$\text{MgBr}_2$ .	$\text{CaSO}_4$ .	$\text{CaCO}_3$ .	$\text{Fe}_2\text{O}_3$ .	Organic matters.	Total.	D <sup>17.50</sup> .
I.	1.357	8.788	2.384	8.991	0.368	0.141	—	trace	—	22.02	1.1546
II.	1.008	7.583	2.898	10.163	0.534	0.090	0.004	0.008	0.020	22.30	1.1823

L. DE K.

**Origin of the Gases Evolved by Mineral Springs.** ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1907, A, 79, 436—439. Compare Abstr., 1904, ii, 306; 1906, ii, 411).—Analysis of the gases liberated on heating

syenite rock from Mt. Sorrel, Leicestershire, and Matopo granite, shows that nitrogen, argon, helium, and neon are present in roughly the same proportions as in Bath gas, which may be regarded as typical of the gases of almost all thermal springs (compare Moureu, *Abstr.*, 1906, ii, 442). The author concludes therefore that the disintegration and partial solution of ordinary rocks by water at a high temperature accounts for the gaseous and solid products obtained from these springs. Other rocks when examined qualitatively were found to give nitrogen, argon, and helium ; neon was not detected, probably because of the small quantity of material dealt with. A sample of commercial pumice-stone, however, gave nitrogen, argon, and neon ; helium could not be detected with certainty.

W. H. G.

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## Physiological Chemistry.

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**Body Temperature, Blood Pressure, and Alveolar Tension in Athletes.** LEONARD E. HILL and MARTIN FLACK (*Proc. physiol. Soc.*, 1907, xi—xii; *J. Physiol.*, 36).—Pulmonary ventilation was found to be more than sufficient to keep the alveolar tensions of oxygen and carbon dioxide normal. There is usually a rise of blood pressure immediately after a race. The panting and distress after a race cannot be entirely due to high body temperature, although this is usually raised, in one case to  $40.4^{\circ}$ . The panting was as marked in those men whose temperature was but little affected. It is attributed to unknown toxic products produced by excessive muscular work.

W. D. H.

**The Chemical Hæmolysins. II.** ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1907, 21, 293—311).—The present work is a continuation of that previously described (Abstr., 1905, ii, 836; 1906, ii, 379), and deals with the hæmolytic action of ammonia, mono- and di-ethylamine, aniline, ethylaniline, phenylhydrazine, acetanilide, phenylurethane, saccharin, antipyrine, and various alkaloids.

G. S. W.

**Hæmolytic Action of Bile Acids and Bile Salts.** B. VON FENYVESSY (*Biochem. Zeitsch.*, 1907, 5, 114—117).—The bile acids and bile salts are hæmolytic. Details are given of this action, and a comparison is drawn between certain mixtures containing these substances and immune serum and complement.

W. D. H.

**Action of Quinine Sulphate on Human Blood.** THOMAS M. WILSON (*Amer. J. Physiol.*, 1907, 19, 445—460).—The bulk of the paper deals with methods of examination of blood. There is evidence that eosinophile and basophile leucocytes are phagocytic. The eosino-

phile has a lower specific gravity than the polymorphous leucocytes. The administration of 15 grains of quinine sulphate increases the opsonic index of healthy persons. The drug *in vitro* inhibits phagocytosis in strong solutions, but stimulates it in dilutions of from 1/15,000 to 1/1,000,000.

W. D. H.

**The Haldane-Smith Method of Estimating the Oxygen Tension of Arterial Blood.** WILLIAM A. OSBORNE (*J. Physiol.*, 1907, 36, 48—61).—Haldane and Lorrain Smith are not justified in concluding from their work that the oxygen tension of arterial blood is higher than that of the alveolar air, because their colorimetric method for estimating carboxyhaemoglobin is not accurate, and, further, they took no account of the counter-diffusion of oxygen and carbon dioxide on the carbon monoxide. Some possible errors in the use of Haldane gas analysis apparatus are also described.

W. D. H.

**Formation of Cyanomethaemoglobin by Coal Gas.** ALBERT S. GRÜNBAUM (*Proc. physiol. Soc.*, 1907, iv; *J. Physiol.*, 36).—If Liverpool coal gas is passed through blood and potassium ferricyanide added, the result is the formation of cyanomethaemoglobin. This is due to the imperfect purification of the coal gas.

W. D. H.

**Action of Muscle Juice on the Heart.** JOHN J. R. MACLEOD (*Amer. J. Physiol.*, 1907, 19, 426—435).—The expressed tissue juice of fresh cardiac or skeletal muscle of the dog, when injected into the fluid perfused through the heart of another dog, usually causes complete inhibition; this is sometimes recovered from, but is usually followed by fibrillary twitchings. The toxic agent is apparently potassium salt. The aqueous solutions of the ash of the juice produce the same effect.

W. D. H.

**Effect of Transfusion of Blood on the Nitrogenous Metabolism of Dogs.** HOWARD D. HASKINS (*J. Biol. Chem.*, 1907, 3, 321—326).—The transfusion of normal blood after hæmorrhage does not prevent the increase of nitrogenous excretion, which hæmorrhage itself produces.

W. D. H.

**The Balance of Acid-forming and Base-forming Elements in Foods.** HENRY C. SHERMAN and J. EDWIN SINCLAIR (*J. Biol. Chem.*, 1907, 3, 307—309).—Examination of the ash constituents of the food enables the excess of acid-forming or base-forming elements to be calculated. Thus the excess of acid-forming elements per 100 Cals. of beef is equal to 10.1 c.c. of *N*-acid solution, of oatmeal 3.15, and of whole wheat 2.62. In peas, milk, and prunes, the base-forming elements are in excess, the numbers being equal to 1.94, 3.31, and 7.92 c.c. of *N*-alkali solution respectively. Any wide deductions from so few experiments are at present regarded as impossible.

W. D. H.

**Nutritive Value of Gelatin. I.** JOHN R. MURLIN (*Amer. J. Physiol.*, 1907, 19, 285—313).—Metabolic experiments on dogs and men are given in detail; their object was to ascertain the amount of

replacement of ordinary protein by gelatin, which is compatible with nitrogenous equilibrium. The figures obtained vary a good deal in relation to the other constituents of the diet; the sparing action of carbohydrate being, for instance, an important factor in obtaining high replacements. The power to utilise gelatin depends also on the protein condition of the organism at the start; the lower the condition the more strongly does the organism lay claim to gelatin as a means of protecting its living substance.

W. D. H.

**The Nutritive Value of Asparagine.** OSCAR KELLNER (*Pflüger's Archiv*, 1907, 118, 641—642)—Polemical against Müller (this vol., ii, 491).

G. S. W.

**Metabolism in Children.** ERICH MÜLLER (*Biochem. Zeitsch.*, 1907, 5, 143—303).—Full details are given of metabolic experiments on thirty-two children between the ages of three and six years, both as regards chemical composition and calorific value of the food taken and the excretions passed. Various factors cause considerable differences in the result, such as age, sex, appetite, amount of sleep, &c. The amount of protein consumed was somewhat lower than that given by previous authors, but it is greater than during the suckling period, or in the adult.

W. D. H.

**Metabolism in Dogs. I.** EMIL ÖSTERBERG and CHARLES G. L. WOLF (*Biochem. Zeitsch.*, 1907, 5, 304—343).—On a nitrogen-free diet of high calorific value carbamide is the substance which is most diminished. By doubling the amount of such food, the relative amounts of the nitrogenous substances in the urine are hardly affected. On adding casein to the diet, creatinine is the only such substance which remains unaltered in absolute amount. The absolute amount of ammonia increases, but relatively to other substances it falls. On a diet of fat and carbohydrate, the sulphur excretion differs from that of inanition and from that when protein is given; the total sulphur and alkali sulphates diminish, whilst alkyl sulphates increase. The residual nitrogen and neutral sulphur increase absolutely, but decrease relatively on giving protein. The amount of indican has no constant relation to the alkyl sulphates. So far as the experiments go, the results on dogs are very like those in man.

W. D. H.

**Carbohydrate Metabolism in Dogs with an Eck's Fistula. II.** FILIPPO DE FILIPPI (*Zeitsch Biol.*, 1907, 50, 38—74. Compare this vol., ii, 707).—Although the amount of hepatic glycogen is greatly reduced in dogs with an Eck's fistula, that in the muscles shows no difference from what is found in normal animals. The glycogenic function of the muscles (that is, the ability to form glycogen from the sugar of the blood) is thus believed to be independent of that of the liver.

W. D. H.

**Metabolism during Starvation. II. Inorganic.** E. PROVAN CATHCART and CHARLES E. FAWSITT (*J. Physiol.*, 1907, 36, 27—32. Compare this vol., ii, 633).—A continuation of observations on the same



person as before. The urinary chlorides fell sharply on the first day of the fast, and continued to fall until the end. When feeding was resumed, the chloride output rose to normal by the fifth day; during the first four days following the fast, there was a retention of 10 to 11 grams of chlorine. The phosphates follow a very similar course, although the actual reduction was not so great. There is also a steady fall of total sulphur from first to last; this is true for the inorganic sulphates and the alkyl sulphates, the daily output of which was very small. The output of neutral sulphur was fairly regular. The acidity fell on the first day of the fast, rose on the second and third, and then gradually fell to the end of the fast. The excretion of calcium and especially of magnesium declined steadily during the fast. Potassium and sodium excretion fell off gradually also, but the latter more rapidly, so that in time the former exceeded the sodium in quantity. This, however, was previously known, and is due to the ready disintegration of those tissues, such as muscle, which are rich in potassium. Acetone and acetoacetic acid were present during the fast, but were not estimated: they disappear from the urine on resumption of feeding.

F. J. CHARTERIS (*Lancet*, 1907, ii, 685—687) gives clinical details about the same man. The pulse fell in rate and for the first week in tension. The number of red corpuscles varied, but no striking effect was produced; the hæmoglobin diminished; there was slight leucocytosis, and an increase of eosinophile cells. The opsonic index for *Staphylococcus* and *Bacillus typhosus* remained unaltered.

W. D. H.

**Granules of Mammalian Liver Cells. Changes in Fat of Liver Cells during Hunger.** V. H. MOTTRAM (*Proc. physiol. Soc.*, 1907, iv, viii; *J. Physiol.*, 36).—Granules are demonstrable in liver cells (free from glycogen) by staining in formol-magenta after fixing in formaldehyde. There is a large increase in fat in the liver cells during the first two days of inanition; this is more marked in some animals than in others. The fat occurs in globules which stain with Scarlet R. This histological appearance has been confirmed by chemical methods.

W. D. H.

**The Fat contained in Liver, Kidney, and Heart.** PERCIVAL HARTLEY (*J. Physiol.*, 1907, 36, 17—26). The higher fatty-acids from the liver, kidney, and heart-muscle include, in addition to saturated acids and acids of the oleic series, considerable amounts of acids of the series  $C_nH_{2n-4}O_2$ ,  $C_nH_{2n-6}O_2$ , and possibly  $C_nH_{2n-8}O_2$ . They undergo on exposure to air a change which diminishes their iodine value and their solubility in light petroleum. The unsaturated fatty-acids yield on bromination additive products insoluble in ether, carbon tetrachloride, alcohol, and acetic acid, thus resembling the bromo-acids of the series  $C_nH_{2n-8}O_2$ .

W. D. H.

**Percentage of Cholesterol in Ox-bile.** JOHN A. GARDNER and G. D. KNOX (*Proc. physiol. Soc.*, 1907, ix—x; *J. Physiol.*, 36).—The average amount of cholesterol in ox-bile is 0.07%, which is much lower than in human bile. Gall stones in oxen appear to be rare.

W. D. H.

**Influence of Bile on Intestinal Movements.** ALBERT SCHUPBACH (*Zentr. Physiol.*, 1907, 21, 365—367).—The influence of the bile on peristalsis was observed in two dogs with a Vella's fistula, and on the surviving intestine of cats and rabbits (Magnus's method). Bile was found to have no influence on the movements of the small intestine, except in some cases to cause inhibition; this was especially noticeable in the surviving intestine of cats, and the intestine of rabbits *in situ*. On the large intestine, however, peristalsis is greatly increased by bile. W. D. H.

**Influence of Nutrition and Inanition on the Glycogen of the Body.** EDUARD PFLÜGER (*Pflüger's Archiv*, 1907, 119, 117—126).—In complete inanition in dogs, the liver and muscles still contain glycogen; this is attributed to a new formation of this substance, either from the fat or protein of the body. If, however, the animal receives only fat, or only protein food, the amount of glycogen is reduced to a minimum or may disappear altogether. If the food given is dextrose, glycogen appears again in large amount. W. D. H.

**Glycogen in Heterothermic Animals.** ERNST WEINLAND and MAX RIEHL (*Zeitsch. Biol.*, 1907, 50, 75—92).—In marmots, the proportion of total glycogen to body-weight remains remarkably constant during the winter sleep. The amount in the liver falls slightly, and that in the muscles rises to a corresponding degree. On waking from sleep, resumption of active respiratory functions leads to rapid lessening of the glycogen, especially in the liver. W. D. H.

**Metabolism in Dogs without a Pancreas.** W. FALTA, F. GROTE, and R. STAEHELIN (*Beitr. chem. Physiol. Path.*, 1907, 10, 199—231).—Dogs without a pancreas lose weight rapidly; this is due to an enormous increase of protein catabolism which runs parallel with sugar excretion. There is also increased combustion of fats. Full details of the excretions, including respiration, are given in relation to experiments on two dogs. W. D. H.

**Heat Development by the Fermentative Hydrolysis of Proteins and of Gelatin.** ERICH GRAFE (*Arch. Hygiene*, 1907, 62, 216—228).—By means of Rubner's apparatus (*Abstr.*, 1904, ii, 505), consisting of a glass flask surrounded by double vacuum spaces to prevent loss of heat by conduction, the temperature changes during the action of pepsin on casein and fibrin and of trypsin on gelatin and fibrin have been observed accurately, special attention being paid to the first twenty-four hours of the reaction. Practically no variation was recorded, and it is considered that the heat development of the fermentative hydrolysis of proteins is zero, and that, further, there is no heat change due to the synthetic processes. It is probable that this zero value of the heat change is the resultant of several factors working in opposite senses; thus heat is developed by the swelling of proteins and absorbed again by their subsequent solution. E. F. A.

**Precipitation of Casein from, and the Nature of the Inhibitory Action on, Rennet in Human Milk.** ERNST FULD and JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1907, 5, 118—142).—Ehrlich's method of keeping animal fluids frozen is no guarantee that they will be the same after thawing as when fresh. After keeping human milk frozen for three days, it is precipitable by acetic acid and coagulated by rennet, which properties it does not possess when fresh. The intensity of the cold makes no difference, but only the length of freezing; precipitability by acetic acid appears first. Sometimes freezing by itself produces the formation of flocculi, and it is believed that the greater readiness to form precipitates is due to an aggregation of caseinogen particles produced by the freezing. Cows' milk is also more readily precipitable after being frozen. W. D. H.

**Erepsin in the Fœtus.** E. JAEGGY (*Zentr. Gynaekol.*, 1907, No. 35).—According to Zweigel, the fœtal digestive organs contain no pepsin or trypsin. In order to estimate the metabolic action of the intestine apart from its digestive action, it is necessary to investigate it in its empty, and therefore best in its fœtal, condition. To this end, a research on its autolytic protein-splitting ferments, its erepsin, and its arginase becomes necessary, and the present communication relates to erepsin only. It is present in the human fœtal intestine (six specimens) as early as the fifth month. Pancreatic erepsin is absent. It is therefore probable that the intestine is an active organ even when not doing digestive work. W. D. H.

**Melanotic Pigments and the Fermentative Formation of Melanin.** OTTO VON FÜRTH and ERNST JERUSALEM (*Beitr. chem. Physiol. Path.*, 1907, 10, 131—173).—Hippomelanin, the pigment of melanotic tumours of lymph glands in horses, is characterised by its resistance to chemical reagents and its insolubility in concentrated solutions of alkalis, and so it can be distinguished from melanins of other origin. On decomposition with boiling fuming hydrochloric acid, it yields volatile fatty-acids, oxalic acid, hydrocyanic acid, ammonia, pyrrole, pyridine, and small quantities of a substance like phenol. Indole, scatole, and methylbutylhexoic acid, described by others in relation to other melanins, do not occur. It is free from iron, and its sulphur appears to be due to an impurity. By oxidation with chromic acid and fusion with potassium hydroxide, the ratio between its nitrogen and carbon, originally 1:6, is altered to approach that of artificial melanin (1:9) prepared from tyrosine. This change of tyrosine, produced by tyrosinases of vegetable origin, leads to a lessening of its hydrogen and rise in its oxygen without any important difference occurring in the nitrogen-carbon ratio. The artificial melanin resembles hippomelanin in its general characters. The influence of various factors, chemical and physical, in the fermentative formation of melanin was investigated. Excess of vegetable tyrosinase leads to inhibition, and of animal tyrosinase to a cessation of formation of melanin. Injection of tyrosinase from butterflies into rabbits did not produce an anti-tyrosinase in the blood-serum. The

importance of a possible fermentative formation of melanin *in vivo* is discussed.

W. D. H.

**Elimination of Water by Salivary Glands.** A. J. CARLSON, J. R. GREER, and F. C. BECHT (*Amer. J. Physiol.*, 1907, 19, 360—387).—There is a lymph flow from quiescent salivary glands, which in the horse does not appreciably change when the glands act. The osmotic pressure of the lymph is variable and bears no constant relationship to that of the blood. In most cases, neither filtration nor osmosis accounts for the formation or flow of lymph. Osmosis also will not explain the separation of water by the active glands from the blood. The transfer is considered to be due to a "hormone" produced by the active gland, which, passing into the lymph, increases the secretory activity of the capillaries.

W. D. H.

**Alimentary Excretion of Carbohydrates.** MARTIN H. FISCHER and GERTRUDE MOORE (*Amer. J. Physiol.*, 1907, 19, 314—327).—Simple hyperglycemia (produced in rabbits by diabetic puncture, injection of morphine, or intravenous injection of sugar) does not produce any elimination of sugar by the alimentary tract, although sugar may pass into the peritoneal fluid. But if a sodium chloride solution is injected intravenously also, sugar is then excreted by the small intestine, and possibly also by the large intestine. Whether the stomach also shares in this is uncertain. The salt seems to render the cells of the intestinal mucous membrane permeable to sugar.

W. D. H.

**Cystinuria and Diamines.** F. H. THIELE (*J. Physiol.*, 1907, 36, 68—80).—The conclusions drawn from a study of cases of cystinuria are: (1) there is evidence that amino-acids are denitrified by the intestinal mucous membrane; (2) in cystinuria a deficit may be present in ferments which remove sulphur, in those which remove nitrogen, or in both. The deficit is most usual in the tissues, but may also occur in the intestinal mucosal ferments; (3) denitrification of thio-amino-acids does not occur until the sulphur has been removed.

W. D. H.

**Relation of Some Aromatic Compounds to the Production of Benzoic and Hippuric Acids. New Method for Estimating Salicylic Acid in Presence of Benzoic or Hippuric Acid.** I. A. BRUNO SCHULZ (*Bied. Zentr.*, 1907, 36, 602—604; from *Mitt. landw. Inst. Univ., Breslau*, 3, 575).—Coniferin, when oxidised with permanganate, yields benzoic acid. In compounds containing hydroxyl and methoxyl groups in the ortho-position, a reduction and elimination of the methoxyl takes place when the compound is oxidised by alkaline permanganate; the same process takes place in the animal organism.

Salicylic acid may be estimated by distillation, precipitation as dibromide, and titration; or it may be separated from benzoic or hippuric acid by the process based on its different behaviour towards bromine water.

When methyl salicylate is added to the food, the salicylic acid formed is mostly secreted in a combined form.

N. H. J. M.

**Excretion of Creatinine in the New-born Infant.** SAMUEL AMBERG and W. P. MORRILL (*J. Biol. Chem.*, 1907, 3, 311—320).—The creatinine coefficient is approximately one-third as great in normal breast-fed infants as in adults, but is quite as constant. Considering the relative percentage of muscle in the adult and the child, the theory that creatinine excretion is an important index of endogenous protein metabolism is favoured. W. D. H.

**Nature of Fæces Fat.** JOHN H. LONG and W. A. JOHNSON (*J. Amer. Chem. Soc.*, 1907, 29, 1214—1220. Compare Abstr., 1906, ii, 875).—Experiments are described which confirm the authors' opinion that fæces fat contains substances of the lecithin type. A large proportion of the lecithins can be precipitated by adding acetone to an ethereal extract of the fat. E. G.

**Chlorides in Nerve-Fibres.** JOHN S. MACDONALD (*Proc. physiol. Soc.*, 1907, iii—iv, xvi—xvii; *J. Physiol.*, 36).—The distribution of chlorides is detected by a microchemical use of silver nitrate and subsequent exposure to sunlight, or treatment with a pyro-soda developer. After the passage of a constant current through a nerve, the chlorides, as indicated by the orientation of the precipitate, are found at all the nodes, but this is least marked near the anode; on the anodal side of each node of Ranvier, the precipitate is more diffuse, and is apparently streaming towards the anode. The "injury current" produces the same effect; the nodes nearer the injury are occupied by a heavier precipitate. The second paper gives further details of the same nature. W. D. H.

**Purine Bases from the Human Placenta.** T. KIKKOJI and RISABURO IGUCHI (*Zeitsch. physiol. Chem.*, 1907, 52, 401—403).—Guanine, adenine, xanthine, and hypoxanthine have been obtained from the human placenta. J. J. S.

**Oxygen, Osmotic Pressure, Acids, and Alkalis in Experimental Parthenogenesis.** YVES DELAGE (*Compt. rend.*, 1907, 145, 218—224).—From exhaustive experiments on the action of oxygen and acids and alkalis in experimental parthenogenesis, the author concludes: (1) that the presence of oxygen is not necessary, but detrimental to the parthenogenesis of star-fish; (2) that hypertony of the solutions is not necessary to the parthenogenesis of star-fish, and is useful, but by no means indispensable, to that of sea-urchins; (3) that bivalent ions are not necessary, the parthenogenesis of sea-urchins can be brought about by a solution containing only sodium chloride; (4) that the essential condition, in the case of sea-urchins, is the treatment of the eggs with a solution at first acid and then alkaline, the first undoubtedly acting as a coagulant and the second as a liquefiant of certain constituents of ovular protoplasm; (5) that the electric charge on the ions has no effect, the efficacy of the reagents varies with their acid or alkaline reaction and chemical properties. E. H.

**Metabolism in Phosphorus Poisoning.** GRAHAM LUSK (*Amer. J. Physiol.*, 1907, 19, 461—467).—The experiments recorded on dogs

disprove the statement that phosphorus reduces the oxidising power of the organism. The reverse is rather the case. The metabolism is raised, partly on account of the fever, and partly on account of the specific dynamic action of the increased protein metabolism in Rubner's sense. The creatinine output is scarcely affected. W. D. H.

**Experimental Glycosuria. I.** JOHN J. R. MACLEOD (*Amer. J. Physiol.*, 1907, 19, 388—407).—When every precaution is taken against asphyxia, glycogenolytic fibres (the action of which is to increase the sugar of the blood at the expense of glycogen) are demonstrable with certainty only in the case of the greater splanchnic nerves. The experiments were made on dogs. W. D. H.

**The Cleavage of Certain Dipeptides Derived from Tyrosine and Phenylalanine during a Case of Alcaptonuria.** EMIL ABDERHALDEN, BRUNO BLOCH, and PETER RONA (*Zeitsch. physiol. Chem.*, 1907, 52, 435—447).—The following polypeptides containing aromatic residues are converted into homogentisic acid when administered *per os* into patients suffering from alcaptonuria: glycyl-*l*-tyrosine, *r*-glycyl-phenylalanine, *r*-phenylalanylglycine, *r*-alanylphenylalanine, *r*-phenylalanylanine, *r*-leucylphenylalanine. The behaviour is thus entirely different from that of the same substances towards enzymes, when asymmetric hydrolysis usually occurs.

The formation of homogentisic acid is practically quantitative in each case.

Subcutaneous injection of glycyl-*l*-tyrosine also produces an increase in the amount of homogentisic acid. The conclusion is drawn that the acid is formed in the tissues and not in the intestine.

Diiodotyrosine is not converted into homogentisic acid.

It was noticed that the amount of urine increases with the amount of homogentisic acid, and also the amount of ammonia with the amount of reducing substances present. J. J. S.

**The Action of Caffeine on the Capacity for Muscular Work.** W. H. R. RIVERS and H. N. WEBBER (*J. Physiol.*, 1907, 36, 33—47).—The method employed was an improved ergographic one, and mental bias was excluded by the subjects of the experiments not knowing what drug they were taking. Caffeine produces an increased capacity for muscular work, but there are differences noted in the two subjects of the experiment. One effect noted was an acceleration of fatigue as measured by the number of the contractions; another effect as measured by the height of the contractions was a diminution of fatigue; the former effect is probably of central, the latter of peripheral, origin. W. D. H.

**The Action of Cocaine, Adrenaline, and Andoline on Surviving Blood-Vessels.** OSKAR B. MEYER (*Zeitsch. Biol.*, 1907, 50, 93—112. Compare Abstr., 1906, ii, 777).—The experiments were made on the freshly-removed subclavian arteries of oxen, and the effects on them of drugs were recorded in curves. Andoline is a soluble "compound" of stovaine and  $\beta$ -eucaine, and has been recently

recommended as a local anæsthetic and reliever of neuralgic pain. Its two components are vaso-dilators, and more powerful ones than atropine or cocaine, and therefore antagonistic to adrenaline. The relative amount of lengthening which occurs in blood-vessels previously shortened by adrenaline enables the action of the drugs to be compared numerically.

W. D. H.

**Action of Muscarine and Atropine.** WALTHER STRAUB (*Pflüger's Archiv*, 1907, 19, 127—151).—Muscarine brings the heart of *Aplysia* to a standstill, although it has not the nervous inhibitory mechanism of the vertebrate heart. The poison is supposed to act on the heart muscle, and to accumulate there, none being found in the blood after a time. There is in this animal no recovery on the application of atropine, the antagonism between the two drugs only occurring in animals the hearts of which have inhibitory nerves.

W. D. H.

**Aspidin and Filmarone.** MAX GONNERMANN (*Pflüger's Archiv*, 1907, 119, 110—116).—Aspidin and filmarone are two crystalline substances contained in the pharmaceutical preparation of male fern. On hydrolysis, they each yield phloroglucinol and butyric acid, and appear to constitute for the most part the active principle of the extract. A detailed description of their physical and chemical characteristics is given; of the latter, the most striking being their stability even when boiled with ammoniacal silver or Fehling's solution. Pepsin, trypsin, and pancreatin do not manifest any splitting action on either of them.

G. S. W.

**Action of Extract of the Hypo-branchial Gland of *Purpura lapillus*.** HERBERT E. ROAF and MAXIMILIAN NIERENSTEIN (*Proc. physiol. Soc.*, 1907, v—viii; *J. Physiol.*, 36).—The extract of the purple gland contains a substance which is allied chemically and physiologically to adrenaline.

W. D. H.

**Poisonous Action of Hydroxylamine and Hydrazine.** OSCAR LOEW (*Chem. Zeit.*, 1907, 31, 912).—Raciborski's experiments on the assimilation of hydroxylamine and hydrazine salts by fungi, from which that author concludes that these bases are not invariably poisonous (this vol., ii, 384), are inconclusive, since the hydroxylamine and hydrazine must have formed oximes and hydrazones respectively with the dextrose and lævulose resulting from inversion of the sucrose employed as culture medium. That the hydroxylamine or hydrazine salt was present in excess was not established; moreover, the presence of large amounts of sucrose might enable the fungus to reduce any poisonous nitrogenous molecules immediately on entrance.

G. Y.

**Toxicological Detection of the Poisonous Principle of *Atractylis gummifera*.** II. FRANCESCO ANGELICO and A. PITINI (*Gazzetta*, 1907, 37, i, 446—449. Compare this vol., ii, 122).—The authors have made experiments on dogs, poisoned either by decoctions of the roots of *Atractylis gummifera* or by potassium atractilate, the

poisonous principle of the plant, the various organs of the animals being examined for the presence of potassium atractilite by heating with sulphuric acid (*loc. cit.*). In none of the organs could the poison be detected, and it is evident that it undergoes immediate transformation in the organism. In the vomited matter as well as in the contents of the stomach and intestines, the poison was, however, found. Traces of the poison, mixed with pastes of the various organs, were detectable even after putrefaction was far advanced. T. H. P.

**The State of Oxidation of the Tissues and the Electrical Charge of Leucocytes as Important Agents in Immunisation.**  
ALEXANDRE DE POEHL (*Compt. rend.*, 1907, 145, 487—489).—If leucocytosis occurs in blood relatively strongly alkaline, spermine,  $C_5H_{14}N_2$ , is found. The effect of the spermine is to reinforce both the leucocytosis and the alkalinity. Other agents do this also, but not so promptly or effectively. Resistance to infection is reduced when the serum alkalinity is reduced, for example, by the lactic acid of fatigue. Hence the spermine in all probability increases the resistance in both ways, provided that the leucocytosis produced is that of the benign kind. It is shown that leucocytes change their electric condition readily, and also that protein in an alkaline medium is negative; hence the leucocytes are negatively charged in an alkaline medium. If the bacteria are positive, alkaline serum causes positive chemiotaxis, that is, a benign leucocytosis; conversely, less alkaline serum causes negative chemiotaxis, namely, malign leucocytosis. From this point of view, Robin's results with colloidal metals may be considered, and it is probable that colloidal metals and spermine will give important therapeutic results.  
G. S. W.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Lipolytic Power of Croton Seeds.** FRANCESCO SCURTI and A. PARROZZANI (*Gazzetta*, 1907, 37, i, 476—482). The authors show that croton seeds contain a lipase as active as that of *Ricinus* seeds, and capable of saponifying fats energetically (compare Dunlap and Seymour, Abstr., 1905, ii, 753) in presence of a small proportion of sulphuric acid (compare Connstein, Hoyer, and Wartenburg, Abstr., 1903, i, 218). It is remarkable that, of the oils examined, the only one which is not appreciably hydrolysed by the lipase of croton seeds is croton oil.

T. H. P.

**Hydrolytic Properties of Croton Seeds.** FRANCESCO SCURTI and A. PARROZZANI (*Gazzetta*, 1907, 37, i, 486—488).—Besides possessing lipolytic properties (compare preceding abstract), croton seeds are capable of: (1) hydrolysing esters of fatty and aromatic acids, such as ethyl butyrate, ethyl ethylhexoate, ethyl benzoate, or phenyl salicylate, converting them into acid and alcohol (or phenol); (2)

hydrolysing sucrose and raffinose, yielding reducing sugars, and  
(3) hydrolysing starch with formation of dextrose T. H. P.

**Presence of a Proteolytic Enzyme in Croton Seeds and its Action on Proteins Associated with it.** FRANCESCO SCURTI and A. PARROZZANI (*Gazzetta*, 1907, 37, i, 488—504).—The authors first give a résumé of previous investigations on proteolytic enzymes in plants and point out that our knowledge in this region is imperfect, that in very few cases has the action of such an enzyme been actually demonstrated, and that it has not been ascertained what part of the changes occurring are due to the chemical transformation of the reserve proteins or what are the terminal decomposition products of the protein molecule.

The experiments described were made with powdered croton seeds, which were digested for about five weeks at 35—40° with water, 0.25% of acetic acid, and a large excess of chloroform. During this time, the nitrogen present in the liquid increased from 0.081 gram per 100 c.c. to 0.397 gram, 0.091 gram being protein nitrogen and 0.306 gram soluble nitrogen. The solution was found to contain arginine, histidine, lysine, glutamine, aspartic acid, leucine, and phenylalanine.

The following conclusions are drawn. Croton seeds, even in a resting state, contain, probably in the form of zymogen, a proteolytic enzyme capable of attacking energetically the proteins associated with it, forming simpler, soluble, and diffusible nitrogen compounds. This enzyme exerts an action similar to that exerted by animal trypsin, and must hence be considered as a vegetable trypsin. As the products formed by its action are identical with those obtained by the action of mineral acids, the enzyme is sufficiently energetic to raise the strength of dilute organic acids to that of boiling mineral acids. The complex phenomena of germination are hence, to some extent, simple hydrolytic actions. The changes produced by the enzyme in the authors' experiments must be analogous to those occurring in the seeds in their passage from a latent state to one of actual life. T. H. P.

**Reduction During Alcoholic Fermentation of Nitrates Occurring Naturally in Certain Musts.** MATTEO SPICA (*Gazzetta*, 1907, 37, ii, 17—22).—Wines prepared from Carricante and Vispara grapes clarify more rapidly in the light than in the dark, the action being accelerated by the presence of air. Reduction of the nitrates in a must to nitrites during fermentation only occurs when there is a scarcity, in both the must and the surrounding medium, of the oxygen required by the yeast; under such conditions, the yeast assumes the functions of an anaërobic organism and makes use of part of the oxygen contained in the nitrates, which thus undergo reduction. Hence, since genuine wines and musts may contain nitrates and, under certain circumstances, nitrites, the presence of these salts is by no means a proof of adulteration with water containing nitrates or nitrites. T. H. P.

**Action of Carbon Dioxide, Oxygen, and Hydrogen on Bacteria at Various Pressures.** BERGHAUS (*Arch. Hygiene*, 1907, 62, 172—200. Compare Hoffmann, *Abstr.*, 1906, ii, 695).—Carbon

dioxide has an inhibitory effect on the development of bacteria at atmospheric pressure. The varying results obtained by different observers are due to small differences in the culture media which markedly influence the resistance. Some bacteria, like yeast, develop equally rapidly in a carbon dioxide atmosphere. As the result of a series of experiments, in which cultures were subjected first to a carbon dioxide pressure ranging from 0 to 16 atmospheres for twenty-four hours and then subsequently allowed to develop in the air, the bacteria are divided into three classes. The first class are absolutely killed by carbon dioxide even at atmospheric pressure; the second do not develop in carbon dioxide, but are not killed even by an exposure to it at a pressure of an atmosphere; the majority develop in carbon dioxide, some even up to a pressure of two atmospheres, and they require exposure to a much higher pressure to prevent their subsequent growth in air. *Bacillus coli* is particularly resistant.

A similar series of experiments in oxygen with the same bacteria showed that development in every case took place up to pressures as high as  $1\frac{1}{2}$  atmospheres, whilst others developed at pressures of  $2\frac{1}{2}$  (*Bacillus coli*) and even 3 (*Staphylococcus aureus*) atmospheres. In most cases, they continued to develop subsequently in air at ordinary pressure even when previously exposed to pressures of 40 atmospheres, whilst *Bacillus coli* resists 75 atmospheres without being killed.

Hydrogen even at 75 atmospheres is practically without influence on the growth of these bacteria, and even those which are pronouncedly aërobic seem to find enough oxygen for growth in the pabulum.

E. F. A.

**Action of Vapours on Yeast Cells.** REGINALD O. HERZOG and FRANZ HÖRTH (*Zeitsch. physiol. Chem.*, 1907, 52, 432—434. Compare H. Buchner and Gruber, D.R.-P. 113181, 137643, 137995).—Experiments were made by placing a small amount of fresh yeast on a dish in a desiccator, the bottom of which contained 50—100 c.c. of alcohol or other volatile liquid. The desiccator was rapidly evacuated (one minute), and the time noted at which liquefaction of the cells occurred. The following are the times: methyl alcohol 1·2, acetone 3·3, ethyl alcohol 6·2, chloroform 13·8, ether 33·8 minutes; benzene 6·8, carbon disulphide 7·3, toluene 17 hours; light petroleum 8 days, and formaldehyde no action. The effect appears to be the most rapid with vapours which dissolve readily in water. The inhibiting action of various liquids on fermentation appears to be closely related to their liquefying effects.

J. J. S.

**Catalysis of Hydrogen Peroxide by Bacteria.** D. RYWOSCH and MARIE RYWOSCH (*Centr. Bakt. Par.*, 1907, i, 44, 295—298).—The oxygen evolved from solutions of hydrogen peroxide by a number of species of bacteria grown on agar plates has been measured quantitatively. The anaërobic bacteria (*Botulinus* and *Tetanus*) hardly act as catalysts, whereas the pronounced aërobic bacteria are very active, a sarcina evolving 7 c.c. per milligram. The *Vibrio* are remarkable in showing a very weak catalytic power. *Staphylococcus aureus* is about three times as active as *Staphylococcus albus*, showing that

the activity is not a group property. Most bacteria evolve the greater part of the oxygen during the first hour, as does a twenty-four hour culture of *Bacillus anthracis*. A forty-eight hour culture, however, evolves very little oxygen in the first hour, although it subsequently gives a large volume. This is regarded as due to the formation of spores, which react more strongly against the poisonous action of hydrogen peroxide, but require time for their coatings to be destroyed and their catalytic power set in action. It is considered that bacteria, like other catalases, function to destroy hydrogen peroxide, which is poisonous to protoplasm, immediately on its formation in the organism.

E. F. A.

**Attempts to Increase the Oxidising Action of Vinegar Bacteria by the Addition of Iron and Manganese Salts.** F. ROTHENBACH and W. HOFFMANN (*Chem. Zentr.*, 1907, i, 1637—1638; from *Deutsch. Essigind.*, 1907, 11, 125—127).—Although acetic acid bacteria contain iron (Buchner and Gaunt, *Abstr.*, 1906, i, 920), and iron is also found together with manganese in many oxydases (Bertrand, *Abstr.*, 1897, ii, 493), the addition of 0.01—0.1% of ferrous sulphate and manganese sulphate does not perceptibly increase the oxidation even when the bacteria have been gradually accustomed to the presence of ferrous sulphate.

E. W. W.

**Formic Acid as a Preservative.** BERNARD H. SMITH (*J. Amer. Chem. Soc.*, 1907, 29, 1236—1241).—Experiments have been made with the object of determining the value of formic acid as a preservative. It has been found that, in the case of stewed tomatoes, formic acid acts as an efficient antiseptic when present in considerable quantity, but is inferior to benzoic or salicylic acid, and that benzoic acid is more active than salicylic acid in preventing fermentation.

In the examination of foods, the separation of formic acid is best effected by steam distillation after acidifying with phosphoric acid. To detect formic acid in presence of acetic acid, the red liquid obtained on addition of ferric chloride is treated with five times its volume of 95% alcohol; this precipitates the formate after a time, the acetate remaining in solution. The test fails in presence of a large excess of acetate. For details the original must be consulted. For estimating the acid, Portes and Ruyssen's method is recommended (this *Journ.*, 1876, ii, 663; compare Sparre, *Abstr.*, 1900, ii, 449).

E. G.

**Proteolytic Changes in Lima Bean during Germination.** SHINKICHI SUZUKI (*J. Biol. Chem.*, 1907, 3, 265—277).—In the cotyledon, all proteins except peptones decrease at the six and twelve day stages of growth. Peptones, amino-derivatives, and ammonia increase at the six day stage and then decrease; these substances must be due to the cleavage of proteins. The decrease of all nitrogen at the twelve day stage must be due to translocation into the stems; this is confirmed by analyses of the stems. The change is more active in sunlight than in darkness; in the stem, the peptones and amino-compounds decrease as the formation of coagulable protein increases.

W. D. H.

**Influence of Magnesium Sulphate on the Growth of Seedlings.** GERTRUDE S. BURLINGHAM (*J. Amer. Chem. Soc.*, 1907, 29, 1095—1112).—Magnesium sulphate in solutions of greater concentration than  $m/3192$  has a toxic action on most seedlings. A solution of that strength is toxic to pea seedlings, but slightly stimulates *Abutilon*, and has a marked stimulating effect on maize. The maximum stimulating effect is produced by solutions from  $m/32768$  to  $m/131072$ . When employed in proper dilution, magnesium sulphate may nearly double the production; in the case of *Abutilon* seedlings, the growth of the primary root was increased fifteen times. At the same time, the lateral roots develop sooner and attain a greater growth.

The results show that, in absence of other salts, magnesium sulphate is not necessarily injurious, and may be highly beneficial.

N. H. J. M.

**Hemicelluloses contained in the Husks of the Seeds of Cucurbita Pepo.** NICOLA CASTORO (*Zeitsch. physiol. Chem.*, 1907, 52, 521—525. Compare Abstr., 1906, ii, 884).—The husks of *Cucurbita Pepo* seeds contain a xylan, as xylose crystals have been isolated from the syrup obtained after the husks had been hydrolysed with sulphuric acid. A galactan is also present, as the mother liquors from the xylose crystals yield mucic acid when oxidised.

J. J. S.

**Constituents of the Seeds of Pinus Cembra.** ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1907, 67, 57—104).—The dry matter of seedlings of *Pinus Cembra* contains about 60% of fat, which shows a high iodine number and, when decomposed, yields a mixture of fatty-acids which remain mostly liquid for several months; the fat contains some phytosterol and very little lecithin. About 15% of the dry matter consists of proteins: globulin, and two proteins insoluble in 10% sodium chloride. The seedlings contain very small amounts of bases; choline and arginine were detected. The carbohydrates consist of starch, sucrose, and at least one other soluble carbohydrate. The cell-wall contains, besides cellulose, hemicellulose, a galactan, and a pentosan. Citric acid and probably oxalic acid were found to be present, whilst, as regards phosphorus compounds, nuclein, lecithin, and phytin were detected. The ash contains much potassium and phosphoric acid.

The seed husks consist chiefly of cellulose, hemicellulose, and a brown dye; they contain little nitrogen, fat, soluble carbohydrates, and mineral matter. The ash contains much potassium, but very little phosphoric acid.

N. H. J. M.

**Fat of the Seeds of Canarium commune.** P. PASTROVICH (*Chem. Zeit.*, 1907, 31, 781—782).—The air-dried kernel of *Canarium commune*, L., contains fat, 65.73%; crude protein, 12.24%; crude fibre, 3.81%; extractive matter free from nitrogen, 6.0%; ash, 3.19%, and water, 9.03%. The whole of the fat is extracted by means of light petroleum, but only 56.12% by pressure; it is obtained as a pale yellow, odourless oil, having a pleasant flavour, and solidifies at 17°.

In the following values for the constants of the oil, where two are quoted, the first is for the oil extracted by light petroleum, the second for the oil obtained by pressure: m. p. 18—28.5°;  $D_{40}^{20}$  0.9050; acid number, 1.31, 0.84; saponification number, 194.28; ester number, 192.97, 193.45; Hehner's number, 95.36, 95.73; Hübl's iodine number, 65.63, 65.12; Wijs' iodine number, 65.94, 65.28; refraction in Zeiss' butter refractometer at 40°, 51.3°, 51.1°; glycerol, 10.53%, 10.56%; unhydrolysable substances, 0.46%; saponification number after acetylation, 197.6, 196.92; Hehner's number for the acetylated fat, 94.59, 94.67.

The insoluble fatty-acids consist of about 29.5% of palmitic, 15.0% of stearic, 43.0% of oleic, and 12.5% of linoleic acids. A fat-hydrolysing ferment was not found in the kernels. G. Y.

**Examination of the Fruit of *Brucea antidysenterica*.** FREDERICK B. POWER and ARTHUR H. SALWAY (*Pharm. J.*, 1907, 79, 126—128).—The following are the more important constituents of the fruit of *Brucea antidysenterica*, an Abyssinian plant: (1) a fatty oil, amounting to about 22% of the weight of the fruit; this oil yields oleic, linoleic, palmitic, and stearic acids, together with small quantities of acetic and butyric acids; phytosterol is also present. (2) A small amount of volatile acids, consisting of a mixture of formic and butyric acids. (3) About 1% of resinous substances. (4) A bitter principle. (5) A considerable quantity of an amorphous, yellow colouring matter. (6) A large amount of dextrose. W. P. S.

**Chemical Examination of the Barks of *Brucea antidysenterica* and *Brucea Sumatrana*.** ARTHUR H. SALWAY and WALTER THOMAS (*Pharm. J.*, 1907, 79, 128—130).—The investigation showed that the bark of *Brucea antidysenterica* contains some bitter substances, but these could not be separated in the form of definite compounds. A considerable amount of dextrose was obtained from the bark, as were also certain resins, phytosterol, and volatile acids. The bark of *Brucea Sumatrana* yielded an amorphous, bitter principle, volatile acids (formic, acetic, and butyric), proteins, and an acid which was probably behenic acid. W. P. S.

**On *Cucumis trigonus* and *Colocynthin*.** WILLIAM A. H. NAYLOR and E. J. CHAPPEL (*Pharm. J.*, 1907, 79, 117—118).—*Cucumis trigonus*, or pseudo-colocynth, contains a principle identical with, or closely related to, colocynthin. From experiments with colocynthin obtained from *Citrullus Colocynthis*, the authors find that this substance is capable of hydrolysis, and that it yields, amongst other products, colocynthein, elaterin, and dextrose. The authors were also able to obtain colocynthin in a crystalline form. W. P. S.

**Migration of Odoriferous Compounds [in Plants].** EUGÈNE CHARABOT and G. LALOUÉ (*Bull. Soc. chim.*, 1907, [iv], 1, 640—646. Compare this vol., ii, 714).—By analysing the various organs of *Verbena triphylla* (1) when in flower and (2) after fructification, the authors obtained further proof of the migration of the odoriferous

principle at the time of inflorescence, the percentages of essential oil in the dry matter of the various parts being as follows :

	During inflorescence (Sept. 16, 1905).	After fructification (Oct. 2, 1905).
Roots .....	0·028	0·049
Stems .....	0·015	0·029
Leaves .....	0·579	0·486
Inflorescence .....	0·544	0·239
Whole plant .....	0·227	0·186

The stem plays the part of a channel, connecting the leaf, which produces the essence, with the flower which consumes the essence. While the flower is carrying out its functions, essence accumulates in the roots and stems, whilst the flowers and leaves lose a fraction of their essence. The plant uses up some of the essence. T. H. P.

**Poisonous Action of Various Salts on Spirogyra and the Antidotal Effect of Calcium Salts.** WILHELM BENECKE (*Ber. deut. bot. Ges.*, 1907, 25, 322—337).—Although *Spirogyra* will grow luxuriantly in suitable complete mineral solutions, they are very sensitive to the single components of such solutions, with the exception of calcium. The chlorides, nitrates, sulphates, and phosphates of sodium, potassium, magnesium, and iron are more or less poisonous ; iron and magnesium being more poisonous than potassium, and potassium more so than sodium, whilst phosphates, sulphates, and nitrates are more poisonous than chlorides. In each case, the injurious effect can be inhibited or diminished by the presence of calcium.

Barium and strontium should exercise a similar protective action; without, however, taking the place of calcium as a nutrient.

N. H. J. M.

**Phosphoric Acid Removed by Crops, by Dilute Nitric Acid and by Ammonium Hydroxide, from a Limed and Unlimed Soil Receiving Various Phosphates.** BURT L. HARTWELL and JAMES W. KELLOGG (*19th Ann. Rep. Rhode Island Agric. Exper. Stat. for 1904—5*, 253—285. Compare Abstr., 1905, ii, 353).—The assimilability of the phosphates and of the soil phosphorus varies with the reaction of the soil. As regards measurement of availability by growing crops, it is found that flat turnips gave useful results, whilst in the case of oats and German millet the range in percentage of phosphoric acid is not wide enough. The relative yield of turnips on limed plots receiving the same amount of phosphoric acid ranges between 1·7 and 27·0, according to the kind of phosphate, as compared with the limed check plot taken as 1. The percentage of phosphoric acid in the dry matter of the roots and tops varied between 0·45 and 0·87 and between 0·31 and 0·83 respectively.

Ammonium hydroxide (*N*/5, *N*/25, and *N*/100) and nitric acid (*N*/5 and *N*/25) failed to indicate uniformly the differences in the availability of the phosphoric acid as shown by the crop results. It is doubtful whether any solvent will extract from all soils amounts of

phosphoric acid corresponding with those removed by a given crop, especially when much of the phosphorus is present in organic forms.

N. H. J. M.

**Field Manurial Experiments on the Action of Ammonium Sulphate as Compared with Sodium Nitrate.** FRIEDRICH KRETSCHMER, HERMANN RÖMER, HANS C. MÜLLER, PAUL BÄSSLER, and M. HOFFMANN (*Bied. Zentr.*, 1907, 36, 586—594; from *Arb. deut. Landw.-Ges.*, 1906, Heft 121; and *Mitt. deut. Landw.-Ges.*, 1906, No. 42).—The results of experiments with different crops conducted in different parts of Germany showed that in the majority of cases sodium nitrate was superior to ammonium sulphate.

N. H. J. M.

**Manurial Experiments with Calcium Cyanamide and Sodium Nitrate on Oats.** RICHARD OTTO (*Bied. Zentr.*, 1907, 36, 634—635; from *Deut. Landw. Presse*, 1906, 33, 32. Compare *Abstr.*, 1905, ii, 126).—Sodium nitrate doubled the production of grain and straw; with cyanamide, the yields were three times as much as without manure.

N. H. J. M.

**Influence of Mineral Manure on Fixation of Nitrogen by Lower Organisms in Soil.** HERMANN WILFARTH and GUSTAV WIMMER (*Landw. Versuchs-Stat.*, 1907, 67, 27—50).—Fixation of free nitrogen takes place in pure sand, inoculated with soil extract, when phosphoric acid is present in addition to potassium, calcium and magnesium, but not in absence of phosphoric acid. The production of organic matter in the form of different algae also depends on the presence of phosphoric acid. The amount of organic matter produced is about 20 to 1 of nitrogen fixed.

N. H. J. M.

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## Analytical Chemistry.

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**Burette Reading.** P. KUSNETZOFF (*Zeitsch. anal. Chem.*, 1907, **46**, 515—516).—The reading is facilitated by using a small mirror ( $3 \times 2$  cm.), half of which is coated lengthwise with asphalt varnish, or covered with black glazed paper.

The burette should stand as vertically as possible and be lighted sideways. The mirror is held behind the burette in such a manner that the border of the black strip is visible at about 2—3 divisions below the meniscus. When the dark part of the visible meniscus is on a level with the eye (the other eye should be closed), the mirror is turned  $45^\circ$ , which causes the lower border of the meniscus to become very black.

L. DE K.

**A Simple Method of Determining the Colour of Small Amounts of Slightly Coloured Liquids and its Use in Microchemical Analysis.** FRIEDRICH EMICH and JULIUS DONAU (*Monatsh.*, 1907, **28**, 825—831).—In microchemical colour reactions, in which

the coloured substance cannot be precipitated on a textile fibre (compare this vol., ii, 296) or by concentration, the sensitiveness of the test can be increased by observing under the microscope the colour of a column of the liquid contained in a thick-walled capillary glass tube of 0.2—0.5 mm. internal diameter and 2—3 cm. in length. The light is transmitted through the length of the capillary. The following are the minimum amounts of the substances named which could be detected in 1 cm. by this method;  $E$  is the "equivalent sensitiveness" (*loc. cit.*). Methylene-blue, 0.002  $\mu\text{g}$ ,  $E=170,000$ ; nitric acid, by the diphenylamine reaction, 0.01  $\mu\text{g}$ ,  $E=6300$ ; colloidal gold, 0.002—0.004  $\mu\text{g}$ ,  $E=22,000$ ; permanganic acid, 0.01—0.02  $\mu\text{g}$ ,  $E=8000$ ; manganese, by oxidation with lead dioxide and nitric acid, 0.05—0.1  $\mu\text{g}$ ,  $E=3600$ ; iron, as ferric thiocyanate, 0.002—0.003  $\mu\text{g}$ ,  $E=6000$ ; platinum, by means of potassium iodide, 0.005  $\mu\text{g}$ ,  $E=10,000$ ; hydrochloric acid or sodium hydroxide, by means of litmus, 0.003—0.006  $\mu\text{g}$ ,  $E=10,000$ . G. Y.

**Iodometric Estimation of Chlorates.** ROBERT LUTHER and TH. F. RUTTER (*Zeitsch. anal. Chem.*, 1907, 46, 521—522).—Ten c.c. of the solution containing about 0.035 gram of the chlorate are mixed with 10 c.c. of  $N$ -potassium iodide, 10 c.c. of  $2N$ -sulphuric acid, and 10 c.c. of  $N/100$  vanadyl sulphate; this acts as catalyst. The solution is heated in a sealed tube or securely-stoppered flask in the boiling water-bath for fifteen minutes. When cold, the contents are diluted to 100 c.c., and the iodine liberated is titrated with  $N/100$  thio-sulphate as usual. L. DE K.

**Microscopic Detection of Very Small Quantities of Bromine.** M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, 12, 316—317).—The dry substance or the solution reduced to about 2 c.c. is heated in a small, round-bottomed flask with a few drops of sulphuric acid and a few drops of saturated chromic acid solution, and the vapours are passed into a small test-tube containing a trace of pure aniline. The precipitate formed when viewed under the microscope is at first flocculent, but then becomes crystalline, and the field is filled with very small and slender prisms. Sometimes the prisms are a little larger, and occasionally long needles are noticed, but the field always has the appearance of a colony of isolated bacteria. Sometimes these bacillar crystals form rose-shaped clusters. Illustrations are given. L. DE K.

**Estimation of Iodine in the Crude Article.** H. CORMIMBŒUF (*Ann. Chim. anal.*, 1907, 12, 307—308).—Three grams of the sample are treated with 25 c.c. of water and 1 gram of iron filings until a pale green liquid is obtained, which is filtered and made up to 250 c.c. Fifty c.c. of the filtrate are then treated with 1 gram of sodium carbonate, dissolved in a little water, and the whole is diluted to 100 c.c. Fifty c.c. of the filtrate are acidified with nitric acid, and after adding one-fourth of the volume of ammonia the iodine is precipitated with silver nitrate. Any chlorine or bromine present in the crude product may be recovered as usual from the ammoniacal filtrate. L. DE K.

**Ignition of Barium Sulphate.** HENRI PELLET (*Ann. Chim. anal.*, 1907, 12, 318—320. Compare Truchot, this vol., ii, 719).—The filter containing the precipitate should not be dried before ignition. A short ignition after the filter has completely burnt suffices to reoxidise any barium sulphide formed.

In case of large precipitates, it is advisable to moisten the ignited barium sulphate with a few drops of nitric acid, containing one drop of sulphuric acid, and to re-ignite. L. DE K.

**Estimation of Sulphur Dioxide in Wine.** V. VETÈRE (*Chem. Zentr.*, 1907, i, 1640; from *Giorn. Farm. Chim.*, 1907, 56, 145—155).—A modification of Ripper's process. A 500 c.c. flask is fitted with a doubly-perforated india-rubber cork, one opening of which is in connexion with a distilling flask and condenser, and the other with a Varrentrap bulb-tube serving as a trap. Into the flask are introduced 100 c.c. of water, 5 c.c. of hydrochloric acid (D 1.1), 10 c.c. of a 10% solution of potassium iodide, and 20 c.c. of a solution of potassium dichromate (3.874 grams per litre), which causes the liberation of exactly 0.2 gram of iodine. Into the bulb-tube are placed 5 c.c. of standard thiosulphate and a little water, and the air from the apparatus is expelled by a current of carbon dioxide. The wine and 5 c.c. of syrupy phosphoric acid are put into the distilling flask, and one-half of the volume is distilled. The contents of the bulb-tube are emptied into the flask, both tube and condenser are well rinsed, and the excess of iodine is titrated as usual. In this manner, all risk of loss of iodine is avoided. L. DE K.

**Detection of Pentathionic Acid in Aqueous Solution.** J. J. P. VALETON (*Chem. Weekblad*, 1907, 4, 553—555).—The ordinary tests employed to distinguish pentathionic acid from the other polythionic acids—the action of strong bases, ammonia, ammoniacal mercuric cyanide, ammoniacal silver nitrate, and ammonia followed by hydrogen sulphide—are valueless, since a pure colloidal solution of sulphur reacts similarly, and all these alkaline reagents decompose pentathionic acid with precipitation of sulphur. There is no test applicable to the detection of pentathionic acid in aqueous solution. A. J. W.

**Standardisation of Sodium Thiosulphate and Estimation of Sodium Sulphide.** ADOLPHE BESSON (*Chem. Zentr.*, 1907, ii, 177—178; from *Collegium*, 1907, 193—198).—Ten c.c. of the clear, approximately *N*/10-thiosulphate are heated for ten minutes in the boiling water-bath with 25 c.c. of *N*/10-alkali and 20 c.c. of neutral hydrogen peroxide (10 c.c. of Merck's "Perhydrol" diluted to 200 c.c.), and the excess of alkali is titrated with *N*/10 acid, with methyl-orange as indicator. Two mols. of sodium hydroxide = 1 mol. of thiosulphate. The presence of sulphite or sulphide does not interfere, but carbonates should be estimated and allowed for.

Sodium sulphide is titrated with *N*/10-iodine, and the liberated sulphur may then be oxidised with hydrogen peroxide as described; 2 mols. of sodium hydroxide = 1 atom of sulphur. In another part of the liquid, the total alkali may be titrated as usual. If the salt is

pure, the results should agree, but a difference points to the presence of free alkali or sulphite. It should be remembered that a sulphite only shows half the amount of alkali present when titrated with acid. Sulphites may be readily titrated, however, by means of *N*/10-iodine after removing the sulphide by means of cadmium carbonate or zinc sulphate. L. DE K.

**Volumetric Estimation of Thiosulphates, also in Presence of Sulphites.** AUGUST GUTMANN (*Zeitsch. anal. Chem.*, 1907, 46, 485—500. Compare this vol., ii, 298).—Twenty to fifty c.c. of approximately *N*/10-thiosulphate solution are mixed with 0.3—1 gram of pure potassium cyanide and 2 c.c. of 15% sodium hydroxide solution, and heated for half an hour on the water-bath. The liquid now contains, besides undecomposed cyanide, sulphites and potassium thiocyanate. After titrating the cyanide with *N*/10-silver, according to Liebig, a definite volume of the latter is added, the liquid is acidified with nitric acid, and then diluted to a definite bulk. The excess of silver is then estimated in an aliquot part of the filtrate with ammonium thiocyanate, according to Volhard. From the silver precipitated is deducted that required by the cyanogen  $\times 2$ ; the difference represents that absorbed by the thiocyanate. One litre of *N*/10-silver = 0.1 mol. of thiosulphate. The presence of additional sulphite does not interfere, but a little more nitric acid should then be added to redissolve any silver sulphite. A large number of test analyses are communicated. L. DE K.

**Estimation of Nitric Nitrogen.** CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1907, 4, 594—595. Compare Abstr., 1900, ii, 242).—Vriens (this vol., ii, 651) has criticised adversely the author's method, and has proposed an alternative method.

The author upholds his own process, and thinks that boiling with a strong acid and excess of a ferrous salt cannot lead to satisfactory results unless the air is rigidly excluded. L. DE K.

**Estimation of Nitrous Acid and its Separation from Nitric Acid.** G. MADERNA and GIULIO COFFETTI (*Gazzetta*, 1907, 37, i, 595—598).—When a solution of a nitrite is treated with acetic, oxalic, tartaric, or citric acid and potassium ferrocyanide, nitric oxide is evolved according to the equation:  $K_4FeCy_6 + KNO_2 + 2C_2H_4O_2 = K_3FeCy_6 + 2KC_2H_3O_2 + NO$ . On this reaction is based the method of estimating nitrous acid devised by the author, who shakes up saturated solutions of citric acid and potassium ferrocyanide with the nitrite solution in a Lunge nitrometer. The method gives results agreeing exactly with those obtained by titration with permanganate, and it can be used with solutions containing large proportions of nitric acid, which does not form nitric oxide under the conditions used. T. H. P.

**Estimation of the Composition of Nitrating Mixtures.** GIULIO COFFETTI and G. MADERNA (*Gazzetta*, 1907, 37, ii, 13—17).—With nitrating mixtures which have been used and contain

organic matter, it is not possible to estimate the nitrous acid by titration with permanganate. The authors give the following methods for analysing such mixtures.

(1) When the mixture contains, besides the ordinary components, acid organic compounds, but no organic nitro-compounds, the sulphuric acid is estimated gravimetrically, the total nitrogen (from nitric and nitrous acids) by means of the nitrometer, and the nitrous acid by the method described by the authors (see preceding abstract). (2) When nitro-compounds, but no organic acids, are present, the estimations made are the total acidity, the sulphuric acid and the nitrous acid, the nitric acid being obtained by difference. (3) When both organic acids and nitro-compounds are present, the following estimations are made: the total acidity, the acidity after elimination of nitrous and nitric acids, the sulphuric acid, and the nitrous acid; the nitric acid is estimated by difference.

These methods are found to give good results.

T. H. P.

**Microchemical Detection of Phosphorus in Microscopical Preparations of Vegetable and Animal Tissues.** ALCESTE ARCANGELI (*Gazzetta*, 1907, 37, ii, 148—151).—The author has investigated the method of detecting phosphorus in sections of animal or vegetable tissues by means of ammonium molybdate solution. It is found that precipitation of ammonium phosphomolybdate does not always take place in such sections, especially when the phosphorus exists in organic combination. The tissues behave irregularly towards ammonium molybdate, so that, after reduction by means of stannous chloride, they assume a more or less intense blue colour independently of the presence, or of the greater or less amount, of phosphorus. The excess of ammonium molybdate cannot be completely removed from the tissues by washing, and hence yields a blue coloration on reduction with stannous chloride. Moreover, the presence of certain substances in the tissues influences and, in some cases, prevents the reaction.

T. H. P.

**Estimation of Free Phosphoric Acid in Superphosphates.** W. MOLLER (*Chem. Zeit.*, 1907, 31, 879—880).—The author in reply to Schultze (*ibid.*, 31, 801) states that free phosphoric acid in superphosphates may be estimated with sufficient accuracy by the conventional "Oxalate Method."

The reason why the insoluble phosphates are but slowly attacked by the free acid is due to the protective action of the calcium sulphate present.

L. DE K.

**Estimation of Boric Acid and Borates in Foodstuffs and Commercial Products.** RODGER J. MANNING and WILLIAM R. LANG (*J. Soc. Chem. Ind.*, 1907, 26, 803—804).—The method described previously (*Abstr.*, 1906, ii, 491) may be employed for the estimation of boric acid in milk and common salt. In the case of milk, 300 c.c. are distilled with 400 c.c. of methylated spirit and 70 c.c. of concentrated sulphuric acid. The distillate is filtered after the addition of barium chloride, but before neutralisation, and the process is then continued

as described. Common packing salt was found to contain 0.88% of boric acid. W. P. S.

**Assay of Sodium Silicofluoride.** S. KOHN (*Chem. Zeit.*, 1907, 31, 794).—Five grams of the sample are dissolved in water and made up to one litre, 100 c.c. of the clear solution are then placed in a porcelain dish, and after adding nearly the requisite amount of *N/2*-alkali the liquid is heated to boiling and mixed with a few drops of alizarin and a sufficiency of calcium chloride solution. The titration is now continued at the boiling heat, the end point being reached when the bright yellow liquid changes to violet. L. DE K.

**New Method of Estimating Potassium [Tarugi's].** RAFFAELLO PAJETTA (*Gazzetta*, 1907, 37, ii, 82—87. Compare *Abstr.*, 1906, ii, 804).—Polemical against Tarugi (this vol., ii, 719). T. H. P.

**Estimation of Potassium Soluble in Mineral Acids in Sulphated Stassfurt Salts and the Influence of Free Hydrochloric Acid in the Estimation of Sulphates or Barium.** BOUWE SJOLLEMA and M. J. VAN'T KRUYSS (*Chem. Weekblad*, 1907, 4, 589—594).—In potassium estimations, it should be remembered that barium sulphate is sensibly soluble in dilute hydrochloric acid; this solubility is, however, much decreased by the presence of either excess of barium or of sulphate. If now only just enough barium chloride is added to convert the sulphates into barium sulphate, the potassium platinichloride obtained in due course will be contaminated with barium sulphate, and the results will be sensibly in excess. If therefore this method should be used, it will be necessary to determine the amount of admixed barium sulphate by extracting the weighed residue with boiling water. Or, better, the free hydrochloric acid should be expelled by evaporation before adding the barium chloride.

L. DE K.

**Estimation of Calcium, Magnesium, and Phosphoric Acid with the Zeiss Immersion Refractometer.** B. WAGNER and F. SCHULTZE (*Zeitsch. anal. Chem.*, 1907, 46, 501—507).—The calcium is precipitated as oxalate, which is then converted by ignition into carbonate. This is then dissolved in acetic acid and evaporated to dryness. The dried mass is dissolved in 5 c.c. of 2% acetic acid, and after diluting to 10 c.c. the liquid is examined with the immersion refractometer at 17.5°. Reference is then made to a table.

In a similar manner, magnesium and phosphoric acid respectively may be determined by washing the triple phosphate with a 1% ammonia solution, and then three times with 1 c.c. of water; the loss on account of solubility in pure water is negligible. The precipitate is dissolved in 10 c.c. of 4% sulphuric acid. The liquid and washings are concentrated and finally made up to 10 c.c., and examined in the refractometer.

For details, the tables and illustrations in the original paper should be consulted. L. DE K.

**Rapid Method for the Estimation of Calcium in Water for Boiler Purposes.** FRANK E. HALE (*J. Amer. Chem. Soc.*, 1907, 29, 1078—1085).—One hundred c.c. of the sample are mixed with 10 c.c. of saturated ammonium chloride solution and 1 c.c. of ammonia (1 : 1), 5 c.c. of saturated oxalic acid solution are added, and the whole well stirred. Five c.c. of a saturated solution of ammonium oxalate are added, and the liquid boiled vigorously for fifteen minutes. The calcium oxalate is collected and washed with hot water in a Gooch crucible. The crucible is replaced in the beaker and covered with boiling water, 10 c.c. of dilute sulphuric acid (1 : 1) are added, and the solution is titrated with  $N/5$  standard permanganate.

The result obtained, coupled with a determination of the alkalinity and the hardness of the sample, enables the magnesia to be calculated, and gives sufficient information as to the suitability of the water for boiler purposes.

L. DE K.

**Estimation of Calcium by the Use of Sugar Solution.** JAMES HENDRICK (*Analyst*, 1907, 32, 320—325).—A process for estimating calcium oxide in burnt limes is described, the oxide being dissolved in sugar solution and then titrated. Five grams of the powdered sample are placed in a 500 c.c. flask already containing 10 c.c. of alcohol, and the flask is then filled to the mark with 10% sugar solution. After being shaken for at least four hours, the mixture is filtered, and 100 c.c. of the filtrate are titrated with standard hydrochloric acid, using methyl-orange as indicator.

The small amount of magnesia present in ordinary burnt lime does not affect the result obtained by the method to any appreciable extent; calcium carbonate is also practically insoluble in the sugar solution, and consequently without influence on the results, but care must be taken that carbonate is not formed by absorption of carbon dioxide from the atmosphere during the estimation.

W. P. S.

**Separation and Estimation of Zinc Oxide in "Zinc White," "Zinc Grey," Paints, and Lithopones.** J. TAMBON (*Bull. Soc. chim.*, 1907, [iv], 1, 823—829).—The method depends on the solubility of zinc oxide, even after ignition, in a mixture of equal parts of ammonia (D 0.924), solution of ammonium carbonate (20%), and solution of ammonium chloride (20%). In the case of "zinc white," 10 grams of the sample are placed in a wide-mouthed stoppered flask and shaken with 300 c.c. of the above solution for a few minutes and then set aside for ten minutes. The insoluble matter is collected, washed, dried, and weighed, and the difference between this weight and that of the original sample is taken as zinc oxide, or the zinc in the ammoniacal solution may be estimated volumetrically by means of sodium sulphide. If soluble zinc salts are present in the "zinc white," they should be removed by washing with warm water before applying this process.

With "zinc grey," the same method is used, but the material is left in contact with the ammoniacal solution for thirty minutes.

Where either of these products is present in oil paints, the organic

matter is removed by a suitable solvent and the residue treated as before, unless Schweinfurth green is present, in which case the green pigment is removed by treatment with ammonia, the zinc oxide being then determined in the residue by the above process.

Lithopones are first thoroughly washed with boiling water to remove soluble zinc salts and the residue treated with the ammoniacal mixture. Zinc sulphide can be estimated in the insoluble portion by any of the usual methods. T. A. H.

**Use of Tin as a Cathode for the Rapid Electrolytic Deposition of Zinc, Copper, Silver, Cadmium, and Nickel.** LAURENCE T. SHERWOOD and GELLERT ALLEMAN (*J. Amer. Chem. Soc.*, 1907, 29, 1065—1074).—The authors have found that under certain conditions a tin cathode may be used instead of a platinum one in the case of zinc, copper, silver, cadmium, and nickel, and probably for other metals as well. For details of the various operations, the original article and tables should be consulted. L. DE K.

**Detection and Estimation of Mercury in Urine.** CARL ENOCH (*Zeitsch. öffentl. Chem.*, 1907, 13, 307—308).—Five hundred c.c. of the urine are rendered alkaline with sodium hydroxide and heated until the phosphates are precipitated. The precipitate, which contains all the mercury, is collected on a filter and washed with a little cold water. The precipitate is then dissolved off the filter in a warm mixture of 5 c.c. of strong nitric acid and 100 c.c. of water, and the filter is washed with hot water until the filtrate measures 150 c.c. To this is then added so much nitric acid that it amounts to one-twentieth of the total volume.

The mercury is then separated electrolytically with the usual precautions, using a current of  $\frac{1}{2}$  ampere. A weighed electrode composed of platinum gauze previously electrolytically coated with copper is used. The smallest amount of mercury is perceptible by the grey colour of the deposit. L. DE K.

**Electrolytic Estimation of Mercury.** VINCENZO BORELLI (*Gazzetta*, 1907, 37, i, 425—429).—None of the text-books dealing with the electrolytic estimation of mercury describe a trustworthy method of drying the mercury deposit before weighing. Heating, even at a low temperature, leads to an appreciable loss of mercury, as also does drying over sulphuric acid, which absorbs mercury vapour. These difficulties are avoided by drying the deposit in a desiccator containing fused potassium hydroxide, four or five hours' drying being sufficient to bring the weight of the deposit to a constant value, which does not change after a further seventy hours. Any very slight loss which may occur in this method may be rendered negligible by placing a small dish of mercury in the desiccator. The nitric acid used to remove the mercury from the platinum capsule on which it is deposited always contains a small quantity of platinum, which has evidently amalgamated with the mercury. T. H. P.

**Volumetric Estimation of Lanthanum as the Oxalate.** W. A. DRUSHEL (*Amer. J. Sci.*, 1907, [iv], 24, 197—198).—Ten to



twenty c.c. of the neutral 1% nitrate solution are mixed with a measured amount of *N*/10-oxalic acid or with *N*/10-ammonium oxalate with addition of a few drops of acetic acid. The lanthanum oxalate is collected in a perforated crucible fitted with an asbestos felt and well washed with water. The crucible and contents are placed in a beaker containing 100 to 300 c.c. of water and 10 to 30 c.c. of dilute sulphuric acid (1 : 4), the liquid is heated to boiling, and at once titrated with *N*/10 permanganate.

By way of a check, the filtrate containing the excess of oxalic acid may be also titrated with permanganate. L. DE K.

**Estimation of Manganese in Water.** ROBERT S. WESTON (*J. Amer. Chem. Soc.*, 1907, 29, 1074—1078).—A suitable quantity of the sample representing about 0.001—0.01 gram of manganese is, if necessary, freed from chlorine by means of silver nitrate and then evaporated to dryness with addition of 25 c.c. of nitric acid, D 1.135. The residue is gently ignited or heated for half an hour at 130° and redissolved in 50 c.c. of nitric acid. 0.5 Gram of sodium bismuthate is added and the liquid heated until the pink colour has disappeared. The cold solution is now mixed with excess of sodium bismuthate, well stirred, and filtered through asbestos contained in a Gooch filter. The filtrate is made up to 100 c.c. with 3% nitric acid and placed in a large Nessler tube. In a similar tube are put 100 c.c. of dilute sulphuric acid (25 c.c. per litre), and the colour of the liquid in the other tube is matched by cautious addition of standard permanganate. L. DE K.

**Estimation of Iron in the Presence of its Oxides.** HENRY G. MARTIN (*J. Amer. Chem. Soc.*, 1907, 29, 1211—1214).—A convenient apparatus for measuring the hydrogen evolved on dissolving a weighed quantity of metallic iron in dilute sulphuric acid is described.

When applying the process to furnace products which contain besides metallic iron also ferrous and ferric oxides, the process cannot lay claim to strict accuracy, as it is assumed that the ferric oxide present is not partially reduced by the hydrogen evolved. If much manganese is present, the results also become uncertain. L. DE K.

**Estimation of Ferrous Carbonate.** PHILIP H. CREWE (*Pharm. J.*, 1907, 79, 115—117, 134).—For the estimation of ferrous carbonate in pharmaceutical preparations, the following methods are recommended, as, by their use, the difficulties due to organic excipients are overcome.

**Saccharated Ferrous Carbonate.**—A weighed quantity of about 1 gram of the sample is stirred for about fifteen minutes with 10 c.c. of 50% phosphoric acid. The solution is then diluted with water to 70 c.c. and titrated with *N*/10-potassium dichromate solution. One c.c. of the latter corresponds with 0.01159 gram of ferrous carbonate.

**Pilula Ferri.**—The method depends on the fact that when hydriodic acid is added to a ferric salt, iodine is liberated and the iron is reduced to the ferrous state. Ten pills are broken up and dissolved in a 200

c.c. flask in diluted sulphuric acid, a little potassium hydrogen carbonate being added, and the solution aided by the application of a gentle heat. The mixture is then diluted to 201 c.c. (1 c.c. being allowed for the insoluble matter), filtered, and 100 c.c. of the filtrate are treated with potassium hydrogen carbonate until the liquid is deep red in colour. Sulphuric acid is now added until this colour just disappears, 3 grams of potassium iodide are introduced, and, after the lapse of thirty minutes, the liberated iodine is titrated with *N*/10-thiosulphate solution, each c.c. of which is equivalent to 0.1789 grain of ferric salt calculated as ferrous carbonate. To a further 50 c.c. of the above filtrate, potassium permanganate is added until a pink coloration is obtained; potassium hydrogen carbonate is then added, and the process continued as described previously. The result gives the total iron calculated as ferrous carbonate, from which the quantity present in the ferric state is subtracted in order to obtain the amount of actual ferrous carbonate.

*Capsule Ferri Carbonas.*—After cutting off the ends of 5 capsules, the contents are washed into a flask with dilute sulphuric acid and chloroform. A little potassium hydrogen carbonate is added, and the mixture is titrated with *N*/10-permanganate solution, each c.c. of which is equivalent to 0.1789 grain of ferrous carbonate.

W. P. S.

**Estimation of Silica and Alumina in Iron Ores.** GRAHAM W. DEAN (*J. Amer. Chem. Soc.*, 1907, 29, 1208—1210. Compare Abstr., 1906, ii, 630).—*Silica only.*—0.5 Gram of the finely-powdered sample is heated in a covered porcelain crucible to dull redness for a few minutes and then boiled in a beaker with 20 c.c. of hydrochloric acid containing 1 gram of stannous chloride in 225 c.c. When all the iron is dissolved, the silica is collected, washed, ignited, and weighed.

*Silica and Alumina.*—0.5 Gram of the finely-powdered ore is placed in a covered porcelain crucible and 0.4 gram of sulphur is sprinkled over it. The whole is heated to dull redness, and the temperature then raised for some ten seconds. The mass is then boiled in a beaker with hydrochloric acid, some nitric acid is added, and the boiling continued for about fifteen minutes. The silica is collected and weighed as before, whilst the alumina is recovered from the filtrate by any suitable method.

L. DE K.

**A New Very Sensitive Method for the Detection of Nickel.** M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1907, 145, 435—436).—The method is based on the fact that nickel molybdate, obtained by double decomposition of a nickel salt with an alkali molybdate, is insoluble in a neutral or slightly acid aqueous solution containing excess of the alkali molybdate, whilst cobalt molybdate is extremely soluble under the same conditions. To apply the test, the mixture of cobalt and nickel sulphides is dissolved in aqua regia, the solution almost neutralised with alkali, treated with a large excess of a saturated solution of ammonium molybdate and heated, with shaking, at 70°. In the presence of cobalt, a rose coloration appears, whilst nickel pro-

duces immediately, or after a few minutes, either an opalescence or a heavy, greenish-white, crystalline precipitate according to the amount present. The formation of a precipitate is absolutely characteristic of nickel in the absence of metals other than cobalt. The method enables the detection of 0.01 gram of nickel in presence of 5 grams of cobalt. A salt of cobaltamine, however, gives a precipitate under the conditions described, but salts of cobaltamine are easily transformed into those of cobalt. E. H.

**Rapid Estimation of Nickel in the Presence of Iron, Chromium, and Manganese.** CHARLES M. JOHNSON (*J. Amer. Chem. Soc.*, 1907, 29, 1201—1208).—A modification of Moore's cyanide process. One gram of steel drillings is dissolved in 20 c.c. of hydrochloric acid (1:1) and 10 c.c. of nitric acid (D 1.20) are added. The liquid is boiled down to 15 c.c. and 8 c.c. of sulphuric acid previously diluted with 24 c.c. of water are added. The solution is now transferred to a 600 c.c. beaker and 12 grams of powdered citric acid are added; in the case of chrome-nickel steel, 24 grams are taken. When dissolved, the liquid is rendered faintly alkaline with ammonia (1:1), and when cold the nickel is titrated in the usual manner with potassium cyanide, using silver iodide as indicator. The only interfering metal is copper, but this is rarely present in steels. L. DE K.

**The Nitroso- $\beta$ -naphthol Method for the Qualitative Separation of Nickel and Cobalt.** WILLIAM H. CHAPIN (*J. Amer. Chem. Soc.*, 1907, 29, 1029—1032).—The sulphides of nickel and cobalt obtained in the ordinary course of analysis are boiled with 10 c.c. of dilute hydrochloric acid (1:4) and 10 c.c. of dilute nitric acid (1:3). The filtrate is evaporated to dryness and the residue dissolved in a few drops of hydrochloric acid and 10 c.c. of water. The cobalt is then precipitated by a slight excess of nitroso- $\beta$ -naphthol and the presence of cobalt in the precipitate confirmed by the borax bead test.

Before testing for nickel, it is necessary to destroy the excess of the reagent, and this is done by adding 5 c.c. of dilute sulphuric acid (1:5) and 1 c.c. of dilute nitric acid (1:3) and evaporating until dense sulphuric fumes appear. When cold, 5 c.c. of water are added, and the liquid neutralised with ammonia. The nickel is then precipitated with hydrogen sulphide and identified with the borax bead. L. DE K.

**Estimation of Nickel as Nickeldicyanodiamide and its Separation from Iron and Aluminium.** HERMANN GROSSMANN and BERNHARD SCHÜCK (*Chem. Zeit.*, 1907, 31, 911—912. Compare this vol., ii, 582).—*Nickel from Iron.*—To the solution containing about 0.2 gram of the metals is added 1 gram of Rochelle salt and then ammonia in excess. The nickel is then precipitated by adding first 10—20 c.c. of a 10% solution of dicyanodiamide sulphate and then a 10% solution of potassium hydroxide. After remaining overnight, the nickel is collected on a filter, washed, dried at 115°, and weighed as  $\text{Ni}(\text{C}_2\text{H}_5\text{ON}_4)_2$ ; it may be also converted into anhydrous sulphate. The iron may be precipitated as impure hydroxide by simply boiling

the solution; the precipitate is then redissolved in acid and reprecipitated with ammonia.

*Nickel from Aluminium.*—The same process is applied, but the aluminium is recovered from the filtrate by evaporation and heating the residue with sulphuric and nitric acid until all organic matter is destroyed. The mass is then dissolved in hydrochloric acid and the aluminium precipitated with ammonia. L. DE K.

**Analysis of Chromic Anhydride and its Solutions.** THOMAS E. WALLIS. (*Pharm. J.*, 1907, 79, 112—113).—The following volumetric method is described for the estimation of chromic acid. A weighed quantity of the sample is dissolved in water, and to the solution are added barium chloride and sodium acetate. The precipitated barium chromate is collected on a filter, washed, and the filtrate is titrated with *N*/10-sodium hydroxide solution, using phenolphthalein as indicator. The reaction proceeds according to the equation:  $\text{BaCl}_2 + \text{H}_2\text{CrO}_4 + 2\text{CH}_3\cdot\text{CO}_2\text{Na} = \text{BaCrO}_4 + 2\text{NaCl} + 2\text{CH}_3\cdot\text{CO}_2\text{H}$ . In case sulphuric acid is present in the sample, it must be estimated separately, or the chromic acid may be titrated with ferrous ammonium sulphate solution. The author considers that the sp. gr. of the official liquor of the pharmacopœia should be changed from 1.185 to 1.208, as the latter value corresponds with a strength of 25% of chromic anhydride. W. P. S.

**Volumetric Estimation of Chromium with Permanganate.** H. BOLLENBACH (*Chem. Zeit.*, 1907, 31, 760—761).—Ten to fifteen grams of potassium nitrate, 2—5 grams of pure lead nitrate, 4—5 grams of barium sulphate, and 100 c.c. of hot water are placed in a flask and permanganate is added until a decided pink colour is obtained. The chromium, which should be present as nitrate or sulphate, is now added, and after diluting to 400 c.c. the solution is heated to boiling and titrated with standard permanganate. Owing to the rapid subsidence of the precipitate formed, the end point is readily visible. One c.c. of *N*/10-permanganate = 0.00107 gram of chromium.

L. DE K.

**Volumetric Estimation of Titanium.** F. WILLY HINRICHSSEN (*Chem. Zeit.*, 1907, 31, 738).—The hydrochloric acid solution is heated and reduced by means of 50% zinc-magnesium, and the trichloride thus obtained is titrated with standard ferric chloride, using potassium thiocyanate as indicator. One atom of iron = 1 atom of titanium. L. DE K.

**Estimation of [Organic] Nitrogen in Water.** MAX RUBNER (*Arch. Hygiene*, 1907, 62, 83—91).—The author points out the great significance of the organic nitrogen in waters and estimates it by means of a slight modification of the Kjeldahl process (see following abstract). The nitrogen present in the suspended matter may be estimated by precipitating 5—20 litres of the sample with ferric acetate at a gentle heat. The precipitate, which also contains the whole of the bacteria present, is then treated by the Kjeldahl process.

L. DE K.

**Estimation of Small Quantities of Nitrogen and its Application to Water Analysis.** S. KORSCHUN (*Arch. Hygiene*, 1907, 62, [i], 92—106).—Two hundred to one thousand c.c. of the sample, which should be practically free from nitrates, are evaporated to about 20 c.c. with addition to 2—3 c.c. of dilute sulphuric acid, and the residue is then treated as usual in a small Kjeldahl flask with 5—8 c.c. of sulphuric acid and 1 gram of potassium sulphate; bumping may be prevented by adding a little talc. When cold, the mass is dissolved in water, neutralised with 15% sodium hydroxide, and a few c.c. of this are added in excess. After making up to 200—250 c.c., the liquid is allowed to settle and an aliquot part is Nesslerised as usual.

The ammonia present in the sample must, of course, be allowed for. Nitric nitrogen may be converted into ammonia by reduction and also allowed for. L. DE K.

**Recovery of Albuminoid Ammonia from Distillates Contaminated with Permanganate.** FRANK E. HALE (*J. Amer. Chem. Soc.*, 1907, 29, 1085—1087).—In the distillation of "albuminoid ammonia," it not unfrequently happens that some of the permanganate finds its way into the distillate. In such cases, the author decolorises the solution by means of 1 c.c. of a solution containing 30 grams of normal sodium sulphite and 350 grams of potassium hydroxide per litre. After being exposed for some time to the air to separate every trace of manganese, the liquid is filtered through a filter which has been well washed with ammonia-free water, and the ammonia in the filtrate is estimated by the Nessler process as usual. L. DE K.

**Estimation of Organic Matter in Sea Water and a Modification of the Kubel-Tiemann Process.** A. DI DONNA (*Zeitsch. anal. Chem.*, 1907, 46, 516—520).—According to Kubel-Tiemann, 100 c.c. of water are acidified with 5 c.c. of dilute sulphuric acid (1 : 3), 10 c.c. of *N*/100-permanganate are added, and the whole boiled for ten minutes. Ten c.c. of *N*/100-oxalic acid are then added and the excess titrated with permanganate. When applying the process to sea water (or well waters charged with chlorides), the results are quite untrustworthy. It is therefore recommended to take 25 c.c. of sea water and to remove the chlorine by means of a calculated amount of silver sulphate. After diluting to 100 c.c., the liquid is titrated as directed. L. DE K.

**Estimation of Ethyl Alcohol with the Zeiss Immersion Refractometer.** B. WAGNER and F. SCHULTZE (*Zeitsch. anal. Chem.*, 1907, 46, 508—515).—A paper fully illustrated with tables and a curve showing the utility of the immersion refractometer for the purpose of estimating the percentage of alcohol in aqueous mixtures. When dealing with strong spirits, it is best to dilute a portion of the sample with water to exactly twice its volume, and to make a fresh observation. The result is then doubled. L. de K.

**Reduction of Alkaline Copper Solutions by Sugars.** STANLEY R. BENEDICT (*Bio-Chem. J.*, 1907, 2, 408—411).—The different coloured

precipitates obtained when urine is heated with Fehling's solution under varying conditions owe their appearance to the proportion of potassium hydroxide present in the solutions, the red precipitate being cuprous oxide and the yellow and green precipitates hydrated forms of this oxide. The author does not agree with Maclean's statement (this vol., ii, 406) that the colour of the precipitate is dependent on the state of division in which the substance exists. W. P. S.

**Application of the Reaction of Potassium Cyanide with Copper Salts in Alkaline Solution to the Estimation of Dextrose.** CARLO CONTI (*Boll. chim. farm.*, 1907, 46, 609—610).—This method of estimating dextrose requires a colourless, freshly-prepared potassium cyanide solution, of which the volume required to decolorise 1 c.c. of Fehling's solution is determined. As the potassium cyanide solution readily undergoes change, its titre must be re-determined from time to time. The dextrose solution having been brought approximately to the concentration of 1% by means of a preliminary test, a known volume of it is added to a certain volume in excess of Fehling's solution. The liquid is boiled for a few minutes, allowed to cool, made up to a known volume, and filtered. A quantity of the filtrate corresponding with 1 c.c. of Fehling's solution is then titrated with the potassium cyanide solution in order to estimate the amount of copper remaining unreacted by the dextrose solution. If the potassium cyanide solution exactly decolorises an equal volume of Fehling's solution, 1 c.c. of it corresponds with 0.005 gram of dextrose. T. H. P.

**The Necessary Duration of the Fermentation in the Detection of Dextrose in Urine.** C. VICTOROFF (*Pflüger's Archiv*, 1907, 118, 583—600).—In the fermentation test for sugar in urine, an evolution of carbon dioxide may be observed, although no sugar is present, if the process is allowed to proceed too long. At the room temperature, the evolution of gas may continue up to thirty-six hours. It is necessary for the precise performance of the test to incubate at 34—36°, the fermentation being then complete in six hours.

G. S. W.

**Detection of Sucrose in Plant Seeds.** ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1907, 52, 404—411).—A simple method for the extraction of sucrose from seeds is to dry, and remove fat by extraction with ether, then to grind and extract at 50—60° with 95% of absolute alcohol. When the alcoholic solution is allowed to evaporate slowly over sulphuric acid, crystals are often obtained. It is sometimes necessary to extract the residue from the alcoholic solution with ether to remove lecithin and then with 95% alcohol, when other carbohydrates are left undissolved. In other cases, it is advisable to dissolve in water, shake out with ether, neutralise with barium hydroxide, evaporate, and extract the sucrose from the residue by means of 95% alcohol. J. J. S.

**Some Applications of Safranin as a Test for Carbohydrates.** HUGH MACLEAN (*Bio-Chem. J.*, 1907, 2, 431—442).—Safranin is a general test for carbohydrates, and is a useful reagent

for determining the presence of traces of these substances; it is unaffected by all the ordinary "interfering" substances of urine except those of a carbohydrate nature. Safranin is not decolorised by albumin after long boiling, but the presence of albumin in the liquid to be tested interferes with the delicacy of the reaction; ammonia in excess acts in a somewhat similar manner. By combining the safranin test with a yeast fermentation, fermentable sugar can be detected in every urine; along with the fermentable sugar, which is probably dextrose, there is always present a definite amount of unfermentable carbohydrates. The ratio of fermentable to unfermentable substances in normal urine varies roughly from 1 : 3 to 1 : 2; if this ratio is much disturbed, the urine is probably pathological. W. P. S.

**Polarimetric Estimation of Starch in Cereals.** CARL J. LINTNER (*Zeitsch. Nahr. Genussm.*, 1907, 14, 205—208).—The following method is recommended as being simple and trustworthy: the starch is dissolved in hydrochloric acid and the solution clarified with phosphotungstic acid before polarisation. 2.5 Grams of the finely-ground flour are well mixed with 10 c.c. of water, care being taken that all lumps are broken up, and 20 c.c. of hydrochloric acid, D 1.19, are added. After the lapse of thirty minutes, the thick solution is rinsed into a 100 c.c. flask with hydrochloric acid, D 1.125, 5 c.c. of 4% phosphotungstic acid solution are added, and the mixture is diluted to a volume of 100 c.c. with the dilute hydrochloric acid. The solution is now filtered and the clear filtrate examined in a 200 mm. tube in the polariscope. The starches obtained from barley, rye, wheat, maize, rice, and potato flours have  $[\alpha]_D^{20}$  202 (average), and from this the percentage of starch in the flour under examination is calculated. The results obtained are from 4 to 6% lower than those yielded by the usual inversion process, probably owing to the fact that, in the latter process, the pentosans are counted as starch. W. P. S.

**Separation of Benzoic and Cinnamic Acids.** K. SCHERINGA (*Pharm. Weekblad*, 1907, 44, 984—986).—To detect benzoic acid in the presence of cinnamic acid, the sample is boiled with water and allowed to cool. To the filtrate is then added ferric chloride, which gives a straw-yellow opalescence in the absence of benzoic acid, but a brownish-yellow coloration if this should be present.

Benzoic acid may be estimated approximately in a mixture of the two acids as follows: about 0.7 gram of the sample is dissolved in ammonia and diluted to 30 c.c. The bulk of the cinnamic acid is then precipitated by addition of calcium chloride. The filtrate is cautiously treated with potassium permanganate to decompose the cinnamic acid still in solution, and the excess of permanganate is at once removed by a few drops of thiosulphate. After removing the manganese precipitate by filtration, the benzaldehyde formed is boiled off, and the benzoic acid is recovered by adding hydrochloric acid and repeatedly extracting with ether. L. DE K.

**Estimation of Salicylic Acid in Milk and Cream.** CECIL REVIS and GEORGE A. PAYNE (*Analyst*, 1907, 32, 286—288).—Twenty

c.c. of the milk, or 20 grams of the cream, are placed in a stoppered flask and neutralised to litmus paper with *N*/1-sodium hydroxide solution, the amount thus added being noted. Forty c.c. of absolute alcohol are now added, the flask is closed securely and placed in water at a temperature of 95°, and shaken at frequent intervals for fifteen minutes. After cooling, an amount of water equivalent to the volume of the proteins and fat, less the quantity of sodium hydroxide used for the neutralisation, is added. For milks, this correction may be taken as 2 c.c., but in the case of cream it depends on the percentage of fat; thus to 20 grams of cream containing 50% of fat, 11.4 c.c. of water must be added; with 40% of fat, 9.3 c.c. of water, and so on. The contents of the flask are then filtered; 40 c.c. of the filtrate are transferred to a 500 c.c. flask, 100 c.c. of water are added with sufficient sodium hydroxide to render the mixture distinctly alkaline, and 60 c.c. are distilled off slowly. The residue is washed into a 250 c.c. flask and, before diluting to the mark, 2 c.c. of potassium mercuric iodide solution are added (the latter solution is prepared by dissolving 1.35 grams of mercuric chloride and 3.32 grams of potassium iodide in 64 c.c. of water and adding 20 c.c. of concentrated sulphuric acid). The solution is filtered and 100 c.c. of the filtrate are shaken out with three successive quantities of 20 c.c. of ether. The ethereal extracts are next shaken out several times with water rendered slightly alkaline with sodium hydroxide, the aqueous extracts being collected in a 100 c.c. flask, to which is added an amount of sulphuric acid equivalent to the sodium hydroxide used, and the whole is then diluted to the mark. This solution is employed for the colorimetric estimation of the salicylic acid in the usual way by the use of iron, alum, and a standard salicylic acid solution. Boric acid has no influence on the results, nor has benzoic acid even when present to the extent of five times the amount of salicylic acid.

W. P. S.

**The Caprylic [Octoic] Acid Value of Butter Fat.** R. K. DONS (*Zeitsch. Nahr. Genussm.*, 1907, 14, 333—342).—By estimating the amount of caprylic [octoic] acid in a sample of butter fat, some indication is afforded of the presence, or absence, of cocoanut oil in the sample. In the process described by the author, the quantity of this acid distilling over during the estimation of the Reichert-Meissl value of the fat is estimated by means of its silver salt; the result, expressed in c.c. of *N*/10-octoic acid solution for the 5 grams of butter fat taken, is termed the "first caprylic acid value." By adding 110 c.c. of water to the distillation flask, distilling over a further 110 c.c., and estimating the additional quantity of octoic acid thus obtained, a "second caprylic acid value" is found for the sample. In the case of pure butter, these two values are approximately the same, varying from 1.0 to 1.6 according to the Reichert-Meissl value of the butter. The addition of 10% of cocoanut oil to the butter causes an increase of from 0.8 to 1.0 in the first value, whilst the second value is influenced to a smaller extent.

W. P. S.



**Method for Estimating the Ratio  $\text{CO}_2/\text{N}$  in the Carbamino-Reaction.** MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1907, 52, 506).—Considerable errors are introduced into the method for estimating the  $\text{CO}_2/\text{N}$  ratio in amino-compounds (Abstr., 1905, ii, 332; 1906, i, 144) when even small amounts of alcohol are present. Even 2 drops of alcoholic phenolphthalein solution affect the result, and it is necessary to use a solution of the indicator in lime water.

J. J. S.

**Estimation of the Cyanogen Group in Slightly Dissociated Salts.** VINCENZO BORELLI (*Gazzetta*, 1907, 37, i, 429—434).—Cyanogen is only precipitated by silver solutions when it exists as a constituent of dissociated cyanides. For cyanogen compounds which are only slightly dissociated in solution, such as the compounds of mercury, the author gives the following method of estimating the cyanogen, which is as exact as, and more rapidly executed than, that of Rose. To the cyanide solution, rendered strongly alkaline with sodium hydroxide solution (12—15 mols.  $\text{NaOH}$  per atom of  $\text{Hg}$ ), halogen-free aluminium powder (4—5 atoms of  $\text{Al}$  per atom of  $\text{Hg}$ ) is gradually added, the liquid being well shaken after each addition. The aluminium dissolves rapidly, and the mercury is deposited first as an aluminium amalgam and ultimately as a liquid globule. When a test made on a small quantity of the liquid shows that all the mercury has been deposited from the solution, the latter is filtered and the cyanogen, now existing as sodium cyanide, estimated either volumetrically or gravimetrically. Analyses of mercuric cyanide, mercuric cyanonitrate, and mercuric cyanoperchlorate by this method show that good results are obtained. The method can also be applied to solutions containing chloride, bromide, iodide, or thiocyanate ions. To estimate cyanogen in the complex iron cyanides, the substance is heated with an excess of mercuric oxide and the cyanogen in the filtered solution, which contains it as mercuric cyanide, estimated by the method described above.

T. H. P.

**A Reaction of Phenylcarbamine.** A. CHWALA (*Zeitsch. angew. Chem.*, 1907, 20, 1366—1367).—The author has found that mercuric chloride is reduced quantitatively to the mercurous state in alcoholic solution on addition of phenylcarbylamine, and proposes to utilise this reaction in the estimation of phenylcarbylamine in the crude product.

L. DE K.

**The Lloyd Reaction as Applied to Heroine and Veratrine.** DANIEL W. FETTEROLF (*Amer. J. Pharm.*, 1907, 79, 317—325).—The action of sulphuric acid and potassium dichromate on a mixture of morphine and hydrastine, which produces a bluish-violet coloration, is known as the Lloyd reaction. The author has tried the test, substituting heroine and veratrine for morphine.

Heroine yields results somewhat similar to morphine and apomorphine. The only difference is that the initial yellow and brownish-yellow colour in the mixtures of morphine, and the yellowish-brown

colour in the mixtures of *apomorphine*, is replaced by a pink or reddish-brown colour with *heroin*. The green colour observed with *morphine* and *apomorphine* at the ordinary temperature does not show with *heroin* unless a large quantity is present and the temperature is raised to 80—90°.

The reaction with *veratrine* is not very characteristic, and is inferior to the ordinary sulphuric acid test.

*Dionine*, as may be expected from its close relation to *morphine*, also gives a bluish-violet coloration.

L. DE K.

**Detection of Quinine.** J. ABENSOUR (*J. Pharm. Chim.*, 1907, [vi], 26, 25—26).—The following modification of the thalleioquinine reaction for detecting quinine is more sensitive than the original method. To about 10 c.c. of the liquid to be examined saturated bromine water is added, drop by drop, until the fluorescence disappears, and to the mixture are then added its own volume of alcohol and one or two drops of ammonia solution. A very brilliant, green coloration is thus obtained if quinine is present. When the amount of quinine is small and the coloration feeble, the liquid should be shaken up with a small quantity of chloroform, which serves to concentrate the colouring matter. If the quinine exists as a salt, it should be dissolved in a little alcohol and the solution diluted with its own volume of water before applying the test as described above.

Slight traces of quinine (0.001 gram per litre) can be detected by adding, to about 10 c.c. of the slightly acidified aqueous solution, one drop of each of the following solutions: semi-saturated bromine water, 1 : 10 potassium ferrocyanide solution, and 1 : 10 ammonia solution; on then agitating with chloroform, the latter assumes a red colour.

T. H. P.

#### Pyrimidines. IV. A Colour Test for Uracil and Cytosine.

HENRY L. WHEELER and TREAT B. JOHNSON. (*J. Biol. Chem.*, 1907, 3, 183—189).—A characteristic purple colour is produced when uracil or cytosine is dissolved in bromine water and the solution treated with barium hydroxide solution. The uracil or cytosine reacts with bromine to form dibromohydroxyhydrouracil; barium hydroxide then converts this into isodialuric acid, which immediately undergoes a rearrangement in the alkaline solution to give the purple barium salt of dialuric acid. The presence of guanine, adenine, thymine, *isocytosine*, or 6-aminopyrimidine does not interfere with the test.

W. D. H.

#### Estimation of Mucoid in Urine, Blood, and Tissue Extracts.

CLARENCE E. MAY and WILLIAM J. GIES (*Proc. Amer. Soc. Biol. Chemists*, 1907, xlii., *J. Biol. Chem.*, 3).—Mucoids are not completely precipitated on acidification; moreover, other proteins are apt to be carried down with the mucoid in flocculent combinations. All data hitherto published as to the amount of mucoid in various fluids and tissues are therefore inaccurate.

W. D. H.

**Benzidine as a Reagent for Blood.** O. SCHUMM (*Pharm. Zeit.*, 1907, 52, 604).—It is pointed out that various samples of benzidine found in commerce show very different sensibilities as regards their reaction with blood. Only such samples as will give a coloration with 1 part of blood in 200,000 should be used. Eight c.c. of blood at this dilution, when mixed with 2 c.c. of saturated alcoholic benzidine solution, 1 drop of acetic acid, and 2 c.c. of 3% hydrogen peroxide, should show a blue coloration within two minutes. W. P. S.

**Guaiacum Reaction of Blood.** ERNST J. LESSER (*Zeitsch. Biol.*, 1907, 49, 571—574).—The author's previous view that the guaiacum reaction in blood is due to the action of a catalase is no longer held. The reaction is given by blood after it is boiled. The constituent of blood to which it is due is the pigment. Iron-free derivatives of hæmoglobin do not give it, and so special importance attaches to the iron. Invertebrate blood containing no hæmoglobin does not give it.

No reference is made to the work of Buckmaster (this vol., ii, 660), who has reached the same conclusions. W. D. H.

**Detection of Blood in Urine: Red Urines.** A. FLORENCE (*J. Pharm. Chim.*, 1907, [vi], 26, 49—55).—The presence or absence of a red colour in urine is no criterion as to the presence or absence of blood. The spectrum of oxyhæmoglobin given by urine containing blood often disappears after the lapse of an hour.

The urine should be examined microscopically for blood-corpuscles, which at first are pale yellow and rounded, and often have indented edges; later the indentations disappear and the globules become vesiculous, the contour alone being partially or wholly recognisable. Blood-corpuscles may be distinguished from spores by drying a preparation and then adding a drop of water, after which no corpuscles are visible, whilst the spores retain their characters.

The preparation of hæmin crystals from urine containing blood is best effected as follows. A little of a solution of 1 gram of citric acid in saturated aqueous picric acid is added to the urine in a long cylinder and the separated, flocculent precipitate centrifuged, thrown on a small filter, and washed with a few drops of water; this precipitate is more or less reddish-brown if it contains blood or its pigments. A little of the moist precipitate is placed on a glass slide, mixed with a trace of sodium chloride, dried at a low temperature (45°), and examined under the microscope to make sure that no uric acid crystals are present. Glacial acetic acid is then added, and the preparation heated gently until the bubbles run together, almost the whole of the acetic acid being then evaporated. When the slide cools, the characteristic crystals of hæmin can be recognised under the microscope. Another simple and rapid test is to dissolve the picric acid precipitate, after complete washing, in a little potassium hydroxide solution and to add a couple of drops of ammonium sulphide solution; the red liquid thus obtained readily exhibits the hæmochromogen spectrum. Other tests are also given. T. H. P.

**Reactions and Estimation of Arrhenal (Disodium Methylarsonate) and Atoxyl (Sodium Anilinoarsonate).** J. BOUGAULT (*J. Pharm. Chim.*, 1907, [vi], 26, 13—20).—The reaction of cacodylic or methylarsonic acid with a hydrochloric acid solution of hypophosphorous acid (Abstr., 1903, ii, 339) is greatly increased in sensitiveness by the subsequent addition of 1 to 2 drops of *N*/10 iodine solution. This reagent has now been applied to the detection and estimation of arrhenal and atoxyl.

It has been shown by Auger (Abstr., 1904, i, 724) that the black powder precipitated when a hydrochloric acid solution of hypophosphorous acid acts on arrhenal has the formula  $(\text{MeAs})_n$ , and that it is oxidised by nitric acid to methylarsonic acid. The author finds that the same oxidation is effected by iodine:  $\text{MeAs} + 4\text{I} + 3\text{H}_2\text{O} = \text{MeAsO}(\text{OH})_2 + 4\text{HI}$ . Both the formation and oxidation of  $(\text{MeAs})_n$  being quantitative, arrhenal may be estimated as follows: 0.15—0.20 gram of arrhenal is dissolved in 1—2 c.c. of water and mixed with 15—20 c.c. of the hydrochloric and hypophosphorous acid mixture. After twelve hours, the liquid is diluted with 15—20 c.c. of water and filtered, the residue being washed with water. The filter and its contents are then introduced into a beaker with a known excess of *N*/10 iodine solution, the whole being well shaken and the excess of iodine estimated with thiosulphate solution. Four atoms of iodine correspond with 1 mol. of arrhenal. The presence of free arsenic in the  $(\text{MeAs})_n$  may be recognised as follows. (1) If after titration of the excess of iodine, the liquid is saturated with potassium hydrogen carbonate, it becomes capable of reducing a further quantity of iodine, since only in alkaline solution does iodine completely oxidise arsenic to arsenic acid. (2) The liquid gives a precipitate with magnesia mixture.

Atoxyl gives the following reactions with a hydrochloric acid solution of hypophosphorous acid. In the cold, a yellow precipitate is obtained which forms gradually when the amount of atoxyl is small. The addition of a trace of iodine renders the reaction very sensitive and changes the colour of the precipitate to orange-yellow. When the liquid is heated at 100°, the precipitate rapidly turns brown and finally black, and then contains a considerable proportion of free arsenic. The estimation of atoxyl is carried out in a manner exactly similar to that described above for arrhenal, 4 atoms of iodine corresponding with 1 mol. of atoxyl.

If 5 c.c. of normal urine is heated at 100° for thirty to forty-five minutes with 10 c.c. of the hydrochloric-hypophosphorous acid reagent and a drop of *N*/10 iodine solution, it assumes a dark brown coloration, whilst if 0.25 milligram of atoxyl or arrhenal is present, the intensification of the colour of the urine is but slight; 0.01 gram of atoxyl per 250 c.c. of urine may be detected with certainty by the use of the hydrochloric-hypophosphorous acid reagent and iodine solution as described above.

T. H. P.

## General and Physical Chemistry.

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**Optical Properties of Solutions and of Dissolved Substances.** I. C. CHÉNEVEAU (*Ann. Chim. Phys.*, 1907, [viii], 12, 145—228).—The original contains a detailed account of the author's experiments on the refractive index of some fifty-three aqueous solutions of mineral acids, bases, or salts. The results obtained in the case of thirty-five of these solutions have already been published (compare *Compt. rend.*, 1904, 138, 1484, 1578; *Abstr.*, 1904, ii, 641).

M. A. W.

**Emission Spectra of Uranium Salts at Low Temperatures.** M. CANTONE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1907, [iii], 13, 149—156. Compare Becquerel, this vol., ii, 213).—The author has investigated the groups of narrow bands exhibited by the spectra of uranium sulphate, uranium ammonium sulphate, ammonium uranate, uranium ammonium fluoride, uranium potassium acetate, uranyl nitrate, and uranium acetate at the temperature of liquid air. It is found that the lines for each of these compounds obey the law  $1/\lambda = A + mB$ , where  $\lambda$  is the wave-length of a line occupying the position  $m$  in the series; the constant  $B$  has the same value, namely, about 84, for all the above compounds, but the characteristic coefficient is, in general, different for the different compounds.

T. H. P.

**Optical Behaviour of Colloidal Metals.** ERNST MÜLLER (*Ann. Physik*, 1907, [iv], 24, 1—24).—In turbid media where the particles are non-conducting, the direction of the maximum polarisation of the diffused light makes an angle of  $90^\circ$  with the incident light. In the case, however, of freshly prepared colloidal gold, platinum, and silver solutions, the polarisation maxima occur at the angles  $125^\circ$ ,  $112^\circ$ , and  $97.5^\circ$  respectively, a result in harmony with Ehrenhaft's observations (*Ann. Physik*, 1903, [iv], 11, 489). It appears therefore that the gold particles are smaller than the platinum particles, and these again smaller than the silver particles. The colour transmitted by colloidal solutions of metals is not due only to the general diffusion of light in these media; these solutions must be regarded as possessing a characteristic colour themselves. When colloidal solutions of metals are kept for a considerable time, or when a trace of acid is added, the colour, in general, changes before the metal is precipitated; this change of colour is accompanied by a change in the position of the polarisation maximum, so that its direction comes to lie at an angle of  $90^\circ$  with the incident light. At the same time, the polarisation alters in degree, increasing markedly in the case of gold and platinum, decreasing in the case of silver. The change of colour and the precipitation of the metals is hindered by the addition of a trace of gelatin, which, however, is without effect on the polarisation changes. The

optical properties of colloidal solutions of metals cannot be interpreted by reference only to the size of the particles. J. C. P.

**Relation between the Rotary Power of Optically Active Substances and their Chemical Constitution.** D. CHARDIN and S. SIKORSKI (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 703—731. Compare Guye, *Abstr.*, 1890, 722; 1893, ii, 204, 561).—Guye's expression for the product of asymmetry contains about twenty-eight unknown quantities; it was therefore simplified by assuming that all the centres of gravity of the side-groups lie on the axes of the asymmetric carbon atom, thus obtaining an expression, I, with four unknowns, namely, the distances of the C.G.'s of the side-groups from the asymmetric carbon atom. This was then further simplified by assuming these distances to be equal to II. All the experimental work which has been performed so far to disprove Guye's theory really only leads to the rejection of formula II. Accepting Guye's general theory and assuming (1) that the distances of the C.G.'s from the asymmetric carbon atom are functions of the internal structure and distances from one another of the atoms in the side-groups; (2) that the atoms rotate round the axes uniting them; (3) that, in general, the distances between the atoms depend only on their nature and not on their position, it is deduced that the C.G. of any side-group describes a curve with its centre on the continuation of the corresponding axis of the asymmetric carbon atom; since therefore the C.G.'s are constantly shifting their plane, the angle of rotation should alter periodically. This alteration is not observed, either because the difference in the angles is too small or the time is too short, consequently the angle observed is the average, and the C.G.'s to be considered in any formula should also be their average position, that is, they will coincide with the centres of the curves and will lie on the axes of the asymmetric carbon atom. Therefore in active aliphatic compounds, formula I is applicable. Formulae are given for calculating the distances of the C.G.'s from the asymmetric carbon, and, by employing these in conjunction with formula I, the distances of the elements from one another can be calculated; thus the distance between two carbon atoms in the pentane derivatives containing one or two asymmetric carbon atoms is found to be 4.10. Again, for the derivatives of the amyl alcohol,  $\text{CHMeEt} \cdot \text{CH}_2\text{R}$  (where  $\text{R} = \text{N}, \text{O}, \text{S}, \text{Cl}, \text{Br}, \&c.$ ), the product of the atomic weight of the element R and its distance from the carbon atom (termed "the atomic product," even if the weight considered is that of a group instead of an atom) is a definite constant for each series in the periodic system, and equals one-half the sum or difference of the atomic product of the normal carbon chain with either one, two, three, &c., carbon atoms, and is positive for the even series, negative for the odd series. For example,  $g_1l_1$  (the atomic product of the carbon chain containing one carbon atom) = 61.5,  $g_2l_2 = 139.4$ ,  $g_3l_3 = 222.7$ , then for the second series, that is, for the elements, nitrogen, oxygen, fluorine, the atomic product = 139.4. For the third series, chlorine, for example, =  $(61.5 + 139.4)/2 = 100.45$ . For the fifth series, bromine =  $(61.5 + 134.9 + 222.7)/2 = -211.9$ . If the replacement of one element by another changes the sign of the angle of rotation, then half the difference must be taken

instead of the sum; thus, in the amyl mercaptan, the atomic product of sulphur  $= (139.4 - 61.5)/2 = -38.9$ . The following further deductions are made. The distance between the carbon and oxygen of the carbonyl group equals  $-1.9$  and is independent of the aliphatic radicle. If in the homologous series of the fatty esters in which the group  $\text{CHMeEt}$  is contained the angle between the oxygen atoms  $= 90^\circ$ , then the sum of the projections of the atomic products of the carbonyl oxygen and of that of the alcoholic radicle,  $OR$ , on the axis of rotation of the carbonyl group is a constant and is independent of  $R$ , also  $X/3n + Y/3n - 1 = \text{constant}$  (where  $X, Y$  are the atomic products of the groups  $OR, CO$  respectively, and  $n$  the number of carbon atoms in the side-chain combined with  $OR$ ). The experiments described were all performed at the boiling point of the substances and with sodium light, and the results agree closely with those calculated by using the equations and deductions described above. Throughout, the angle of rotation referred to is that of the specific, not the molecular, rotation. The product of asymmetry itself bears no relation to the sign of the angle of rotation, but the latter is shown to depend on the position of the C.G. of the whole molecule on one side or other of the plane passing through the centre of the molecule and dividing into two equal parts the edges of the tetrahedron starting from the apex corresponding with the C.G. of the heaviest side-chain and directed towards the C.G.'s of the two side-chains next in weight. Thus, if the introduction of a new element alters the position of the C.G. of the molecule with respect to this plane, the sign of the angle of rotation will change; if it does not do so, the sign will remain the same. Z. K.

**Polarimetric Researches. III. CHR. WINTHER** (*Zeitsch. physikal. Chem.*, 1907, **60**, 563—589. Compare Abstr., 1902, ii, 589; 1904, ii, 4).—The rotation and rotation dispersion have been determined for solutions: (1) of nicotine in water, methyl alcohol, ethyl alcohol, formamide, ethylene dibromide, aniline, benzene, chloroform, and *iso*-butyl alcohol; (2) of camphor in benzene, chloroform, ethylene dibromide, and acetic acid; (3) of ethyl tartrate in formamide, ethylene dibromide, chloroform, benzene, water, and methyl, ethyl, and *iso*-butyl alcohols.

For the pure active substances employed, the following constants were obtained at  $20^\circ$ : nicotine,  $[\alpha]_D - 163.85^\circ$ ; ethyl tartrate,  $[\alpha]_D + 7.48^\circ$ . The curve showing the variation of the specific rotation of nicotine with temperature rises regularly until about  $80^\circ$ , where there is a marked bend in the curve; this is probably connected with the changes which nicotine so readily undergoes. If  $[\alpha]_D^{45^\circ}$  for nicotine is taken as unity, the values of the specific rotation at the same temperature with red, green, light blue and dark blue light are respectively  $0.767, 1.252, 1.803$ , and  $2.061$  (compare Gennari, Abstr., 1896, ii, 286). The specific rotation of nicotine, dissolved to the extent of 11% in formamide, is lowered to  $-73.74^\circ$ , a lower value even than the specific rotation in the corresponding aqueous solution. In ethylene dibromide, the rotation of nicotine is increased. The dispersion coefficients deduced for nicotine are independent of the

solvent (water and formamide being exceptions), and therefore also of the concentration.

In dilute solutions of camphor in chloroform, the rotation increases with the dilution. The rotation of camphor is increased by solution in ethylene dibromide.

The specific rotation of ethyl tartrate, deduced from the rotation of an infinitely dilute solution in formamide at  $20^{\circ}$ , is  $+30.4^{\circ}$ , the highest value yet observed for any solution of this substance. Very concentrated solutions of ethyl tartrate in formamide, like ethyl tartrate itself, exhibit anomalous dispersion, but this disappears in the more dilute solutions. In this respect, as also in regard to the increase of the specific rotation, the influence of formamide is closely analogous to that of water (compare Walden, *Abstr.*, 1906, ii, 149). The specific rotation of ethyl tartrate, deduced from the rotation of an infinitely dilute solution in ethylene dibromide, is  $-19^{\circ}$ , the highest negative rotation yet recorded for this substance. The results obtained for solutions of ethyl tartrate in the various solvents are in harmony with the rule that the maximum rotation of this substance is displaced towards the red end of the spectrum as the rotation is lessened.

A few determinations of molecular weight have been made by the cryoscopic method. The molecular weight of camphor in ethylene dibromide is approximately normal in very dilute solution, and increases slowly with the concentration.

The molecular weight of ethyl tartrate in ethylene dibromide is normal only in very dilute solution; it increases rapidly with the concentration. From experiments with carbamide dissolved in formamide, it appears that the freezing-point depression constant of the latter substance is about 3200, and on the basis of this value it is shown that the molecular weight of ethyl tartrate in formamide is normal. The values obtained by the cryoscopic method for the molecular weight of ethyl tartrate in ethylene dibromide (as just recorded) and in benzene (see Patterson, *Trans.*, 1902, 1132) have been generally confirmed by partition experiments in which ethyl tartrate was allowed to distribute itself: (1) between ethylene dibromide and water, (2) between benzene and water.

There are recorded also in the table a number of densities: (1) for mixtures of nicotine and ethyl alcohol, (2) for mixtures of nicotine and water, at temperatures between  $0^{\circ}$  and  $40^{\circ}$ . J. C. P.

**Theory of Optical Rotation.** III. IV. V. (General Theory of Solution. I.—III.). CHR. WINTHER (*Zeitsch. physikal. Chem.*, 1907, 60, 590—625, 641—684, 685—705. Compare *Abstr.*, 1906, ii, 320, 822; also preceding abstract).—The basis of the author's theory (*loc. cit.*) is widened, and emphasis is laid on the part played by the internal pressure. In order to determine the actual internal pressure of a solution, it is necessary to know the actual volume of one of the constituents of the solution, and the author's work shows that under certain conditions it is possible to determine the actual volume of dissolved substances. In this connexion, approximate values are calculated for the internal pressure of a number of liquids. The calculation is based on the applicability of van der Waals'



equation, and Amagat's data on the compressibility of liquids are employed. The following are the values obtained, expressed in atmospheres and valid for 0°: water, 4900; glycerol, 3493; acetic acid, 3143; methyl alcohol, 2420; carbon disulphide, 2200; ethylene dibromide, 2114; ethylene dichloride, 2063; ethyl alcohol, 2030; propyl alcohol, 1900; carbon tetrachloride, 1824; benzene, 1792; acetone, 1790; methyl acetate, 1709; chloroform, 1680; toluene, 1638; ethyl chloride, 1536; ethyl acetate, 1486; ethyl ether, 1220.

In proceeding to show the bearing of the internal pressure on the phenomena of optical rotation, the author formulates three fundamental propositions from which he starts: (1) isothermal volume changes in homogeneous systems are due exclusively to change of pressure (either external or internal), to change of the degree of association, dissociation, or combination, or to the simultaneous action of both causes; (2) every alteration in the rotation of an optically active substance is causally related to a volume change; (3) every volume change which is due alone to change of pressure, without the degree of association, dissociation, or combination being affected, is accompanied by a change of rotation which is proportional to the change of volume.

In this paper, these principles are applied chiefly to the changes in volume and rotation which are observed when an optically active substance is dissolved, or when the solution so obtained is diluted. The proportionality between change of rotation and change of volume referred to in proposition (3) may be shown to be valid for the following solutions: nicotine in acetone, ethyl ether, water, benzene, methyl, ethyl, and propyl alcohols, and formamide; nicotine acetate in water; camphor in phosphorus trichloride, carbon disulphide, ethylene dibromide, benzene, chloroform, methyl, ethyl, propyl, and butyl alcohols, formic, acetic, propionic, and butyric acids; *l*-turpentine oil in benzene, ethyl alcohol, and acetic acid; lithium, ammonium, sodium, potassium, calcium, and barium camphorates in water.

In further developing his theory of the relation between the internal pressure of liquids and the change of rotation with concentration and temperature, the author deals with the case in which the active substance is associated. If the specific volume is dependent on the degree of association, then the single and double molecules must have different specific volumes, and consequently different rotatory powers. The influence of varying degree of association on the change of specific rotation is thus shown to be causally related to the internal pressure.

The case also where the constituents of the mixture or solution form a compound is discussed, and it follows that each substance present in such a mixture or solution has a constant specific volume and a constant rotatory power, independent of the concentration.

So long as a mixture does not contain more than two active substances with different rotatory powers, the relation  $\Delta[\alpha] = k \cdot \Delta\phi$ , where  $\phi$  is the "actual" solution volume of the active substance, must be fulfilled exactly. A similar equation is valid for the "calculated" solution volume, when the constituents form a single compound with each other. In all other cases, the use of the "calculated" solution

volume instead of the "actual" solution volume robs the equation of its validity.

In all cases where the constituents of a mixture form no compounds, the influence of the solvent on the rotation of the dissolved active substance at infinite dilution depends only on the difference of the internal pressures. When therefore the various solvents are arranged according to the magnitude of this influence, the order is the same with different active solutes.

It is shown that in those cases where change in degree of association is unaccompanied by any change in volume, the variation in molecular weight with concentration must be in harmony with the law of mass action.

The author finds that in the process of electrolytic dissociation, the volume of the active part of the electrolyte remains constant, so that the rotatory power is not altered directly by the dissociation process. There arises indirectly, however, a parallelism between degree of dissociation and rotatory power by virtue of the total volume change which accompanies dissociation.

The curves showing the variation in value of certain physical constants with concentration in aqueous solutions of nicotine acetate exhibit marked discontinuities. These are due to the fact that within a very small concentration interval a new compound of solute and solvent is formed.

In the third paper, the author proceeds to apply his theory to rotation dispersion and to the influence of temperature on rotatory power. In the latter case, only pure active substances are considered. The constancy of the solution dispersion coefficients has been verified by exact measurements with ethyl tartrate solutions.

The importance of the study of specific rotation in relation to the general theory of solution is emphasised. Whereas the properties of solutions generally depend on the alterations of the properties of *both* constituents and are therefore difficult to interpret, a study of the change of specific rotation throws light on the behaviour of *one* of the constituents. The study of optical activity is regarded as, at present, the only trustworthy method of investigating the constitution of concentrated solutions.

J. C. P.

**Fluorescence and Chemical Constitution. Reply to Kauffmann.** ARTHUR HANTZSCH (*Ber.*, 1907, 40, 3536—3543. Compare this vol., i, 214, 513; ii, 519).—Polemical. The salts, both of benzoquinoldisulphonic acid and of resorcinoldisulphonic acid,  $C_6H_2(OH)_2(SO_3K)_2$ , do not fluoresce when pure and in pure aqueous solution. The marked fluorescence of the quinol derivative observed by Kauffmann is due to traces of decomposition products, the formation of which can be brought about even by minute traces of alkali derived from the water or glass vessels used. The colourless salt solutions, when made alkaline, not only fluoresce, but become yellow.

E. F. A.

**Spectrophotometric Investigations on the Absorption and Fluorescence of Resorufin.** FRANCES G. WICK (*Physikal. Zeitsch.*, 1907, 8, 681—692).—The absorption and fluorescence of resorufin in

ethyl-alcoholic solution have been studied. The absorption varies with the thickness of the absorbing layer according to the exponential law which expresses the behaviour of optically normal substances. An increase in concentration has the same effect as an increase in the thickness of the absorbing layer if dilute solutions are used, but this does not hold for concentrated solutions. Change in concentration of the solution is found to have no influence on the typical fluorescence spectrum.

H. M. D.

**Fluorescence Absorption in Resorufin.** FRANCES G. WICK (*Physikal. Zeitsch.*, 1907, 8, 692—698. Compare preceding abstract).—An examination of the absorption phenomena exhibited by fluorescing resorufin has shown that the increased absorption during fluorescence is independent of the intensity of the transmitted light. When the thickness of the absorbing layer reaches a certain value, further increase has no influence on the fluorescence absorption. The bands observed in the fluorescence absorption spectrum coincide with the fluorescence bands.

H. M. D.

**Photochemical Reactions. I. Influence of Light on the Phosgene Equilibrium.** FRITZ WEIGERT (*Ann. Physik*, 1907, [iv], 24, 55—67).—The influence of light on the reversible reaction,  $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$ , is purely catalytic, and experiments in the neighbourhood of  $500^\circ$  have shown that the position of equilibrium suffers no displacement when the system is exposed to light. For the purpose of the investigation, a furnace is described in which the gaseous mixture could be heated at  $500^\circ$ , and at the same time exposed to the action of light.

J. C. P.

**The Laws of the Action of Light on Glucosides, Enzymes, Toxins, and Antitoxins.** GEORGES DREYER and OLAV HANSEN (*Compt. rend.*, 1907, 145, 564—566).—It is well known that many photochemical actions, such as the decomposition of oxalic acid and hydriodic acid and the union of carbon monoxide and chlorine, are subject to the ordinary law of mass action. The action of light on glucosides, like saponin and cyclamin, enzymes, like rennet and trypsin, and on toxins and immune-serum has been investigated. A strong light impairs all the substances named, the action being largely due to the ultra-violet rays absorbed by the glass. The weakening action proceeds regularly, and may be expressed by means of the ordinary equation for a unimolecular reaction. It is further shown that under the action of a strong light, the glucosides yield sugar, and also that light is capable of coagulating liquids containing albumin.

J. J. S.

**Fluorescence of some Salicylic Acid Preparations under the Influence of  $\beta$ - and  $\gamma$ -Rays of Radium.** CHR. JENSEN (*Chem. Zentr.*, 1907, ii, 402—403; from *Zeitsch. wiss. Photograph. Photophys. Photochem.*, 5, 187—194).—In order to estimate the fluorescence of salicylic acid preparations when exposed to the action of radium rays, strips of cardboard smeared with the substance have been compared photometrically with a standard barium-platinocyanide strip, the

strips being exposed under a millimetre scale until they showed the same intensity. The relative intensity was calculated from the distance between the centres of the surfaces and the radium preparation. The method gave accurate results, the average error not being more than 1%. Salipyrine, salicylamide, barium, cadmium, strontium, and zinc salicylates showed the most intense fluorescence. The fluorescence of salipyrine is 4.8 times that of barium platinocyanide. The phenomenon is mainly due to the action of  $\beta$ -rays. The fluorescence induced by Röntgen rays does not resemble that caused by  $\beta$ -rays.

E. W. W.

**Thermal Determination of the Radioactivity of Ordinary Substances.** HEINRICH GREINACHER (*Ann. Physik*, 1907, [iv], 24, 79—104).—The amount of heat liberated by a radioactive substance does not stand in a direct relationship to the ionisation which it produces. The radioactivity of an ordinary substance, although its ionising power is very small (compare McLennan and Burton, *Abstr.*, 1903, ii, 621), might yet be considerable and might be detected by a thermal method. From this point of view, the author has examined zinc, cadmium, mercury, lead, uranyl nitrate, zinc, cadmium, and magnesium sulphates, and lead nitrate in a Dewar vacuum vessel. In no case except the last is the temperature difference between the substance and its surroundings greater than  $0.01^{\circ}$ . In the case of lead nitrate, the unexplained observation was made that its temperature remains one or more hundredths of a degree below the temperature of its surroundings.

J. C. P.

**Rate of Transformation of the Radium Emanation.** G. RÜMELIN (*Phil. Mag.*, 1907, [vi], 14, 550—553.\* Compare Sackur, *Abstr.*, 1905, ii, 367; Curie, 1903, ii, 50; Rutherford and Soddy, *ibid.*, 347).—The period of decay of the radium emanation has been measured by a method which avoids the measurement of ionisation currents over a wide range of intensity, the liability of escape of emanation, and disturbances of the homogeneous distribution during the process of transference of the emanation into the testing-vessel. The mean value obtained in eight experiments is 3.75 days, the separate value ranging from 3.70 to 3.80 days.

H. M. D.

**Radiation of Uranium-X.** MAX LEVIN (*Physikal. Zeitsch.*, 1907, 8, 585—589. Compare Moore and Schlundt, *Abstr.*, 1906, ii, 721).—The rays emitted by uranium-X have been examined by absorption experiments and also by the method of Bragg and Kleeman. The emission of  $\alpha$ -rays is very improbable according to the absorption phenomena, the easily absorbed rays emitted consisting of  $\beta$ -rays. The data obtained in the second series of experiments confirm this result, and the conclusion is drawn that  $\alpha$ -rays of ionisation-range greater than 2 mm. are not emitted by uranium-X.

H. M. D.

**New Radioactive Element.** BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1907, [iv], 24, 370—372. Compare this vol., ii, 62).—Evidence has been obtained that uranium minerals contain a previously

\* And *Physikal. Zeitsch.*, 1907, 8, 803—805.

unknown radioactive element, which emits  $\alpha$ - and  $\beta$ -rays, produces no emanation, and resembles thorium in its chemical properties. The range of the  $\alpha$ -particle in air is smaller than that of the particles from any other known radioactive element. The  $\beta$ -radiation is less penetrating than that from uranium. The name *ionium* is proposed for the new substance, which is supposed to be a disintegration product of uranium, and probably the immediate parent of radium.

H. M. D.

**Corpuscular Rays Produced in Different Metals by Röntgen Rays.** C. D. COOKSEY (*Amer. J. Sci.*, 1907, [iv], 24, 285—304).—The readily absorbable type of radiation emitted by heavy metals when subjected to the action of Röntgen rays has been examined. The absorption by aluminium indicates that this radiation is corpuscular, the velocity of the particles being of the same order as that of the cathode ray particles. The more penetrating the primary Röntgen rays the more penetrating is the corpuscular secondary radiation. For the more penetrating primary rays, all the metals tested, with the exception of nickel, give corpuscular rays of nearly the same penetrating power. For the less penetrating primary rays, the secondary corpuscles vary with the nature of the metal, those from lead being the least penetrating. The first-mentioned secondary corpuscles are homogeneous, the second are not homogeneous if the radiation from tin and silver is excepted.

For equal absorptions of the primary rays by different metals, the number of corpuscles produced compared with the number produced in a standard substance (lead) increases with the density of the metal. Silver is an exception when highly penetrating primary radiation is used for the comparison.

H. M. D.

**Canal Rays in Hydrogen, Helium, and Argon.** ERNST DORN (*Physikal. Zeitsch.*, 1907, 8, 589—590).—A list of the spectral lines for which the Doppler effect has been observed in hydrogen, helium, and argon is given.

H. M. D.

**Zeeman Effect with Magnesium, Calcium, Strontium, Zinc, Cadmium, Manganese, and Chromium.** WILLIAM MILLER (*Ann. Physik*, 1907, [iv], 24, 105—136).—The spectra of the metals named have been examined, and the observed lines are recorded in full.

J. C. P.

**Potential and Nature of Alloys.** NICOLAI A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 869—897. Compare this vol., ii, 774).—The alloys of lead with copper, silver, bismuth, antimony, and arsenic are not chemical compounds. With the exception of the lead-copper alloys, they form solid solutions of very low concentration, although in the case of the lead-bismuth alloys these solutions are not indicated on the potential curve.

As the metals, chromium, manganese, iron, cobalt, and nickel, are added to tin, the alloys become gradually harder and more brittle. The potential curve indicates no solid solutions, but the following com-

pounds exist,  $\text{NiSn}$ ,  $\text{CoSn}$ , both having a potential lower than either of the metals of which they are composed:  $\text{SnMn}_2$ , at the composition 66% manganese, and  $\text{Mn}_3\text{Sn}$ , which is crystalline and contains 75% manganese;  $\text{Fe}_4\text{Sn}$ . Tin and chromium form very soft alloys and give no definite compounds. The metals of the first three groups of the periodic system combine with those of the 5th, 6th, and, to some extent, of the 4th group, according to certain well-defined types, but the chemical nature of some of these compounds, especially the bronzes, does not agree with the commonly accepted ideas on valency, and a detailed study of these compounds would probably serve to bridge over the gulf that still exists between the metallic and non-metallic elements. A concise summary of all the results so far obtained is given, as well as tables and potential curves of the alloys here described. Z. K.

**Action of Depolarisers.** FRITZ WEIGERT (*Zeitsch. physikal. Chem.*, 1907, 60, 513—552).—A preliminary communication of the results has already been made (Abstr., 1906, ii, 417). Details of the work are now given, and the action of hydrogen and hydrogen iodide as anodic depolarisers is described, in addition to the depolarisers previously examined. J. C. P.

**Thermodynamics of Normal Cells. III.** ERNST COHEN, FREDERICK D. CHATTAWAY, and W. TOMBROCK (*Zeitsch. physikal. Chem.*, 1907, 60, 706—727. Compare Abstr., 1900, ii, 520, 703).—The potential difference at a copper electrode immersed in copper sulphate is not very constant, and therefore the ordinary form of the Daniell cell is quite unsuited for accurate work. The authors show, however, that the potential difference at a copper amalgam electrode (prepared electrolytically) is very steady, and independent of the concentration of the amalgam between 1% and 16% of copper. Cells were accordingly constructed of the type:

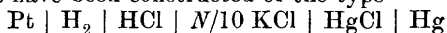
Zinc amalgam.		Saturated solution of zinc sulphate.		Saturated solution of copper sulphate.		Copper amalgam.
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The zinc amalgam used contained 1 part of zinc to 9 parts of mercury; the copper amalgam used contained 12% of copper. The *E.M.F.* is very constant at all temperatures, and the authors consider that a Daniell cell of this construction may be classed alongside the Clark and Weston cells.

The validity of the Gibbs-Helmholtz equation  $E = E_c/n\epsilon + T.dE/dT$  is established for the Daniell cell. The value of  $E_c$  at  $15^\circ$  is calculated from the thermochemical data to be 55,189 cal., whereas the electrical measurements lead to the value 56,089 cal. J. C. P.

**Neutral Point of the Hydrogen Electrode.** RICHARD LORENZ and A. MOHN (*Zeitsch. physikal. Chem.*, 1907, 60, 422—430).—The "neutral point" of the hydrogen electrode means the *E.M.F.* of a platinised platinum electrode charged with hydrogen at 1 atmosphere pressure and immersed in pure water. This *E.M.F.* cannot be determined directly, but it may be deduced from a study of the hydrogen electrode in acid and in alkali solutions of different concentrations,

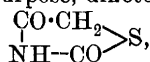
The potential of the electrode,  $\text{Pt} | \text{H}_2 | \text{acid}$ , increases gradually as the concentration of the acid diminishes; that of the electrode,  $\text{Pt} | \text{H}_2 | \text{alkali}$ , diminishes as the concentration of the alkali diminishes. Subject to the necessary corrections, the mean of the two potential values found for an acid and an alkali of equal concentration represents the neutral point of the hydrogen electrode. A number of cells have been constructed of the type



and  $\text{Pt} | \text{H}_2 | \text{NaOH} | N/10 \text{ KCl} | \text{HgCl} | \text{Hg}$ , and the *E.M.F.*'s of these have been determined with different concentrations of acid and alkali. The mean value thus found for the neutral point of the hydrogen electrode, measured against the calomel electrode, is  $-0.75$  volt. The negative sign is inserted in accordance with Luther's system, since in all cases the current in the cells flows from the hydrogen to the mercury electrode, that is, the hydrogen electrode is the negative pole of the cells.

J. C. P.

**Ionisation of Water at  $0^\circ$ ,  $18^\circ$ , and  $25^\circ$ , derived from Conductivity Measurements of the Hydrolysis of the Ammonium Salt of Diketotetrahydrothiazole.** CLARENCE W. KANOLT (*J. Amer. Chem. Soc.*, 1907, 29, 1402—1416).—Although the degree of ionisation of water has already been determined in several ways, yet in no case can the value obtained be regarded as highly accurate. It was therefore considered desirable to re-determine this constant by measuring the increase in conductivity produced by adding to a partially hydrolysed salt of a weak acid and a weak base an excess of the acid or of the base. For this purpose, diketotetrahydrothiazole,



was selected as the acid and ammonium hydroxide as the base. The ionisation of both substances at various concentrations was determined by conductivity measurements at  $0^\circ$ ,  $18^\circ$ , and  $25^\circ$ . The conductivity was also determined of solutions of the salt of  $0.02N$  and  $0.05N$  concentration, both alone and in presence of the equivalent amount and half the equivalent amount of the free acid and also of the free base. The conductivity of the completely ionised salt was determined by measurements with  $0.002N$  solutions. The method employed in carrying out the experiments is described with the aid of a diagram.

The following values for the ionisation constants were obtained. Ammonium hydroxide,  $13.91 \times 10^{-6}$  at  $0^\circ$ ;  $17.15 \times 10^{-6}$  at  $18^\circ$ , and  $18.06 \times 10^{-6}$  at  $25^\circ$ . Diketotetrahydrothiazole,  $0.0711 \times 10^{-6}$  at  $0^\circ$ ;  $0.146 \times 10^{-6}$  at  $18^\circ$ , and  $0.181 \times 10^{-6}$  at  $25^\circ$ . Water,  $0.089 \times 10^{-14}$  at  $0^\circ$ ;  $0.46 \times 10^{-14}$  at  $18^\circ$ , and  $0.82 \times 10^{-14}$  at  $25^\circ$ . The concentration of the hydrogen ions in pure water is  $0.30 \times 10^{-7}$  at  $0^\circ$ ;  $0.68 \times 10^{-7}$  at  $18^\circ$ , and  $0.91 \times 10^{-7}$  at  $25^\circ$ . These values of the hydrogen ion concentration of water are from 16% to 20% lower than those of Kohlrausch and Heydweiller (*Abstr.*, 1894, ii, 375). From the variation of the values with the temperature, the heat of ionisation of water was calculated and found to be 14.5 Cal. at  $9^\circ$  and 14.2 Cal. at  $21.5^\circ$ , which agrees closely with the values obtained by Wörmann (*Abstr.*,

1906, ii, 148) for the heats of neutralisation of potassium and sodium hydroxides by hydrochloric and nitric acids. E. G.

**Conductivity of Dilute Acids.** FRIEDRICH KOHLRAUSCH (*Zeitsch. Elektrochem.*, 1907, 13, 645—646. Compare Bogdan, this vol., ii, 734).—The author does not agree with the conclusion drawn by Bogdan that the electrical conductivity values of dilute solutions of hydrochloric and nitric acid are those required by the mass-action dissociation formula. The data are more closely expressed by the formula  $\Lambda_{\infty} - \Lambda = Pm^{\frac{1}{2}}$ , in which  $P$  is a constant,  $\Lambda$  and  $\Lambda_{\infty}$  the equivalent conductivity at concentration  $m$  and at infinite dilution respectively. This formula is, moreover, capable of representing the observed data for solutions which are five times as concentrated as the strongest solutions for which Bogdan claims agreement with the dilution formula. H. M. D.

**Electrical Conductivity of Methylamine Solutions.** EDWARD C. FRANKLIN and HARRY D. GIBBS (*J. Amer. Chem. Soc.*, 1907, 29, 1389—1396).—Since Gibbs (Abstr., 1906, i, 933) has shown that liquid methylamine is a good solvent for many substances, it was considered desirable to study the electrical conductivity of the solutions. The apparatus was constructed on the same lines as that employed by Franklin and Kraus (Abstr., 1900, ii, 382). Determinations have been made of the conductivity of methylamine solutions of potassium iodide, acetamide, benzenesulphonamide, *m*-nitrobenzenesulphonamide, and silver nitrate. The results are tabulated and plotted as curves.

The conductivity curves for potassium iodide and *m*-nitrobenzenesulphonamide in methylamine are similar to those of the cyanides of the heavy metals in liquid ammonia (Franklin and Kraus, Abstr., 1905, ii, 298). In the case of silver nitrate, the molecular conductivity at first increases with the dilution, then decreases, and afterwards increases again. An explanation of this peculiar behaviour is suggested. E. G.

**Electrical Conductivity of Solutions of Organic Acids in Liquid Hydrogen Chloride and Bromide.** EBENEZER H. ARCHIBALD (*J. Amer. Chem. Soc.*, 1907, 29, 1416—1439).—It has been shown previously (this vol., ii, 526) that most of the organic hydroxy-compounds dissolve in liquid hydrogen bromide to form solutions of considerable conductivity. The investigation has now been extended to the organic acids.

Walker, McIntosh, and Archibald (Trans., 1904, 85, 1098) found that several of the organic acids yield conducting solutions with liquid hydrogen chloride, but that in the case of hydrogen bromide solutions the conductivity was so small as to be scarcely measurable. The method followed in the present investigation, however, has shown that the conductivity of many acids when dissolved in hydrogen bromide can be determined over a considerable range of dilution.

The monobasic acids of the benzene series and the lower members of the paraffin series give conducting solutions with both solvents; formic acid, however, does not dissolve in hydrogen bromide, and yields only a feebly conducting solution with hydrogen chloride.



The dibasic acids of the oxalic acid group seem to be insoluble in both solvents, whilst those of the ethylene group, racemic and fumaric acids, although not yielding conducting solutions with hydrogen bromide, show fair conductivity in hydrogen chloride.

Glycollic and lactic acids do not give conducting solutions. Salicylic acid shows considerable conductivity in both solvents, whilst *p*-hydroxybenzoic acid conducts slightly in hydrogen chloride, but not at all in hydrogen bromide. Phthalic acid forms good conducting solutions with hydrogen chloride, but *isophthalic* acid appears to be insoluble in this liquid.

Mono- and di-hydroxy-dibasic acids do not yield conducting solutions with either solvent. In general, the greater the number of carboxyl or hydroxyl groups in the molecule, the less likely is the substance to dissolve.

The molecular conductivities and temperature coefficients of conductivity of several acids are tabulated; the former are also plotted as curves. The molecular conductivity of the hydrogen bromide solutions decreases rapidly with increasing dilution, except in the case of salicylic acid, in which it increases with dilution. The molecular conductivity of the more dilute hydrogen chloride solutions increases as the dilution increases, but in all the concentrated solutions it increases rapidly with decreasing dilution.

In the paraffin series, the conductivity of hydrogen chloride solutions increases in the order butyric, propionic, acetic acid, but formic acid has a much lower conductivity than any of these.

The temperature coefficients are positive in all cases, but vary greatly in magnitude for different acids of the same series. It has been found that the temperature coefficient increases with the concentration.

Acetic, butyric, and benzoic acids have a higher conductivity in halogen hydrides than in aqueous solutions of the same concentration.

In cases in which the molecular conductivities as calculated from the expression  $\kappa V$  decrease with dilution, recalculation from the expression  $\kappa V^n$ , where  $n$  is the number of molecules of the solute associated with the solvent to form the electrolyte, gives values which vary with dilution in the same way as the molecular conductivities vary for aqueous solutions of inorganic electrolytes (compare Steele, McIntosh, and Archibald, *Phil. Trans.*, 1905, 205, 99). E. G.

**Conductivity of Electrolytes in Aqueous Solutions of Gelatin.** A. DUMANSKI (*Zeitsch. physikal. Chem.*, 1907, 60, 553—562).—The electrolytes chiefly studied were potassium chloride, sulphate, and phosphate. If  $\alpha_g$  represents the specific conductivity in the gelatin solution,  $\alpha_w$  the specific conductivity of the same electrolyte in water, and  $\pi$  the diminution in the section of the conductor, owing to the presence of the non-conducting gelatin, then, according to the author's experiments,  $\alpha_g/(1-\pi)$  is not very different from  $\alpha_w$ . It is shown that potassium chloride has almost the same concentration in the gelatin as in the water, and favours the swelling of the gelatin. It is found that for salts which favour the swelling of gelatin and lower its setting point,  $\alpha_n/(1-\pi)$  is always less than  $\alpha_w$ . J. C. P.

**The Electrolytic Dissociation of Fused Salts.** KURT ARNDT (*Ber.*, 1907, 40, 3612—3614. Compare this vol., ii, 598).—A reply to Lorenz (this vol., ii, 665). The coefficient of internal friction of a completely dissociated fused salt is a function of the three coefficients of friction between the cations and anions, between the cations and cations, and between the anions and anions. Fousereau's law that the electrical resistance of a fused salt is proportional to its coefficient of internal friction applies only when this is proportional to the coefficient of friction between the cations and anions, which alone is concerned with the electrical conductivity. G. Y.

**Thermoelectricity of Nickel (Influence of Foreign Metals).** HECTOR PÉCHEUX (*Compt. rend.*, 1907, 145, 591—593. Compare Abstr., 1906, ii, 758).—Examination of three specimens of nickel containing: (1) 0.80% of copper, 0.20% of carbon and silicon, and traces of iron and cobalt; (2) 0.20% of copper, 0.15% of cobalt and traces of iron, and (3) 1.5% of iron, 0.5% of cobalt, 0.1% of carbon and silicon, and traces of copper, shows that the first is hard, brittle, and the most fusible, the second soft and of intermediate fusibility, and the third rather hard and the least fusible. Thus copper rather than carbon increases the fusibility, whilst iron diminishes it; carbon increases the hardness.

Thermoelectric couples of these samples of nickel with pure copper have been made and the variation of the *E.M.F.* with temperature studied. The curves representing this variation are roughly parabolic, exhibiting maximum and minimum points at  $t_m$  and  $t_n$  respectively. The values of  $t_m$  and  $t_n$  are (1) 240° and 380°; (2) 235° and 398°; (3) 220° and 366°. The three curves are not parallel, inversion takes place between samples (1) and (2) at 402°, between (1) and (3) at 200°, and between (2) and (3) at 180°. Annealing the couples for twenty hours at 640° increases the *E.M.F.*, but not to the same extent. The inversion temperature of (1) and (3) remains 200°, but that of (1) and (2) is reduced to 390°. After annealing, the *E.M.F.* of the couples remains constant. The simultaneous existence of copper and cobalt in nickel apparently produces more marked deviations in the variation of the *E.M.F.* E. H.

**Electrolytic Valve Action Exhibited by the Metals Magnesium, Antimony, and Bismuth.** GÜNTHER SCHULZE (*Ann. Physik*, 1907, [iv], 24, 43—45).—Magnesium exhibits a valve effect, not only in potassium hydroxide and carbonate solutions, but also in a solution of sodium phosphate containing ammonia. Antimony and bismuth exhibit the effect in nearly all electrolytes, and the potential difference against which the "valve" holds out is in some cases as high as 600—700 volts. The valve effect is in all cases due to the formation of a layer of oxide on the surface of the anode metal (compare Taylor and Inglis, Abstr., 1903, ii, 260; Fischer, *ibid.*, ii, 587). J. C. P.

**Platinum Resistance Furnace for Melting Points and Combustions.** SAMUEL A. TUCKER (*J. Amer. Chem. Soc.*, 1907, 29, 1442—1444).—A small furnace is described, suitable for obtaining

temperatures between 800° and 1300°. It consists essentially of a quartz tube wound with platinum tape to the ends of which short pieces of platinum wire are welded to serve as leads. The walls of the furnace are made of sheet asbestos, and the space between the walls and the quartz tube is filled with infusorial earth. A diagram of the apparatus is given.

E. G.

**Calorimetric Resistance Thermometers and the Transition Temperature of Sodium Sulphate.** H. C. DICKINSON and E. F. MUELLER (*J. Amer. Chem. Soc.*, 1907, 29, 1381—1388).—The construction of a form of resistance thermometer for calorimetric work is described which has been found suitable for temperature determinations between 0° and 100°. Two of these thermometers were compared with four standard mercury thermometers of the U.S. Bureau of Standards, and were calibrated by means of Callendar's formula,  $t - pt = \delta\{(t/100) - 1\}t/100$ . The transition temperature of sodium sulphate was determined with these thermometers and found to be 32.384°, which is practically identical with the value obtained by Richards and Wells (*Abstr.*, 1903, ii, 401). The calibration of resistance thermometers can be carried out very accurately by using Callendar's formula and determining the constant  $\delta$  from the transition temperature of sodium sulphate. It is shown that these thermometers can be used to reproduce the international hydrogen scale to within about 0.002°.

E. G.

**Condensation Nuclei produced by Cooling Gases to Low Temperatures.** GWILYM OWEN and A. LL. HUGHES (*Phil. Mag.*, 1907, [vi], 14, 528—538).—Different gases, after having been cooled to a sufficiently low temperature, show the presence of condensation nuclei on admission to the cloud chamber of a Wilson expansion apparatus. For each gas there is a more or less definite critical temperature below which it must be cooled before the formation of these nuclei can be detected. Below this temperature, the number of nuclei increases rapidly with the degree of cooling, the maximum effect being obtained when the cooling is sufficient to cause some of the gas to turn (or to be on the point of turning) into the liquid state. The number of nuclei is independent of the time of cooling and of the amount of the expansion to which the gas is subjected in the cloud apparatus. The nuclei are very persistent, and the small degree of supersaturation required to cause condensation in them indicates that they are of considerable size. For a particular gas, the "critical temperature" falls with the pressure of the cooled sample. For air, under pressures of 101, 80, and 41 cms. of mercury, the observed "critical temperatures" were respectively -140°, -145°, and -160°. No nuclei were ever detected in hydrogen until it had been cooled to -175°. For carbon dioxide at pressures of 117, 80, and 35 cms., the observed temperatures were -66°, -70°, and -73° respectively.

It is shown that the production of the nuclei cannot be due to any direct action on the walls of the cooled containing vessel or to traces of water vapour in the gas. As an explanation of the phenomena, it

is tentatively suggested that, at temperatures considerably higher than the liquefaction temperatures, the molecules of the gas form aggregations of considerable size (incipient liquefaction) capable of persisting for a long time after the gas has regained its normal temperature.

H. M. D.

**Specific Heat of Nitrogen, Carbon Dioxide, and Water Vapour up to 1400°.** LUDWIG HOLBORN and FRITZ HENNING (*Ann. Physik*, 1907, [iv], 23, 809—845. Compare Abstr., 1906, ii, 147; also Holborn and Austin, *Wiss. Abh. der Phys.-Techn. Reichsanstalt*, 1905, 4, 131).—The determinations of the mean specific heat of nitrogen, carbon dioxide, and water vapour previously carried out up to 800° have now been extended to 1400°. For this purpose, the nickel tubes in the original apparatus have been replaced by platinum tubes. For a description of the calorimeter and the heating apparatus, the original must be consulted. The following formulæ are given as representing the dependence of the mean specific heat ( $c_{0,\theta}$ ) between 0° and  $\theta^\circ$  on the temperature: nitrogen,  $c_{0,\theta} = 0.2350 + 0.000019\theta$ ; carbon dioxide,  $c_{0,\theta} = 0.2010 + 0.0000742\theta - 0.0718\theta^2$ ; water vapour, (1)  $c_{100,\theta} = 0.4669 - 0.0000168\theta + 0.0744\theta^2$ ; (2)  $c_{100,\theta} = 0.4544 + 0.006925 \times 10^{-6} \theta^{0.007513\theta}$ .

The variation of the specific heat of nitrogen with the temperature agrees with the results obtained in explosion experiments by Mallard and Le Chatelier and by Langen. For carbon dioxide and water vapour, the specific heat values obtained in these experiments are considerably smaller than those given by the explosion method.

H. M. D.

**Character of Melting-Point and Clearing-Point Curves for Fluid-Crystalline Substances and their Mixtures.** ALEX. D. BOGOJAWLENSKY and N. WINOGRADOFF (*Zeitsch. physikal. Chem.*, 1907, 60, 433—440).—*p*-Azoxyphenetole and *p*-azophenetole are isomorphous and form a complete series of mixed crystals. The freezing-point curve and clearing-point curve are both almost straight lines. They intersect each other, so that there is in the temperature-concentration diagram a field of stable and a field of labile fluid crystals. The clearing point for pure *p*-azophenetole is 155°, 4.5° below its freezing point, and can be observed by allowing the fused substance to become supercooled in a sealed glass tube. *p*-Azophenetole has a transition point at 97.2°; the temperature at which this transition takes place is very markedly lowered by increasing addition of *p*-azoxyphenetole.

The freezing-point curve for mixtures of *p*-azoxyanisole and *p*-azoisole has a eutectic point, and the clearing-point curve cuts that branch along which separation of *p*-azoisole takes place. Observation of the clearing point has been possible only with mixtures containing from 60—100% of *p*-azoxyanisole, but extrapolation of the directly observed freezing-point curve indicates that if it were possible to supercool *p*-azoisole to such an extent, it would be found to have a clearing point about 108°. The existence of a fluid-crystalline modification like this (that is, at temperatures below the freezing point) may be described as latent, and the fluid crystals formed in such a case are to be regarded as labile.

The freezing-point curve of *p*-azophenetole and *p*-azoanisole has a eutectic point. The clearing points of pure *p*-azophenetole (as already mentioned) and of several mixtures containing gradually increasing quantities of *p*-azoanisole are found to lie below their respective freezing points. Two clearing points have been observed also on the other side of the eutectic; there the distance of the clearing-point curve below the freezing-point curve becomes much greater. Extrapolation indicates again that the labile clearing point of *p*-azoanisole would lie about  $108^{\circ}$ .

The results obtained by the authors throw light on recent observations made on fluid crystals (see Lehmann, *Abstr.*, 1906, ii, 837; Vorländer, this vol., ii, 70; Vorländer and Gahren, this vol., ii, 441).  
J. C. P.

**Molten Hydrated Salts as Solvents for the Freezing-Point Method.** II. J. LIVINGSTON R. MORGAN and F. T. OWEN (*J. Amer. Chem. Soc.*, 1907, 29, 1439—1442).—Morgan and Benson (this vol., ii, 747) have given an account of a study of fused hydrated calcium chloride, lithium nitrate, and sodium chromate as solvents for the determination of molecular weights by the freezing-point method. The investigation has now been extended to three other fused hydrated salts, namely, calcium nitrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , fr. p.  $42\cdot31^{\circ}$ ; zinc nitrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , fr. p.  $44\cdot07^{\circ}$ , and manganous nitrate  $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , fr. p.  $34\cdot81^{\circ}$ . The freezing-point constants for these salts are  $59\cdot4^{\circ}$ ,  $58\cdot6^{\circ}$ , and  $67\cdot4^{\circ}$  respectively. The depressions of the freezing point of these fused salts produced by various substances are tabulated.

The heats of fusion of zinc nitrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and manganous nitrate,  $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , have been calculated from the freezing-point constants, and found to be 34·3 and 28·09 cal. per gram respectively.

E. G.

**Determinations of Molecular Weight and Conductivity in Nitrobenzene.** ERNST BECKMANN and GEORG LOCKEMANN (*Zeitsch. physikal. Chem.*, 1907, 60, 385—398).—The authors confirm Hansen's conclusions (*Abstr.*, 1904, i, 725) as to the hygroscopic nature of nitrobenzene. The freezing point of freshly distilled and crystallised nitrobenzene can be raised  $0\cdot4^{\circ}$  by prolonged passage of carefully-dried air. The value 70 hitherto taken for the freezing-point depression constant of nitrobenzene is valid only for the moist substance; with properly dried nitrobenzene, the value of the constant is 80 or more, as deduced from experiments with the solutes iodine and benzil. Benzoic acid associates in nitrobenzene to double molecules, whilst cinnamic acid also associates, although to a less extent. Hydrogen chloride in nitrobenzene is associated; the association is greater in the perfectly dried than in the moist nitrobenzene and increases with dilution; in the most dilute solutions, the calculated molecular weight has about five times the normal value. The molecular conductivity of hydrogen chloride dissolved in nitrobenzene is exceedingly small, and in the dried solvent is only a third or a fourth of what it is in the moist solvent; the molecular conductivity increases with dilution.

The hygroscopic nature of nitrobenzene is probably responsible for the variations that have been observed in several of its physical constants.

The results obtained for hydrogen chloride dissolved in benzene are, in general, analogous to those obtained with nitrobenzene as solvent.

J. C. P.

#### Lower Critical Temperature of Solution of Two Liquids.

V. I. DOLGOLENKO (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 841—854).—The effect on the solubility of secondary butyl alcohol in water by a rise or fall in temperature was determined by the appearance or disappearance of turbidity in the solution. By this method, which is sensitive to  $0.05^\circ$ , various fractions of the same alcohol were tested, with the result that they were not found to be identical, and suggested the admixture of a small quantity of the tertiary alcohol, and possibly also hydrates of alcohol, which decompose at higher temperatures. This was confirmed by various tests and also by the addition of the tertiary alcohol, when the curve altered in accordance with the theory. The presence of a lower critical temperature of solution is not considered to be the normal condition of a binary system, but is in all cases due to the presence of a third substance. Contrary to Rothmund (*Abstr.*, 1898, ii, 503) and Timmermann (*this vol.*, ii, 229), the natural curve for any pair of liquids is considered to be of a parabolic form.

Z. K.

[Calorimetric Studies.] ADOLF WINKELMANN (*Zeitsch. physikal. Chem.*, 1907, 60, 626—637. Compare Bose, *this vol.*, ii, 332, 333).—The author records results obtained by him more than thirty years ago for the heat of mixture of ethyl alcohol and water in various proportions and at three different temperatures. The results are in good agreement with those recently published by Bose (*loc. cit.*).

J. C. P.

#### Position Isomerism and Heat of Combustion.

LAWRENCE J. HENDERSON (*Zeitsch. physikal. Chem.*, 1907, 60, 413—421. Compare *Abstr.*, 1905, ii, 145).—Available thermochemical data are employed to show that the difference in the heat of combustion involved in the replacement of one group by another may vary according to the position occupied by some other group in the molecule. The most striking case recorded in the paper is the influence of the carboxyl group on the replacement of a methyl group by a carboxyl group. This will be made clear by the following lines, in which the numbers represent differences in the heats of combustion :

$\text{CH}_3 \cdot \text{CO}_2\text{H}$ .....	—	$\text{CO}_2\text{H} \cdot \text{CO}_2\text{H}$ .....	147 Cal.
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ...	—	$\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .....	157 Cal.
$\text{CH}_3 \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$ —	—	$\text{CO}_2\text{H} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$ .....	163 Cal.
$\text{CH}_3 \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ —	—	$\text{CO}_2\text{H} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ .....	162 Cal.
$\text{CH}_3 \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{H}$ —	—	$\text{CO}_2\text{H} \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{H}$ .....	161 Cal.

When the second carboxyl group is in the  $\alpha$ -position, the change in the heat of combustion associated with the change  $\text{CH}_3 \rightarrow \text{CO}_2\text{H}$  is 13 Cal. less than the "normal" value reached when the second carboxyl group is very distant; with this group in the  $\beta$ -position, the difference is 3 Cal. less than the normal value; with the second carboxyl group in the  $\gamma$ ,  $\delta$ , or  $\epsilon$ -position, the difference is about 2.5 Cal. greater than the normal value; thereafter, approximation is made to the normal value. The conclusion drawn is that the valency energy of the linking between two atoms varies with the conditions. J. C. P.

[Application of Thermal Analysis to Ternary Systems.] R. SAHMEN and A. VON VEGESACK (*Zeitsch. physikal. Chem.*, 1907, 60, 507—509. Compare this vol., ii, 532).—A reply to Jänecke (this vol., ii, 666). J. C. P.

Action of Methylene-Blue on Cotton Fibre. J. O. WAKELIN BARRATT and EDWARD S. EDIE (*Bio-Chem. J.*, 1907, 2, 443—457).—The action is best interpreted as a mixed process of chemical combination and adsorption, the former being the chief process. W. D. H.

Influence of Electrolytes and of other Conditions on the Osmotic Pressure of Colloids. RALPH S. LILLIE (*Amer. J. Physiol.*, 1907, 20, 127—169).—The osmotic pressure of gelatin and egg-white was measured by a direct method. It is not affected by non-electrolytes, is increased by acid and alkali, and decreased by salts in an order which is stated; the depression is a function of both anion and cation. The influence of shaking, temperature, mode of preparation, rate of admixture with electrolyte and other factors is also considered. W. D. H.

Relations between Solvents and Solutes. IWAN OSTROMYSLENSKY (*J. pr. Chem.*, 1907, [ii], 76, 264—267).—Solvents for organic substances may be divided into two classes: the solvent power of those of the first class, which includes solvents such as water, alcohol, and ether, is not dependent on the constitution of the solute; the solvents of the second class, on the other hand, are constitutionally related to the solute. The relations between the solute and the solvents of the first class are generalised, so far as known, in the statement that the majority of the members of a group of compounds are soluble or insoluble in a given member of the first class; thus all hydrocarbons are insoluble, or only very sparingly soluble, in water. The author enunciates now the following three of the laws regulating the relation of a solute to solvents of the second class.

- (1) All compounds are soluble in their homologues.
- (2) All position-isomerides are soluble in each other.
- (3) All polysubstitution derivatives of a substance are soluble in each other, so long as one and the same group is substituted for hydrogen.

These three laws are discussed and illustrated by reference to a number of organic compounds and their solubilities. G. Y.

Common Critical Curve for Solutions in Pentane. MIECZYSLAW CENTNERSZWER and A. KALNIN (*Zeitsch. physikal. Chem.*, 1907, 60, 441—450).—The critical phenomena exhibited by solutions of the

relatively non-volatile substances, phenanthrene, triphenylmethane, anthraquinone, dibromonaphthalene, quinol, benzil, anthracene,  $\alpha$ -naphthylamine, and diphenylamine in isopentane have been studied on the lines already followed (Abstr., 1906, ii, 341). From the results obtained, it is shown that all these solutions in isopentane have a common critical curve, given by the equation:  $\pi = \pi_o + A(\theta - \theta_o)$  (compare *loc. cit.*). In this case, the value of  $A$  is 0.33. For isopentane, the molecular increase of the critical pressure is 135, and the molecular rise of the critical temperature is 455. J. C. P.

**Solubilities in Mixed Solvents. V.** WALTER HERZ and G. ANDERS (*Zeitsch. anorg. Chem.*, 1907, 55, 271—278. Compare Abstr., 1904, ii, 709; 1905, ii, 510, 709; this vol., ii, 159).—The solubility of potassium chloride, bromide, and iodide in mixtures of methyl alcohol and water in varying proportions at 25° has been determined and the results are tabulated. In all cases,  $L-l$  ( $L$ =observed solubility,  $l$ =solubility calculated on the assumption that the components exert their effect independently) is negative and reaches a maximum value in each case for the mixture containing 2—3 mols of water to 1 mol. of alcohol. The ratio  $L-l/l$ , however, increases regularly with increasing proportion of alcohol and finally attains a constant value.

The electrical conductivity and the viscosity of the solutions have also been determined. The molecular conductivity curves show minima and the viscosity curves maxima which, however, do not coincide, but the maxima of the viscosity curves coincide with the maximum values of  $L-l$ .

The solubility of potassium and sodium chlorides and of sucrose in mixtures of ethyl alcohol and water, of certain alkali halogen salts, of iodine, and of succinic acid in mixtures of glycerol and water, previously determined by Herz and Knoch (*loc. cit.*) and others, are also tabulated. In all cases except the last,  $L-l$  is negative; the abnormal result in the case of succinic acid probably depends on some chemical action between the latter and the solvent. For the alkali halogen salts in ethyl alcohol and water, the maximum value of  $L-l$  occurs in a mixture containing 1 mol. of alcohol to 3 mols. of water; for glycerol and water, in a mixture containing 1 mol. of the former to 4 mols. of water. For iodine in mixtures of glycerol and water,  $L-l$  does not attain an intermediate maximum value. G. S.

**Studies of the Processes Operative in Solutions. II. The Displacement of Chlorides from Solution by Alcohol and by Hydrogen Chloride.** HENRY E. ARMSTRONG, JOHN V. EYRE, ARTHUR V. HUSSEY, and W. P. PADDISON (*Proc. Roy. Soc.*, 1907, A, 79, 564—576. Compare Caldwell, this vol., ii, 14).—The influence of alcohol, a representative non-electrolyte and weak dehydrant, on the solubility at 25° of sodium, potassium, and ammonium chlorides, potassium iodide and bromide has been determined, as also the similar influence of hydrogen chloride, a representative electrolyte and moderately powerful dehydrant, on the solubility of sodium, potassium, and ammonium chlorides. As the authors' object was to find the relative concentrating effect of alcohol and hydrogen chloride in competition with that of the



salts, *weight-normal* solutions have been used throughout. To illustrate the method of treating the experimental data, the following may be quoted. The weight of sodium chloride dissolved by 1000 grams of pure water is 361.4 grams; the weight dissolved by 1000 grams of water, containing also 1 gram-molecule of alcohol, is 344.3 grams. The weight of water which this quantity of salt would normally saturate is calculated and deducted from 1000 grams, the difference being regarded as the weight of water associated with one molecule of alcohol. In this way, the apparent molecular hydration of the precipitant (alcohol or hydrogen chloride) is deduced. The values thus obtained for the hydration of alcohol, which is added in varying amount, lie between 1 and 4 (roughly), according to the salt, and to the concentration of the alcohol. The highest values are obtained with potassium chloride and the lowest with ammonium chloride, an isolated negative value being recorded in the latter case. The values deduced for the apparent molecular hydration of hydrogen chloride lie between 6.3 and 7.8 when ammonium chloride is the dissolved salt, between 8.3 and 12.6 with sodium chloride, and between 8.4 and 13 with potassium chloride. The conclusion is drawn that, although alcohol is less active than hydrogen chloride, the same kind of influence is exerted by both precipitants.

It appears that the condition of the salts in highly concentrated solutions is different from that which they assume in presence of a considerable proportion of the precipitant. The conclusion is drawn that sodium and potassium chlorides exist in an easily precipitable form in the concentrated solutions; this easily precipitable form is probably a complex polymerised molecule, closely related to the solid form. Emphasis is laid on the necessity of allowing for the existence in solutions of monadic and polymerised molecules, both anhydrous and hydrated, and, in some cases, for the existence of compounds formed by the association of the admixed solutes. Doubt is expressed whether it will ever be possible to develop any simple theory of solutions.

J. C. P.

**Studies of the Processes Operative in Solutions. III. The Sucroclastic Action of Nitric Acid as Influenced by Nitrates.** R. WHYMPER (*Proc. Roy. Soc.*, 1907, A, 79, 576—579. Compare Caldwell, this vol., ii, 14, and preceding abstract).

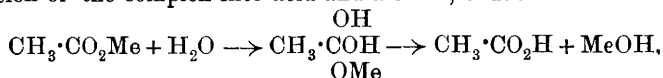
The method employed by Caldwell (*loc. cit.*) in determining the average degree of hydration of the chlorides in solution has been applied similarly in the case of nitrates. The average hydrates indicated in this way for 25° and weight-normal solutions are  $\text{AgNO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{NH}_4\text{NO}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{KNO}_3 \cdot 8\text{H}_2\text{O}$ ,  $\text{NaNO}_3 \cdot 11\text{H}_2\text{O}$ ,  $\text{LiNO}_3 \cdot 13\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2 \cdot 18\text{H}_2\text{O}$ . These results are inconsistent with the view that nitrates are not hydrated in solution.

J. C. P.

**Studies of the Processes Operative in Solutions. IV. Hydrolysis of Methyl Acetate in Presence of Salts.** HENRY E. ARMSTRONG and JOHN A. WATSON (*Proc. Roy. Soc.*, 1907, A, 79, 579—586. Compare preceding abstracts).—The method of deducing the average molecular hydration of a dissolved salt

from the concentrating influence which it exerts on the activity of acids in the inversion of sucrose (see Caldwell, this vol., ii, 14, and Whymper, preceding abstract) is extended to the hydrolysis of methyl acetate by hydrochloric and nitric acids. Methyl acetate in water is probably hydrated only to a very slight extent, whereas sucrose is moderately hydrated; it is therefore to be expected that the values deduced for the average molecular hydration of chlorides and nitrates from their influence on the hydrolysis of methyl acetate should be, if anything, higher than the values deduced from their influence on the hydrolysis of sucrose. It is found, however, that they are actually lower, notably in the case of nitrates, where the values of the average molecular hydration obtained by the two methods differ by 7—10 units.

If it is assumed that the hydrolysis of methyl acetate involves the association of the two molecules (ester and water) and the subsequent partition of the complex into acid and alcohol, thus:



then the retarding influence of salts may be explained by supposing that they also enter into association with the ester, and thus hinder the association of ester and hydrolyst.

The results obtained by the authors are considered to be quite irreconcilable with the doctrine of ionic dissociation. J. C. P.

**Studies of the Processes Operative in Solutions. V. The Discrimination of Hydrates in Solution.** HENRY E. ARMSTRONG and ROBERT J. CALDWELL (*Proc. Roy. Soc.*, 1907, A, 79, 586—597. Compare Caldwell, this vol., ii, 14, and preceding abstracts).—The ionic dissociation hypothesis is criticised, and it is contended that the only respect in which electrolytes and non-electrolytes certainly differ is in their affinity for water, which appears to combine more readily and intimately with the former than with the latter. From this point of view, it becomes of importance to determine the extent to which different substances are hydrated in aqueous solution. The values for the hydration of salts deduced by the authors and others (*loc. cit.*) are accordingly compared with the values deduced from the influence which salts exert on the solubility of hydrogen, oxygen, nitrous oxide, nitrogen, carbon dioxide, phenylthiocarbamide, salicylic acid, and ethyl acetate (compare Philip, *Trans.*, 1907, 91, 711). The fact that the two sets of values agree as closely as they do, taken in conjunction with the results of the authors' hydrolytic studies, seems to support the view that solubility, even in the case of a gas, is a chemical phenomenon. The values for the hydration deduced from the effect of neutral salts on the hydrolysis of sucrose are regarded as likely to be the more accurate, although they are probably rather low.

The bearing of hydration on the phenomenon of electrolysis is discussed. The increase in molecular conductivity which accompanies dilution is probably due to the gradual breaking up of the more or less polymerised salt molecules into simple molecules or monads. These electrically effective monads are probably hydrated or even hydroxylated,

and the process of electrolysis is pictured as consisting of a series of interactions among the hydroxylated monads. The way in which these monads are polarised is represented by a diagrammatic arrangement resembling a Grotthus chain. It is suggested that physicists should re-examine the grounds on which they have rejected the Grotthus explanation of electrolysis. J. C. P.

**Process of Formation of Hydrosol and Hydrogel. I.** ALFRED LOTTERMOSER (*Zeitsch. physikal. Chem.*, 1907, 60, 451—463. Compare Abstr., 1905, ii, 586; 1906, ii, 429; this vol., ii, 78).—The author rehearses and elaborates the conclusions to be drawn from his own previous investigations (*loc. cit.*) and from those of other workers, criticises in some points the methods of Duclaux (*J. Chim. Phys.*, 1907, 5, 29) and Malfitano (Abstr., 1905, ii, 459), and indicates the lines on which fresh work is being carried out. J. C. P.

**The Passivifying, Passivity, and Activifying of Iron.** HENRY L. HEATHCOTE (*J. Soc. Chem. Ind.*, 1907, 26, 899—917).—The subject is discussed at considerable length, not only with reference to experiments made in the past, but also to many new observations which are described in detail. The test which is recommended for passivity consists in plunging the piece of iron into nitric acid of sp. gr. 1.2 at 15—17° and, after shaking for a moment, ascertaining whether chemical action is visible at the surface to the naked eye. The conditions under which iron can be rendered passive by acids and salts in solution, either with or without an external current, are first dealt with; subsequently the conditions which cause passive iron again to become active are considered. The following questions are discussed. (1) Whether “blued iron” is passive, and whether passivity is due to a coating of ferric oxide. (2) The transmission of activity and passivity along iron rods. (3) The nature of the “pulsations” or intermittent solution occurring with iron in nitric acid, and the character of the current oscillations accompanying this phenomenon. The following conclusions are finally drawn.

Iron becomes passive as follows. When immersed in a solution, the ferrous ions in the metal pass into the liquid from all parts of the surface, but as the solution pressure is not the same at every point, probably being greater on the average at a convex apex than round a concave hollow, local electric currents arise, and if the solution will act as a depolariser at the cathode of the local current the latter may persist until it causes the iron at the local anode to become passive. In this way, a number of very small cathode areas might be associated in rendering passive a very much larger local anode area, so that the surface might become passive nearly at the same moment all over. If the solution is not a vigorous hydrogen depolariser, or if its action on iron is vigorous, considerable time may elapse before the metal becomes passive, and various stages of “semi-passivity” will be observed. When one particle becomes passive, it may at once be rendered active again, but as the current density on a small passive area at the end of a rod is half what it would be if the same area were at the middle, passivity may be expected to be established at the ends

first. If the rate of action of the solution on the passive particle is small and if the solution can depolarise it, currents between the passive part and the adjacent active iron will not make the passive part active, but the active metal passive. In this way, passivity spreads over the surface. But as the resistance to or from a mathematical point is infinite, the last remaining point on the surface will remain active; probably minute active areas are also to be found at the bottom of cracks and crevices, and these will give rise to small currents which will persist so long as the rod remains passive. These active particles will generate current so long as the liquid continues to combine with the electrolytic products, and thus prevent the passive part from becoming active. If the depolarisation fails, the rod will become active, and the activity will spread from the active particles and especially from the ends of the rod. The "active spots" which appear in experiments made in a vacuum, the blue spots which are sometimes visible on a rod made passive by potassium ferricyanide, and the fact that "pulsations" nearly always start from one end of the rod are considered to confirm the above theory of passivifying.

The actual cause of passivity is still uncertain, but no theory seems to fit the facts so well as that which assumes the formation of a layer of the magnetic oxide,  $\text{Fe}_3\text{O}_4$ . Measurements are given showing that the *E.M.F.* of fused magnetic oxide|acid is nearly the same as that of passive iron|acid in nitric acid of D 1.2, 1.3, and 1.4 respectively.

W. A. D.

**Kinetic Examination of the Autoxidation of Ferrous Hydrogen Carbonate dissolved in Water.** GERHARD JUST [with TERRES] (*Ber.*, 1907, 40, 3695—3701).—This, the first kinetic investigation in this field, was accomplished by continuously passing a stream of oxygen and carbon dioxide through a ferrous hydrogen carbonate solution at 25°, air being carefully excluded during the preparation of the solution. The ferrous iron was estimated by potassium permanganate.

The partial pressures of oxygen and carbon dioxide remained constant, and the reaction is shown to be of the first order and is independent of the velocity with which the oxygen is passed through the carbonate solution, and consequently the reaction is between oxygen in solution and the iron salt. In another series of experiments, the oxygen percentage was altered, and as  $K/\text{O}_2$ , where  $K$  is the constant in each series of experiment and  $\text{O}_2$  the volume % of oxygen, is constant, whereas  $K/\sqrt{\text{O}_2}$  diminishes rapidly, the conclusion is made that oxygen reacts as a molecule and not as the atom O.

The reaction velocity is next proved to be inversely proportional to the square of the carbon dioxide concentration, and therefore  $dx/dt = K.(C_{\text{iron salt}} \text{CO}_2)/(\text{C}_{\text{CO}_2})^2$ .

The reaction is a non-reversible one, and these results are explained on basis of the ionic theory.

W. R.

**Ester Formation.** HEINRICH GOLDSCHMIDT and OLAF UDBY (*Zeitsch. physikal. Chem.*, 1907, 60, 728—755. Compare Goldschmidt and Sunde, *Abstr.*, 1906, ii, 219).—The esterification of organic acids

in alcoholic solution is accelerated by the addition of strong acids. A theoretical discussion of this process leads to the view that the hydrogen ion which acts catalytically in promoting esterification is associated with the alcohol to form a complex ion,  $(C_2H_5O, H)^+$ .

Numerous experiments have been made on the rate of esterification of phenylacetic, acetic, propionic, *n*-butyric, monochloroacetic, dichloroacetic, trichloroacetic, and benzoic acids. The rate of esterification is represented by a very complicated formula, which, however, by one or two simplifying assumptions is reduced to:  $Kct = (n + r + a) \log_e a / (a - x) - x$ , in which  $c$  is the concentration of the catalytic agent (generally hydrogen chloride, sometimes sulphosalicylic acid),  $n$  is the concentration of the water present, and  $r$  ( $=0.15$ ) is the hydrolytic constant of the complex ion. Whereas the velocity coefficient calculated for a unimolecular reaction falls off as esterification proceeds, the values of  $Kc$  found by the foregoing formula are, in general, satisfactorily constant. This result supports the view that the hydrogen ion is associated with the alcohol.

The foregoing formula does not satisfactorily represent the course of esterification either in the case of dichloroacetic and trichloroacetic acids, or where the ratio  $c/n$  is very small. The want of agreement in the latter case is probably due to the fact that the extent of dissociation in mixtures of alcohol and water is imperfectly known.

The experiments show that the catalytic influence of sulphosalicylic acid is rather less than that of hydrogen chloride. J. C. P.

**Esterification of  $\alpha$ - and  $\beta$ -Naphthoic Acids by Means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Monatsh.*, 1907, 28, 1069—1089. Compare Abstr., 1906, ii, 659; this vol., i, 849; ii, 158, 242, 243).—The velocities of esterification of  $\alpha$ - and  $\beta$ -naphthoic acids at  $25^\circ$  by means of hydrogen chloride in alcoholic solutions containing varying amounts of water have been measured by the method described previously. With both acids, the velocity constant in presence of much water increases more rapidly than the concentration of the hydrogen chloride, but slightly more slowly in concentrated alcohol. The relations of the velocity constants to the concentrations of the water and hydrogen chloride are represented by the expressions. For  $\alpha$ -naphthoic acid:  $1/k = 23.00 + 31.21/c + 0.7617/c^2 + (-51.76 + 70.85/c + 15.21/c^2)w + (-70.8 + 110.7/c + 17.95/c^2)w^2$ , which applies to solutions having the concentration of the water,  $w = 0.01 - 1.3$ , and that of the hydrogen chloride,  $c = 0.16 - 0.66$ . For  $\beta$ -naphthoic acid:  $1/k = 9.12 + 13.24/c + 0.0172/c^2 + (-35.36 + 16.49/c + 10.63/c^2)w + (-59.6 + 97.60/c - 3.234/c^2)w^2$ , which applies to solutions having  $w = 0.01 - 1.3$ , and  $c = 0.16 - 0.67$ .

The behaviour of the naphthoic acids on esterification is shown to be analogous to that of the acids studied previously. G. Y.

**Chemical Statics and Dynamics of the Mercury-Ethylene Compounds.** RICHARD ABEGG (*Zeitsch. physikal. Chem.*, 1907, 60, 431—432).—In reference to Sand and Breest's recent paper (this vol., ii, 537), it is pointed out that Sherrill's work (Abstr., 1903, ii, 534, 649) covered only a certain area of concentration. It is quite

possible that  $\text{HgX}_4''$ , which he found to be the predominant type of complex within that area, may not be the predominant type at other concentrations.

J. C. P.

### Catalysis by Means of Uranium Salts in the Sunlight.

RAYMOND F. BACON (*Philippine J. Sci.*, 1907, 2, 129—137).—As was shown by Seekamp (*Annalen*, 1862, 122, 113; 1865, 133, 253), oxalic acid is decomposed by sunlight in the presence of uranium salts with the formation of carbon monoxide, carbon dioxide, and formic acid. It is found that the rate of decomposition is not affected to any great degree by the relative amounts of uranium salt and oxalic acid present. Iron salts produce an acceleration, brucine, quinine, atropine, cinchonine, and strychnine a diminution, in the rate of decomposition. Thorium salts act like uranium salts, but that radioactivity is in no way connected with the catalytic process is shown by the fact that a solution of pitchblende in nitric acid induces a slower rate of decomposition than a solution of a uranium salt equivalent in amount to the uranium present in the mineral. Propionic, tartaric, pyrotartaric, malic, lactic, mandelic, citric, and malonic acids are also decomposed by sunlight in the presence of uranium acetate, but not formic acid.

The author considers the catalytic action to be intimately connected with the fluorescent nature of the solutions of uranium salts.

W. H. G.

**The Catalytic Action of Acids.** DMITRI P. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 825—841. Compare this vol., ii, 334; Nernst and Hohmann, *Abstr.*, 1893, i, 449).—The experimental results of the interaction of hydrocarbons and acids do not all agree with Nernst's and Hohmann's formula:  $(a-x)(1-x)/vx = K$ , I (where  $v$  = volume of the system,  $a$  = the original number of hydrocarbon molecules,  $x$  = the number of ester molecules formed, and the original number of acid molecules = 1). The action of trichloroacetic acid on  $\Delta^{\beta}$ -isoamylene was therefore re-investigated at various temperatures and with and without the use of different solvents. Equilibrium is established most quickly when no solvent is employed, next, with any hydrocarbon as solvent, but when a simple or complex ester is employed, the reaction is much slower and the limit of the reaction is much lower, whilst if the volume of ester is sufficiently great, no reaction takes place even after months. For all solvents, the amount of ester produced is greater the lower the temperature of the reaction and the higher the concentration. The formation of amylic salts is regarded as being due to the decomposition of the acid ester first formed, in two directions, (1) forming a hydrocarbon and acid; (2) a normal ester and acid, the formulæ proposed to express these reactions being  $K_1 = (a-x)(1-x-y)/yv^2$ , II, and  $K_{11} = (x-y)(1-x-y)/yv$ , III (where  $y$  = the number of molecules of acid ester). The results calculated by means of these formulæ agree closely with those obtained by experiment.  $K_1$  rises rapidly with the temperature; thus at  $65^\circ$  it is twenty times its value at  $18^\circ$ . Nernst's and Hohmann's results are also shown to conform far better with

formula II than with I. Formula II can also be employed to determine the amount of acid ester formed under given conditions. The reaction is thus one of apparent catalysis, and depends on the ability of acids to form unstable compounds with esters. The more active the acid the more pronounced is this tendency, and on this depend the speed and the limit of the reaction. Z. K.

**Catalysis of Sulphonic Acids.** JAMES M. CRAFTS (*Bull. Soc. chim.*, 1907, [iv], 1, 917—929).—The author has studied the hydrolysis of various aromatic sulphonic acids by strong acids of different concentrations, the velocity constant being calculated from the expression  $\log K = [C + C_1 + \log_{\text{nat.}}(C + C_1)]\alpha + \beta$ , where  $C$  and  $C_1$  are the gram-mols. per litre of the mineral and sulphonic acid respectively.

The curves of the velocity constants of hydrolysis in presence of hydrochloric acid are of the same form for all the compounds examined with the exception of mesitylene derivatives, for which  $\alpha$  has a higher value. The catalytic effect is the same for 1 mol. of hydrochloric, hydrobromic, hydriodic, or sulphuric acid, and, when the concentration is increased from 1 to 13, the corresponding acceleration in the rate of the reaction is calculated by multiplying the velocity constant by a factor varying from 1.86—4.76. The velocity of hydrolysis is increased by introducing a methyl group into the benzene nucleus of the sulphonic acid, especially in the ortho- or para-position with respect to the sulpho-group. The substitution of an amino-group instead of methyl produces a marked retardation in the speed of hydrolysis; the relation between concentration and velocity is then quite different from that observed with the acids containing no amino-group.

For solutions containing more than 1 gram-mol. of acid per litre, the generally accepted law, according to which the catalytic action is proportional to the number of free ions in the solution, is no longer applicable. The author suggests that the hydrolysis of sulphonic acids is regulated by the number of molecules which become resolved into the ions  $C_6H_5$  and  $SO_3H$ , not  $C_6H_5 \cdot SO_3$  and  $H$ ; with the former pair of ions, it is easy to see how the action of water can yield hydrocarbon and sulphuric acid. T. H. P.

**Catalysis. IV.** SALOMON F. ACREE and J. M. JOHNSON (*Amer. Chem. J.*, 1907, 38, 258—355. Compare Acree and Johnson, this vol., i, 506).—This paper contains a discussion of the reactions between urazoles and alkyl halides (compare this vol., i, 259), the rearrangement of acetylhalogenaminobenzenes, the reactions of carbonyl compounds with hydroxylamine and phenylhydrazine, the inversion of sucrose, the hydrolysis of amides, and the formation and hydrolysis of esters. It is shown that acids, bases, and salts may act as positive or negative catalysing agents and cause an increase or decrease in the velocity of a reaction, as they effect an increase or decrease in the concentration of the particular ions or molecules entering into the reaction.

The velocity of rearrangement of acetylphenylchloroamine and acetyl-*p*-tolylchloroamine by hydrobromic acid has been determined

Measurements have also been made of the velocity of transformation of both these amines by hydrochloric acid, and of acetylphenylchloroamine by sulphuric acid and by acetic acid. The results are tabulated and compared with those obtained by Blanksma (Abstr., 1902, ii, 646).

The velocity of the reactions of acetone with hydroxylamine and its hydrochloride, and with phenylhydrazine and its hydrochloride, has been determined. The reaction between acetone and hydroxylamine is finished in a few minutes at  $100^{\circ}$  and in two hours at  $65^{\circ}$ . Although the reaction goes nearly to completion, it seems to be reversible. The velocity constant of the reaction between  $N/10$  acetone and  $N/10$  hydroxylamine at  $1^{\circ}$  is 0.0040, whilst at  $65^{\circ}$  it is 0.060. The constant for acetaldehyde and hydroxylamine in  $N/10$  solutions at  $10.5^{\circ}$  is 0.035, and that for  $N/10$  solutions of diethyl ketone and hydroxylamine is 0.005 at  $35^{\circ}$  and 0.010 at  $65^{\circ}$ . The velocity of reaction between acetone and hydroxylamine is increased by the addition of hydrochloric or hydrobromic acid, owing to catalytic action. The acids, by acting on the hydroxylamine, increase the concentration of the hydroxylammonium ions, which then react more rapidly with the acetone. In presence of hydrochloric acid, however, the reaction does not proceed as far as it otherwise would, since the oxime is partly hydrolysed into acetone and hydroxylamine hydrochloride. The changes in the equilibrium, brought about by changes in the amounts of acetone and hydrochloric acid, have been studied.

Experiments are recorded which show that the reaction between phenylhydrazine and acetone seems to go nearly to completion, but that the reaction of phenylhydrazine hydrochloride with the ketone is very slow and appears to be reversible.

In discussing the formation and hydrolysis of esters, reference is made to the observations of several authors that esters act as weak bases and form salts with acids. It is shown that the addition of small quantities of methyl acetate, ethyl acetate, methyl benzoate, 3-ethoxy-1-phenylurazole, 3:5-diethoxy-1-phenylurazole, or benzaldehyde to alcoholic or aqueous hydrochloric acid causes a lowering of the conductivity sufficient to indicate the formation of small quantities of ester salts.

The reversible reactions taking place in the system, water, acid, alcohol, and hydrochloric acid, are due to reactions of the complex cations formed by the union of a very small amount of the hydrogen ions with a very small amount of the ester and organic acid. This affords an explanation of the facts that the velocity of hydrolysis and formation of esters increases in direct proportion to the concentration of the hydrogen ions and that the equilibrium of the system is not appreciably changed by a change in the concentration of the hydrogen ions.

The hydrochlorides of the ordinary esters do not decompose appreciably into the alkyl chlorides and organic acids. It has been shown, however, by Kastle, Murrill, and Frazer (Abstr., 1898, i, 140) that, when sulphonic esters are treated with water and hydrochloric acid, two independent side-reactions take place, one of which is the hydrolysis of the ester into the sulphonic acid and alcohol, and the other the decomposition of the ester hydrochloride into the alkyl



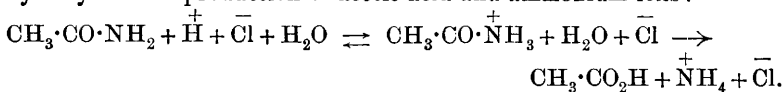
chloride and sulphonic acid. It is shown that by treating the sulphonic ester with alcoholic hydrochloric acid, it should be possible to suppress the former change and enable the latter to become the chief reaction. 3-Ethoxy-1-phenylurazole is not hydrolysed by aqueous hydrobromic acid, but is decomposed quantitatively by alcoholic hydrochloric acid into phenylurazole and ethyl chloride.

The three so-called laws of catalysis are quoted, and it is shown that in certain cases they are not valid. A general discussion is given of catalytic reactions, of the experimental grounds on which the laws of catalysis are based, and of the conditions in which the latter do not hold.

E. G.

**Catalysis. V. Hydrolysis of Amides by Acids.** SALOMON F. ACREE and SIDNEY NIRDLINGER (*Amer. Chem. J.*, 1907, 38, 489—507).—In a previous paper (Acree and Johnson, preceding abstract), a discussion has been given of the theory that various catalytic reactions involve the formation of intermediate compounds of the acid with the substance undergoing hydrolysis. This hypothesis has now been further tested by a study of the hydrolysis of acetamide by hydrochloric acid. Measurements have been made of the velocity of the reaction at 65°.

The results afford strong evidence that the hydrogen ions of the hydrochloric acid unite to some extent with the feebly basic amide to form acetamide cations,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}_3^+$ , which subsequently undergo hydrolysis with production of acetic acid and ammonium ions:



This reaction may be complicated to a very slight extent by the hydrolysis of the free acetamide and the undissociated acetamide hydrochloride.

It has been observed that the velocity constant tends to increase during the course of the reaction, and it was thought that this might be due to an acceleration of the velocity by the ammonium chloride formed. Experiments were therefore made to determine the influence of certain chlorides. Potassium, sodium, chromium, and aluminium chlorides were found to effect an increase in the value of the velocity constant, whilst lithium chloride seemed to lower its value.

E. G.

**Fermentation of Sugar without Enzymes.** H. SCHADE (*Zeitsch. physikal. Chem.*, 1907, 60, 510—512. Compare Abstr., 1906, i, 931).—Some of the author's previous conclusions are admittedly wrong (see Buchner, Meisenheimer, and Schade, this vol., ii, 17). Other conclusions are sustained and their significance is further discussed.

J. C. P.

**Capacity of the Elements for Entering into Chemical Combination.** GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, 55, 289—296. Compare Abstr., 1906, ii, 346).—The binary chemical

compounds present in alloys, the formulæ of which have been established with certainty by the investigations of Heycock and Neville, of Kurnakoff, and more particularly of the author and his co-workers, are tabulated, and it is shown (1) that the formulæ of binary compounds, exclusive of salts or compounds allied to them, are not determined by the ordinary valencies of the component elements; (2) that the two rules already enunciated (*loc. cit.*) with regard to the mutual combining capacity of the elements remain valid in the light of the more abundant data now available.

Out of about one hundred compounds, the formulæ of only twenty-six agree with the ordinary valencies of the metals in their salts, and these are probably largely accidental, as the valency varies only within comparatively narrow limits. The metal whose compounds corresponds most closely with the ordinary valencies is antimony, and this is probably connected with the fact that it has many analogies with the non-metals. Further, the formulæ of the compounds which a metal forms with the members of a natural group in the narrower sense are by no means always analogous; for example, the compounds of sodium with zinc, cadmium, and mercury show no correspondence in their formulæ.

The second rule previously advanced, referring to the combining capacity of an element for the members of a natural group, is shown to hold for the zinc and copper groups and for the nickel, palladium, and platinum groups. It does not apply when there is a change from the non-metallic to the metallic character in a group; for example, there is a great difference between the combining capacity of antimony and of bismuth for other elements. G. S.

**Compressibilities of the Elements and their Periodic Relations.** THEODORE W. RICHARDS, WILFRED NEWSOME STULL, FRANCIS N. BRINK, and FREDERICK BONNET (*Carnegie Inst. Publ.*, 1907, No. 76 \*).—The compressibilities of a large number of elements have been determined by the method previously used (see Abstr., 1904, ii, 384), slight modifications only being introduced to suit particular cases. Among others, the alkali metals have been examined, and the numbers obtained for their compressibilities are almost proportional to the respective atomic volumes; it is found also that the greater the compressibility the greater is its decrease with increasing pressure. For a complete list of values of compressibility, the original must be consulted, but the following results may be recorded here. The compressibility of silicon is not over  $0.16 \times 10^{-6}$ , silicon being the least compressible of the thirty-five elements so far investigated. The compressibility of carborundum is only a little greater than that of silicon. The compressibility of red phosphorus is less than half the value for white phosphorus. The values of the compressibilities of sulphur and selenium are  $12.5 \times 10^{-6}$  and  $11.8 \times 10^{-6}$  respectively.

When all these results as well as others for a number of heavy metals are considered, it is seen that compressibility is a periodic property of the elements, and that it is probably, in part, associated with the same causes which determine atomic volume and volatility.

J. C. P.

\* And *Zeitsch. physikal. Chem.*, 1907, 61, 77—99, 100—113.

**Extractor for Use with Small Quantities of Material.**  
C. LORING JACKSON and JOAQUIN E. ZANETTI (*Amer. Chem. J.*, 1907, 38, 461—464).—This apparatus consists of a flask fitted with a vertical reflux condenser, and a piece of wide glass-tubing, which is a little narrower than the neck of the flask, is open at both ends, and contains the solid to be extracted. The tube is placed in the flask in a slightly inclined position, the lower end resting on the bottom of the flask and the upper end standing immediately under the condenser tube. When the solvent in the flask has commenced to boil at the proper rate, the apparatus works automatically. Experiments are quoted to prove the efficiency of this extractor. The following advantages are claimed for it. It is simpler, less expensive, less fragile, more compact, and acts more rapidly than the Soxhlet apparatus; it can be used with a smaller quantity of the solvent and is well adapted for extraction with solvents of high b. p. E. G.

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## Inorganic Chemistry.

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**Absorption of Hydrogen by Thin Metal Films.** WALTER HEALD (*Physikal. Zeitsch.*, 1907, 8, 659—662).—The absorption of hydrogen by various metals in the form of thin films on glass has been studied. The thin films were obtained by condensation of the vapours formed by electrical heating of the metal serving as the anode in a specially constructed discharge tube containing hydrogen at a pressure of 1 to 6 mm. of mercury. With cadmium, iron (steel), and silver, absorption of hydrogen takes place for some time after the formation of the metallic deposit. No definite absorption is observed in the case of zinc, but with aluminium and platinum a very considerable diminution of pressure immediately takes place when the metals are heated and converted into vapour. The rate of absorption of the hydrogen by these two metals is much too rapid to be followed by observations of the fall of pressure in the tube. H. M. D.

**Preparation of Hydrogen Peroxide.** EMANUEL MERCK (D.R.-P. 179771 and 179826).—When a suspension of barium peroxide in water is treated with excess of carbon dioxide, only a comparatively small portion of the barium compound is decomposed into hydrogen peroxide and barium carbonate, and it has now been found that the excess of carbonic acid leads to the production of the comparatively stable barium percarbonate. A quantitative conversion of barium peroxide into a hydrogen peroxide and barium carbonate is effected by keeping the barium peroxide in excess.

*Barium percarbonate*,  $\text{BaCO}_4$ , which is produced by the interaction at low temperatures of carbon dioxide and barium peroxide, either anhydrous or hydrated, is a convenient reagent for the preparation of

hydrogen peroxide, because, on treatment with water or preferably water and an acid yielding an insoluble barium salt, it gives rise to a neutral solution of the peroxide. G. T. M.

**Basicity of Hydrofluoric Acid.** GIOVANNI PELLINI and L. PEGORARO (*Zeitsch. Elektrochem.*, 1907, 13, 621—622; *Atti R. Accad. Lincei*, 1907, [v], 16, ii, 273—279).—In order to determine the basicity of hydrofluoric acid, measurements of the specific conductivity after the addition of successive quantities of potassium hydroxide, sodium hydroxide, and ammonia have been made. The conductivity curves indicate that the acid behaves as if dibasic on neutralisation with each of the three bases used. On the other hand, the properties of solutions of the free acid and of the normal salts can only be explained on the assumption that these are binary electrolytes. H. M. D.

**Vapour Pressure of Sulphur at Low Temperatures.** HIPPOLYTE GRUENER (*J. Amer. Chem. Soc.*, 1907, 29, 1396—1402).—The vapour pressure of sulphur between 200° and 400° has been determined by Matthies (Abstr., 1906, ii, 663). Determinations have now been made of the pressure between 50° and 120° by passing known volumes of an inert gas (carbon dioxide, hydrogen, and, at the lower temperatures, air) over sulphur heated to the desired temperature. The volatilised sulphur was condensed on the walls of a cold tube, and from its weight the pressure was calculated. A series of determinations were made at 100°, in which the vapour pressure was calculated from the amount of sulphur volatilised with known amounts of water. In these experiments, water containing sulphur in suspension was boiled and the steam passed over a column of sulphur and afterwards condensed. In most of the determinations, the sulphur was used in the form of small crystals obtained by melting sulphur and stirring it as it solidified. The vapour pressure was studied more closely at 100° than at any other temperature, and some determinations were made at this temperature with the prismatic and rhombic forms of sulphur.

The results show that the vapour pressure of sulphur can be calculated from the expression:  $p = ab^t$ , where, for temperatures between 50° and 100°,  $\log a = 7.9225$ ,  $\log b = 0.0395$ , and  $t$  is the number of degrees C, and for temperatures somewhat above 100°,  $\log a = 3.8725$ ,  $\log b = 0.0316$ , and  $t$  = the number of degrees C. - 100. E. G.

**Specific Gravity and Allotropic States of Certain Varieties of Sulphur.** Observations on the Determination of the Specific Gravity of Powders. WALTHER SPRING (*Bull. Soc. chim. Belg.*, 1907, 21, 243—257; *Rec. trav. chim.*, 1907, 26, 357, and *J. Chim. Phys.*, 1907, 5, 410. Compare Abstr., 1906, ii, 607).—The amorphous sulphur, obtained by decomposing potassium polysulphide with hydrochloric acid, is almost white, completely soluble in carbon disulphide, and has  $D_{15}^{20}$  2.0545 in fine powder and  $D_{10}^{20}$  2.0511 after compression into compact cylinders. It passes into rhombic sulphur slowly at the atmospheric temperature, and more rapidly on heating. Its thermal capacity is less than that of rhombic sulphur.

The sulphur obtained by passing hydrogen sulphide into a solution

of ferric chloride is a mixture of two amorphous varieties, of which one, identical with that described above, forms 96·8% of the mixture. The second variety is insoluble in carbon disulphide, has  $D_{18}^{16}$  1·8686 in powder, and  $D_{18}^{18}$  1·7852 after compression into compact cylinders. No sulphur hydrate appears to be formed in either of these reactions.

In determining the specific gravity of these amorphous sulphurs, they were mixed with water in platinum vessels, and exposed under reduced pressure until the powders had apparently settled. It was observed, however, that at this stage the weights had not become constant, and they continued to augment for several days. This phenomenon, which is discussed in detail in the original, is due to incomplete sedimentation. The rate of increase in weight is irregular at first, but after a time becomes proportional at any instant to the mass of the powder still in suspension.

T. A. H.

**Combustion of Sulphur in Air and Oxygen.** JOSEPH H. KASTLE and J. S. MCHARGUE (*Amer. Chem. J.*, 1907, **38**, 465—475).—Hempel has stated (Abstr., 1890, 1050) that when sulphur is burnt in oxygen under atmospheric pressure, the resulting gas contains 2% of sulphur trioxide and 98% of the dioxide. The average result of experiments, which have now been made under somewhat different conditions, shows 2·76% of the sulphur to have been converted into the trioxide. When sulphur is burnt in air instead of oxygen, about 7% is converted into the trioxide. The relative proportions of the oxides produced by the combustion of sulphur in air are not appreciably affected by moisture or increased quantities of carbon dioxide. Moisture is also without influence on the combustion of sulphur in oxygen, but the presence of carbon dioxide causes a slightly larger proportion of the trioxide to be produced. The fact that the quantity of the trioxide formed by the combustion of sulphur in air is so much greater than that produced on combustion in oxygen is considered to be due to the presence of nitrogen. When mixtures of oxygen and nitrogen are employed containing smaller quantities of nitrogen than are present in air, the quantity of the trioxide formed is considerably diminished. As an explanation of this phenomenon, it is suggested that the nitrogen acts as a carrier of oxygen, small quantities of one of the higher oxides of nitrogen being formed which effects the oxidation of the sulphur dioxide.

E. G.

**Dissociation of Hydrogen Sulphide.** GERHARD PREUNER (*Zeitsch. anorg. Chem.*, 1907, **55**, 279—288).—The equilibrium in the reaction  $2H_2 + S_2 \rightleftharpoons 2H_2S$  has been investigated by Löwenstein's method (Abstr., 1906, ii, 272) at 830°, 950°, 1050°, 1140°, and 1240°. The observations were somewhat disturbed by the slow formation of platinum sulphide on the surface of the small platinum tube used as a semi-permeable membrane.

At 830°, 1050°, and 1240°, the partial pressures of hydrogen amounted to 6·5, 16·5, and 25·6 cm. respectively. The mean value for the heat development of the reaction, calculated from the equilibrium results at different temperatures, is 39,400 cal., from which the approximate percentage dissociation of hydrogen sulphide at

different temperatures has been calculated as follows: 2.3% at 627°, 16.4% at 947°, 31.7% at 1137°, 49.2% at 1327°, and 76.1% at 1727°.

The above results are only in moderate agreement with those calculated by Nernst's equation connecting equilibrium constants and temperature; this is partly, at least, owing to the fact that little is known as to the specific heat of hydrogen sulphide.

These results are employed to obtain an estimate of the heat of dissociation of gaseous sulphur, from which it appears that the reaction  $S_8 = 4S_2$  absorbs about 43,200 cals., but other considerations indicate that this figure is too small.

G. S.

**Sulphides and Double Sulphides.** ALFRED DITTE (*Ann. Chim. Phys.*, 1907, [viii], 12, 229—276).—A detailed account of the preparation and properties of the sulphides of mercury, tin, antimony, bismuth, copper, silver, and gold, and of the double compounds they form with the alkali sulphides; the results have already been published (compare Abstr., 1882, 1030; 1883, 156, 716; 1884, 18, 19, 893, 963, 964; 1886, 309, 429; 1895, 223, 273, 274). Stannous sulphide, selenide, and telluride have sp. gr. 5.0802, 6.179, and 6.478 respectively.

M. A. W.

**Action of Alkalis on Tetrathionates.** IV. AUGUST GUTMANN (*Ber.*, 1907, 40, 3614—3622. Compare Abstr., 1905, ii, 384, 813; 1906, i, 149).—According to Fordos and Gelis (*Annalen*, 1842, 44, 227), the action of sodium hydroxide on sodium tetrathionate leads to the formation of the sulphite and thiosulphate, whereas, according to Kessler (*Ann. Phys. Chem.*, 1848, [ii], 74, 253), sodium thiosulphate, sulphate, and sulphide are formed. A re-investigation of the reaction shows that with 15% sodium, potassium, calcium, strontium, or barium hydroxide, it takes place according to Fordos and Gelis' equation:  $2Na_2S_4O_6 + 6NaHO = 3Na_2S_2O_3 + 2Na_2SO_3 + 3H_2O$ , but that if highly concentrated (1:1) aqueous sodium hydroxide solutions are employed the reaction takes place to a small extent also according to the equation:  $3Na_2S_4O_6 + 12NaHO = 3Na_2S_2O_3 + 5Na_2SO_3 + Na_2S + 6H_2O$ ; traces of the sulphide being formed together with the thiosulphate and sulphite; sodium sulphate is not formed.

G. Y.

**Continuous Production of Ammonia from its Elements.** KARL KAISER (D.R.-P. 181657).—Calcium nitride when heated in a current of hydrogen is decomposed, yielding ammonia and calcium hydride. Conversely, calcium hydride when heated in nitrogen gives rise to calcium nitride and ammonia, in this respect differing from barium hydride, which furnishes barium nitride and hydrogen. Accordingly, a continuous production of ammonia is effected when calcium is heated alternately in a current of nitrogen and hydrogen. This operation takes place more readily when the metal is in a finely-divided condition, as, for example, when deposited on asbestos. The reaction sets in at about 150°, and the best results are obtained between 200—400°.

G. T. M.

**Oxidation of Hydrazine.** I. ARTHUR W. BROWNE and F. F. SHETTERLY (*J. Amer. Chem. Soc.*, 1907, 29, 1305—1312 \*).—It has been shown previously (Abstr., 1905, ii, 449) that azoimide is produced by the action of certain oxidising agents on hydrazine sulphate.

It is now found that azoimide can also be obtained by the action of ammonium metavanadate on hydrazine sulphate, and the conditions for its formation have been studied. The maximum yield, 13·55%, as calculated from the equation:  $2\text{N}_2\text{H}_4 + 2\text{O} = \text{N}_3\text{H} + \text{NH}_3 + 2\text{H}_2\text{O}$ , was obtained by adding ammonium metavanadate solution drop by drop to a solution containing 10 grams of hydrazine sulphate and 19·2 grams of concentrated sulphuric acid, and maintained at a temperature of 80°.

The use of ammonium metavanadate in the estimation of hydrazine by Hofmann and Küspert's method (Abstr., 1898, ii, 255) leads to inaccurate results on account of the formation of azoimide. If the estimation is based on the volume of nitrogen evolved, the error amounts to about 4·5%, but if it is carried out by the oxidation of the vanadyl sulphate with potassium permanganate the error is only about 1%. E. G.

**Estimation of the Oxides of Nitrogen and Theory of the Lead-chamber Process.** GEORG LUNGE and ERNST BERL (*Zeitsch. angew. Chem.*, 1907, 20, 1713—1722).—Polemical. A reply to Raschig (this vol., ii, 455). The authors have repeated their experimental work criticised by Raschig, and find the results previously recorded to be correct. Fresh evidence is also brought forward in support of their theory of the lead-chamber process (Abstr., 1906, ii, 438). W. H. G.

[**Estimation of Oxides of Nitrogen and Theory of the Lead-chamber Process.**] FRITZ RASCHIG (*Zeitsch. angew. Chem.*, 1907, 20, 1809—1811).—Polemical. The author in a reply to Lunge and Berl (preceding abstract) upholds the accuracy of his results and conclusions (Abstr., 1905, ii, 23, 700; this vol., ii, 455).

W. H. G.

[**Preparation of Nitrogen Peroxide from Nitrogen and Oxygen at High Temperatures.**] WESTDEUTSCHE THOMASPHOSPHATWERKE (D.R.-P. 182297).—At high temperatures, a mixture of air and steam or its dissociation products interact to produce nitrogen peroxide, but when the products are left in contact with each other the hydrogen produced reduces the oxide, regenerating nitrogen and water. This inverse reaction is avoided when the initial change is effected in a porous vessel. The mixture of air and steam or the products of its dissociation are passed through a thin-walled porous porcelain tube; the hydrogen diffuses through this material, whilst the oxygen and nitrogen combine to form the nitrogen peroxide, which is converted into nitric acid. The tube must be heated at least to 1300°, and the best result is obtained at 1600°. The diffusion of the hydrogen is accelerated by increasing the pressure of the reacting gases and diminishing the pressure outside the porous tube.

G. T. M.

\* And *Ber.*, 1907, 40, 3953—3962.



**Quantitative Vaporisation of Phosphoric Acid from its Salts in a Current of Chlorine Charged with Carbon Tetrachloride.** PAUL JANNASCH and W. JILKE (*Ber.*, 1907, 40, 3605—3608. Compare Abstr., 1906, ii, 745).—Phosphoric acid can be distilled off quantitatively from its salts without previous admixture with charcoal if these are heated in a current of chlorine which has been passed first through carbon tetrachloride heated at 85—95°. Details are given of experiments carried out in this manner with ammonium phosphate and magnesium phosphate. It is observed that free phosphoric acid and ammonium phosphate are more easily vaporised than might be thought from statements in the literature; the ammonium salt vaporises in a platinum crucible over a bunsen flame or when heated in a current of carbon dioxide. G. Y.

**Organic Solvent for some Varieties of Carbon.** IWAN OSTROMYSSLENSKY (*J. pr. Chem.*, 1907, [ii], 76, 268—273).—As amorphous carbon, obtained as the final distillation product of coal tar, has been considered to have a polycyclic structure, the author has sought for a solvent for graphite amongst the high molecular, polycyclic hydrocarbons. It is found that small fragments of graphite disappear when treated at 485° with decacyclene, m. p. 402° (387°: Dziewonsky, Abstr., 1903, i, 431). The process may be one of solution of the graphite or merely of disintegration of the graphite resulting from solution of some impurity. To avoid decomposition of the decacyclene, the operation must be carried out in an atmosphere of carbon dioxide; otherwise, on removal of the decacyclene by boiling successively with aniline, xylene, nitrobenzene, and alcohol, the residue exceeds in weight the graphite taken up by the decacyclene. Fused decacyclene is brownish-black and opaque; the supposed solution, which may contain 10% of graphite, is black and opaque.

Graphite is not dissolved by phenanthrene, chrysene, pyrene, picene, or triphenylene, nor is the diamond dissolved by decacyclene.

G. Y.

**Action of Carbon Dioxide on Sodium and Calcium Sulphides and of Hydrogen Sulphide on Sodium Carbonate.** ERNST BERL and AUGUST RITTENER (*Zeitsch. angew. Chem.*, 1907, 20, 1637—1642. Compare Lunge and Rittener, this vol., ii, 51).—When crude caustic soda is treated with carbon dioxide, considerable amounts of sodium hydrogen carbonate are formed before the decomposition of the sulphides is complete. This has been explained by Lunge as resulting from the mass action of the two acids. A quantitative study of the reaction has yielded results confirming this view. It is found that the decomposition of sodium sulphide by carbon dioxide at 14° is complete only when the sodium has been converted totally into the hydrogen carbonate. The whole reaction is represented by the equations: (1)  $\text{Na}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} = \text{NaHS} + \text{NaHCO}_3$ ; (2)  $\text{NaHS} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NaHCO}_3 + \text{H}_2\text{S}$ . The proportions of sodium sulphide, hydrogen sulphide, and hydrogen carbonate present at any stage of the reaction are shown to depend on the composition of the gaseous phase.

At 80°, a certain amount of sodium carbonate is formed by a side-reaction.

Similarly, it is found that the action of hydrogen sulphide on sodium carbonate at 170° takes place in the two stages: (1)  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{S} = \text{NaHCO}_3 + \text{NaHS}$ ; (2)  $\text{NaHCO}_3 + \text{H}_2\text{S} \rightleftharpoons \text{NaHS} + \text{CO}_2 + \text{H}_2\text{O}$ ; the latter stage is the reverse of the second in the action of carbon dioxide on sodium hydrogen sulphide. At 52° and 90°, sodium hydrogen carbonate and hydrogen sulphide are converted partially into the carbonate and sulphide respectively. The composition of the mixture of salts is related, as in the previous case, to the composition of the gaseous phase. The value  $k=1.96$  is found for the constant in the equation:  $[\text{NaHCO}_3][\text{H}_2\text{S}]/[\text{NaHS}][\text{CO}_2]=k$ , at 18°; the value calculated is  $k=2.31$ .

The action of carbon dioxide on calcium hydrogen sulphide, the first product of the action of the gas on calcium sulphide, takes place in aqueous solution according to the equation:  $\text{Ca}(\text{HS})_2 + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + 2\text{H}_2\text{S}$ . It is of importance that, even when 30% carbon dioxide is employed, the proportion of hydrogen sulphide in the gaseous phase remains, almost to the end of the reaction, above the minimum limit for combustion of hydrogen sulphide to sulphur and water, whereas in the action of carbon dioxide on sodium sulphide this limit is exceeded only in the first stages.

G. Y.

**Ammonium Amalgam.** MORRIS W. TRAVERS (*Ber.*, 1907, 40, 3949—3950).—Reply to Smith (this vol., ii, 615).

C. S.

**Double Decomposition of Silver Nitrate and Potassium Halides in the Absence of a Solvent.** IWAN A. KABLUKOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 914—922).—When a dry, powdered potassium halide is added to melted silver nitrate, the former dissolves with development of much heat, but when the solute added is equal to  $\frac{1}{2}$  gram-mol. to 1 gram-mol. of solvent, the liquid divides into two sharply-defined layers, the lower being coloured and opaque, whilst the upper is almost colourless and transparent. If the addition of the halide is continued, streams of the coloured liquid are observed to separate from the upper layer and sink to the bottom, until, when the substances are present in equivalent proportions, the upper layer becomes quite colourless and consists of pure potassium nitrate. This separation is effected because the lower layer of silver chloride is insoluble in melted potassium nitrate. To determine what actually occurs in the first stage of this process, the depression in the m. p. of silver nitrate on addition of silver and potassium halides respectively was investigated. The results are plotted on a composition-depression curve, the first part of which indicates that, when potassium chloride is introduced into silver nitrate, almost complete double decomposition occurs, whilst the second part shows the possible formation of double compounds. There seems to be a definite relation between the effect of the potassium halides on the m. p. of silver nitrate and the heat effects of their reaction with it.

Z. K.

**Composition and Properties of the Salts Formed in the Fixing of Silver Bromide and Chloride Gelatin Plates.** AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1907, [iv], 1, 946—953).—The solution of silver bromide and chloride in 15% or 45% sodium thiosulphate solution yields double thiosulphates of sodium and silver which are different in the two cases and have not the composition usually attributed to them. The saturated solution of silver bromide in thiosulphate represents a double salt containing 5 mols. of the bromide to 9 mols. of crystallised thiosulphate. This salt only exists in solution, and, on slow evaporation or precipitation by alcohol, readily yields the compound:  $2\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , which, in sufficiently concentrated aqueous solution, is converted gradually into the insoluble double salt,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . Saturation of sodium thiosulphate solution with silver chloride takes place when the proportions of the salts correspond with the composition  $2\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , but the solution deposits an insoluble double salt,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ; the two double salts obtained in the case of silver bromide have also been isolated from this solution. These results confirm the danger of using fixing solutions until they are saturated with silver haloid, especially silver chloride.

T. H. P.

**Some Reactions During Water Treatment.** EDWARD BARTOW and J. M. LINDGREN (*J. Amer. Chem. Soc.*, 1907, 29, 1293—1305).—The observations recorded in this paper were made during attempts to improve the water of the University of Illinois water supply.

On treating a water containing hydrogen carbonates of alkali and alkali earth metals with calcium hydroxide, changes take place in the following order, depending on the amount of the reagent added: (1)  $\text{Ca}(\text{OH})_2 + 2\text{CO}_2 = \text{CaH}_2(\text{CO}_3)_2$ ; (2)  $\text{Ca}(\text{OH})_2 + \text{CaH}_2(\text{CO}_3)_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O}$ ; (3)  $\text{Ca}(\text{OH})_2 + 2\text{NaHCO}_3 = \text{CaCO}_3 + \text{Na}_2\text{CO}_3$ ; (4)  $2\text{Ca}(\text{OH})_2 + \text{MgH}_2(\text{CO}_3)_2 = 2\text{CaCO}_3 + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$ .

If sodium hydroxide is used instead of calcium hydroxide, the reactions take place in the following stages: (1)  $2\text{NaOH} + 2\text{CO}_2 = 2\text{NaHCO}_3$ ; (2a)  $2\text{NaOH} + \text{CaH}_2(\text{CO}_3)_2 = \text{Na}_2\text{CO}_3 + \text{CaCO}_3$ ; (2b)  $\text{Na}_2\text{CO}_3 + \text{CaH}_2(\text{CO}_3)_2 = \text{CaCO}_3 + 2\text{NaHCO}_3 + 2\text{H}_2\text{O}$ ; (3)  $\text{NaOH} + \text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ ; (4)  $4\text{NaOH} + \text{MgH}_2(\text{CO}_3)_2 = \text{Mg}(\text{OH})_2 + 2\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$ .

On treating water containing hydrogen carbonates and sulphates of alkali earth metals with sodium carbonate, reactions occur in the following order: (1)  $\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2\text{NaHCO}_3$ ; (2a)  $\text{Na}_2\text{CO}_3 + \text{CaH}_2(\text{CO}_3)_2 = \text{CaCO}_3 + 2\text{NaHCO}_3$ ; (2b)  $2\text{NaHCO}_3 + \text{MgSO}_4 = \text{MgH}_2(\text{CO}_3)_2 + \text{Na}_2\text{SO}_4$ . If calcium hydroxide is now added, the following changes take place:  $\text{Ca}(\text{OH})_2 + \text{CaH}_2(\text{CO}_3)_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O}$ ;  $2\text{Ca}(\text{OH})_2 + \text{MgH}_2(\text{CO}_3)_2 = \text{Mg}(\text{OH})_2 + 2\text{CaCO}_3$ .

During the first and second stages of the treatment of a water with calcium hydroxide, about 50% of the alkali earth carbonates are removed, but to remove the maximum amount (about 80% in the waters examined) nearly three times as much of the reagent is required. Neither calcium hydroxide nor sodium carbonate alone will remove a maximum amount of the incrusting constituents from a water

containing sulphates, but, if either is used alone, sodium carbonate is the more effective. E. G.

**Absorption of Nitrogen by Calcium Carbide.** FERDYNAND E. POLZENIUSZ (*Chem. Zeit.*, 1907, 31, 958—959).—The absorption of nitrogen by calcium carbide is accelerated by the presence of other oxygen-free calcium compounds, which melt at comparatively low temperatures, and therefore dissociate partially at the temperature of the reaction. The absorption is accelerated also by addition of salts, such as alkali chlorides, bromides, or iodides, or ferrous chloride, which react with calcium carbide, forming the corresponding calcium salt, the free metal, and carbon, the acceleration produced being the greater and the temperature at which absorption takes place the lower, the lower the m. p. of the resulting calcium salt. Bromides and iodides cause a greater acceleration than do chlorides, with the exception of lithium chloride; the abnormally great acceleration caused by this is ascribed to the formation of calcium chloride and lithium nitride. The sulphides, which melt at high temperatures, are without influence on the rate of absorption of nitrogen by calcium carbide, whilst calcium fluoride, m. p. about  $900^{\circ}$ , and the alkali fluorides, which react readily with the carbide, forming calcium fluoride, accelerate the absorption very slightly and only at high temperatures. Acceleration is not observed at  $800^{\circ}$  on addition of metals, oxides, or salts of oxy-acids.

It is suggested that the acceleration in question may result from the action of the ions of the dissociated salt on the nitrogen, forming calcium nitride, and on the carbide, forming the corresponding calcium salt, the calcium nitride and carbon reacting with a further amount of nitrogen with formation of the cyanamide. G. Y.

**Calcium Sulphate in Aqueous Solutions of Sodium Chloride.** FRANK K. CAMERON (*J. Physical Chem.*, 1907, 11, 495—496. Compare Abstr., 1902, ii, 75).—Arth and Crétien (Abstr., 1906, ii, 853) state that the solutions prepared by dissolving calcium sulphate in sodium chloride solutions below  $62.5$ — $65^{\circ}$  contain more lime than is equivalent to the acid present, whilst at higher temperatures the reverse is the case. In the present paper, it is shown that in all the solutions investigated, from  $25^{\circ}$  to  $80^{\circ}$ , the calcium and sulphuric acids are present in equivalent proportions; the results obtained by Arth and Crétien are due to errors in the ordinary analytical processes. Methods by which these errors may be eliminated are given.

Calcium sulphate does not form a double salt in solutions of sodium chloride. G. S.

**Supposed Ammonium Syngenite.** JAMES M. BELL and WALTER C. TABER (*J. Physical Chem.*, 1907, 11, 492—494. Compare Abstr., 1906, ii, 352).—D'Ans (Abstr., 1906, ii, 751) has ascribed the formula,  $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , to a double sulphate of calcium and ammonium stable at  $25^{\circ}$ , but the authors point out that by the method used by D'Ans for removing the mother-liquor (washing with 50% alcohol) the double salt suffers partial decomposition, and show by two independent methods that the compound in question contains  $2\text{H}_2\text{O}$  in accordance with their former results (*loc. cit.*). G. S.

**Occurrence of Passive Phenomena in Magnesium.** RUDOLF LOHNSTEIN (*Zeitsch. Elektrochem.*, 1907, 13, 612—614).—The solvent action of dilute acetic acid on magnesium is inhibited if potassium dichromate is added in sufficient quantity to the solution. The magnesium only loses its power of dissolving spontaneously in the solution, for, if it is made the anode by connecting with the positive pole of a battery, it dissolves readily. The concentration of the dichromate required to produce the passive condition increases with the concentration of the acetic acid. If solution still takes place, the rate is greatly diminished by the dichromate. The passive condition may be destroyed by the addition of an alkali or magnesium salt of a strong acid, the rate of solution of the active magnesium increasing with the concentration of the added salt. It is suggested that the phenomena are of catalytic nature. H. M. D.

**Precipitation of Metals by Hydrogen Sulphide. Action of Hydrogen Sulphide on Zinc Salts.** STANISLAUS GLIXELLI (*Zeitsch. anorg. Chem.*, 1907, 55, 297—320. Compare Baubigny, Abstr., 1882, 1031).—It is shown that, contrary to the assumption of Ostwald and others, the reaction  $\text{ZnSO}_4 + \text{H}_2\text{S} = \text{ZnS} + \text{H}_2\text{SO}_4$  is not reversible, but that very persistent false equilibria occur in acid solution.

Zinc sulphide, precipitated from alkaline solution ( $\beta$ -sulphide), contains more water than that obtained from dilute acid solution ( $\alpha$ -sulphide), but there is no evidence of the existence of definite hydrates, and the water is probably present in the "adsorbed" condition. The differences in the behaviour of the two sulphides may be due to differences in the state of division.

The zinc is removed almost completely from 1/4 and 1/2 molar sulphate solutions by long-continued passage of hydrogen sulphide at atmospheric pressure. The solubility of the sulphides in 0.001 to 0.25 molar sulphuric acid under a variable pressure of hydrogen sulphide (due to the gas set free during the reaction) has been determined at 25°; the results are represented satisfactorily by the ionic equation  $[\text{Zn}]^+[\text{H}_2\text{S}][\text{H}^+]^2 = \text{constant}$ . The  $\beta$ -sulphide is about forty-six times more soluble than the  $\alpha$ -form.

The rate of precipitation of the sulphide from sulphate solutions containing varying proportions of sulphuric acid falls off as the acid concentration increases, and the time which elapses before the appearance of a precipitate, the induction period, also increases with the acid concentration; in solutions 1/2 molar with respect to zinc sulphate and acid, there is practically no precipitation, although the solution contains about one hundred times as much zinc as corresponds with the solubility in that strength of acid. These false equilibria can be passed over by the addition of zinc, cadmium, or copper sulphides as well as by silicic acid; the action is mainly a surface one. Attempts to determine the limits of the false equilibria in acid solutions of different strengths have not led to very conclusive results.

The separation of zinc from nickel and cobalt in acid solution with hydrogen sulphide does not depend on differences of equilibrium, but of the periods of induction. G. S.

**Hardness and Microstructure of Alloys of Cadmium and Zinc.** A. V. SAPOSHNIKOFF and M. SACHAROFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 907—914).—There is a close connexion between the chemical nature of an alloy and its mechanical properties. A metal is harder on the surface than within, but the hardness of the surface also depends on the inner structure, being the greater the more homogeneous the mass. Cadmium and zinc give no definite compounds and no solid solution, except possibly at 93—95% of zinc. At the composition 17·6% of zinc, a eutectic mixture is formed when the hardness of the alloy reaches a relative maximum, after which the hardness and resistance falls, until at the composition 80% of Zn there is a sudden rise to an absolute maximum. At this point, the alloy is more homogeneous than at any other composition.

Z. K.

**Non-Existence of  $\beta$ -Cadmium Iodide.** JOHN F. SNELL (*J. Amer. Chem. Soc.*, 1907, 29, 1288—1293).—Bödeker found that cadmium iodide had D 4·576. Clarke and Kebler (*Abstr.*, 1884, 394) examined specimens of the salt prepared by several different methods and, in most cases, found the value of D to lie between 5·61 and 5·73 at temperatures from 10·5° to 18·2°. Specimens, however, which were prepared by the action of hydriodic acid on cadmium or cadmium carbonate gave D 4·60—4·69 at 14—19°, and it was therefore assumed that cadmium iodide exists in two forms, the ordinary or  $\alpha$ -form and the form of low sp. gr. or  $\beta$ -form.

A study of the so-called  $\beta$ -form has now been made. It is found that products of low sp. gr. can be prepared by crystallising cadmium iodide from hydriodic acid, but that these always contain hydriodic acid and water as impurities. The conclusion is drawn that the  $\beta$ -form does not exist, and that pure cadmium iodide cannot be obtained of lower sp. gr. than 5·6.

E. G.

**The Production of Sparingly Soluble Compounds of the Distillable Heavy Metals.** CARL LUCKOW (D.R.-P. 179305).—The heavy metal is distilled under diminished pressure into a circulating apparatus in which its vapour comes into intimate contact with water or a solution of some appropriate reagent. For instance, lead vapour is subjected to the action of sodium carbonate solution introduced into the exhausted apparatus in the form of a fine spray. White lead is produced, and is collected without interrupting the circulation of the alkaline solution.

G. T. M.

**Hardness and Microstructure of Alloys of Lead and Antimony.** A. V. SAPOSHNIKOFF and I. KANEWSKY (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 901—907).—As antimony is added to lead, the hardness and the resistance to pressure of the alloy increases. At the eutectic point, that is, at a composition 13% of antimony, the alloy is most homogeneous, and its hardness and resistance is greater than any of the other neighbouring alloys. The hardness of alloys containing more than 30% of antimony depends mainly on the presence of antimony crystals in the eutectic mixture. The two metals form no

definite compounds, but solid solutions possibly do exist. Alloys containing 12—90% of antimony have been investigated. Z. K.

**The Ternary System Pb—Cd—Hg.** ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1907, 60, 399—412).—The solid phases separating from fused mixtures of lead, cadmium, and mercury are six in number; they are lead, cadmium, and four kinds of mixed crystals, which may be represented by the symbols:— $\text{PbHg}\alpha$ ,  $\text{HgPb}\beta$ ,  $\text{CdHg}\alpha$ , and  $\text{CdHg}\beta$ . Lead and cadmium do dissolve in each other to solid solutions, but to a very small extent, and no great error is made by neglecting this mutual miscibility. The author has studied in detail the equilibrium between the aforementioned solid phases and the fused mixtures from which they separate. The results are represented in the usual graphical manner. J. C. P.

**Lead Oxide and Silica.** WL. MOSTOWITSCH (*Metallurgie*, 1907, 4, 647—655).—The behaviour of a series of fused mixtures of lead oxide and silica has been studied. Clear rock-crystal, powdered and extracted with hydrochloric acid, and lead oxide, prepared by igniting pure electrolytic lead peroxide, were melted together in a platinum crucible in an electric furnace. The two oxides combine together to form a silicate at 700—790°. These mixtures solidify as glasses, and it has not therefore been possible to construct a freezing-point curve for the binary system. Separation of lead oxide takes place with great development of heat on cooling glasses containing less than 11.94% of silica, the separation taking place over a considerable temperature interval, owing to the high viscosity of the mass. The lead silicate mixtures are therefore to be regarded as solutions of lead oxide in lead glass, the composition of the latter being undetermined.

The silicates are readily reduced by heating in hydrogen; becoming blackened. C. H. D.

**Acid Function of Lead Hydroxide.** NICOLA PARRAVANO and G. CALCAGNI (*Gazzetta*, 1907, 37, ii, 264—268. Compare Bellucci and Parravano, this vol., ii, 86).—The authors have compared (1) the conductivities of solutions of potassium plumbate of various concentrations with those of solutions of potassium hydroxide of equivalent concentrations, and (2) the diminution of alkalinity with time in solutions of potassium plumbate in presence of ethyl acetate with that occurring in corresponding solutions of potassium hydroxide under the same conditions. Both series of measurements show that the more concentrated solutions of potassium plumbate contain a small proportion of undecomposed salt, the amount of which diminishes as the dilution is increased. In a solution of concentration  $N/82.48$ , all the plumbate is resolved into alkali and colloidal plumbic acid. The series silicon, lead, tin, represents the order of increasing basicity of these elements, and the series lead, silicon, tin, the order of increasing acidity.

T. H. P.

**Silicon-Copper.** M. PHILIPS (*Metallurgie*, 1907, 4, 587—592, 613—617).—Although it has not been found possible to bring about

a cementation of massive copper by metallic or amorphous silicon, an intimate mixture of copper turnings and powdered silicon, heated for five hours at 700—750°, is found to react, the copper turnings taking up as much as 9.56% of silicon and becoming brittle without change of shape.

Alloys of copper and silicon may be prepared by heating the components in a graphite crucible at 1200°. It is not possible to isolate the silicide from alloys containing an excess of copper, as solvents which extract the copper convert the silicon into dioxide. Concentrated potassium cyanide solution dissolves these alloys without residue, the silicide being first converted into copper silicate.

Alloys containing an excess of silicon may be attacked by nitrohydrochloric acid, the residue containing silica and free silicon. On ignition, a part of the silicon is oxidised; therefore the quantity of free silicon found on analysing such mixtures is always low. A method of analysis is described, consisting in dissolving the residue in hot potassium hydroxide solution. Both substances dissolve, the free silicon evolving hydrogen according to the equation  $\text{Si} + 4\text{KOH} = \text{K}_4\text{SiO}_4 + 2\text{H}_2$ . The volume of this hydrogen is measured. Estimations of the free and combined silicon in a number of alloys lead consistently to the formula  $\text{Cu}_7\text{Si}_2$  for the silicide ( $\text{Cu}_2\text{Si}_3$ : de Chalmot, Abstr., 1896, ii, 362; 1897, ii, 262;  $\text{Cu}_2\text{Si}$ : Vigouroux, Abstr., 1896, ii, 362;  $\text{Cu}_4\text{Si}$ : Lebeau, Abstr., 1906, ii, 29, 168; Vigouroux, *ibid.*, 168). There is no difference in the proportion of combined silicon between alloys slowly cooled and those quenched suddenly in water, but the latter are far more brittle and do not show any crystallisation.

The alloys become red in moist air, especially those approaching the silicide  $\text{Cu}_7\text{Si}_2$  in composition. They decompose water at 65—70°, forming cuprous silicate and evolving hydrogen free from silicon hydride.

A review of previous work on copper silicides is given. C. H. D.

#### Cuprammonium Salts. IV. Cuprammonium Sulphate.

DAVID W. HORN (*Amer. Chem. J.*, 1907, 38, 475—489. Compare Abstr., 1906, ii, 231; 1907, i, 595).—Horn and Taylor (Abstr., 1904, ii, 662) found that a 0.1*N*-solution of the salt,  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , behaves differently from a solution of the same concentration made by adding the calculated quantity of ammonia to a 0.1*N*-solution of copper sulphate. Dawson (*Trans.*, 1906, 89, 1674), however, after examining 0.1*N*-solutions of cuprammonium sulphate, stated that the data obtained agreed satisfactorily with those obtained in the examination of solutions containing a larger quantity of ammonia, that is, solutions prepared by adding excess of ammonia to copper sulphate solution. The present investigation was carried out with the object of studying this point more closely.

A solution, made by adding ammonia to copper sulphate solution, which has a concentration 0.1*N* with respect to copper sulphate and 0.4*N* with respect to ammonia, may be left in a stoppered bottle for a year without visible change. If, however, a solution of the salt  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , of concentration 0.1*N* with respect to copper, is kept under the same conditions, a blue, crystalline substance is



gradually deposited, although the dry salt is very stable. A study has been made of the rate at which this change takes place, and it has been found that it begins directly the salt is dissolved and continues for some time, crystals becoming visible in about thirty-two hours. The crystalline substance has the composition  $4\text{CuO}, \text{SO}_3, 2\frac{2}{3}\text{NH}_3, 4\frac{1}{3}\text{H}_2\text{O}$ . After a solution had been kept for two months, one portion of the supernatant liquid was transferred to another bottle, whilst a second portion was left in contact with the basic salt. In neither case was any further quantity of the basic salt deposited, even when left for a year. On adding alcohol to the clear solution from which the basic salt had separated, a compound was obtained in lilac-blue needles which had the composition of ordinary cuprammonium sulphate,  $\text{CuSO}_4, 4\text{NH}_3, \text{H}_2\text{O}$ . The changes occurring are expressed by the equations:  $36(\text{CuSO}_4, 4\text{NH}_3, \text{H}_2\text{O}) + \text{H}_2\text{O} = 12\text{CuO}, 3\text{SO}_3, 8\text{NH}_3, 13\text{H}_2\text{O} + 24(\text{CuSO}_4, 4\text{NH}_3, \text{H}_2\text{O})$  (precipitated by alcohol)  $+ 9(\text{NH}_4)_2\text{SO}_4 + 28\text{NH}_3$ . These results prove conclusively that the behaviour of a freshly-prepared 0.1*N*-solution of cuprammonium sulphate differs from that of a solution of the same strength prepared from copper sulphate and ammonia.

E. G.

**Constitution of the Aluminium Bronzes.** B. E. CURRY (*J. Physical Chem.*, 1907, 11, 425—436. Compare Guillet, *Abstr.*, 1905, ii, 712; Carpenter and Edwards, Eighth Rep. to the Alloys Research Com.)—The complete equilibrium diagram for these alloys above  $400^\circ$  has been constructed, and the results, taken in conjunction with microscopic observations, indicate that only one compound,  $\text{CuAl}_2$ , and six series of solid solutions exist.

The melting-point curve (determined with rising temperatures only) consists of seven branches; there is a maximum at 87.5% by weight of copper, which does not appear to correspond with a chemical compound, and two minima at 90.5% and 32% of copper respectively. The limits within which the seven phases separate from the fused alloy are as follows:  $\alpha$ -mixed crystals, 100—91%;  $\beta$ -crystals, 91—84%;  $\gamma$ -crystals, 84—71%;  $\delta$ -crystals, 71—60%;  $\epsilon$ -crystals, 60—53%;  $\text{CuAl}_2$ , 53—32%, and  $\eta$ -crystals, 32—0% by weight of copper respectively. The compound  $\text{CuAl}_2$  melts at  $585^\circ$ .  $\beta$ -Crystals are only stable above  $566^\circ$ ; at the latter temperature they break down into a mixture of  $\alpha$ - and  $\gamma$ -crystals.  $\delta$ -Crystals are only stable between  $845^\circ$  and  $570^\circ$ ; at the latter temperature they break down into  $\gamma$ - and  $\epsilon$ -crystals. Under equilibrium conditions at  $500^\circ$ , aluminium dissolves 11% of copper. The equilibrium conditions in the solid alloys above  $400^\circ$  have been determined by annealing at different temperatures and then rapidly cooling; for details as to the limits of the various fields, the original must be consulted.

The  $\beta$ -alloys crystallise in long needles, the  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -alloys in leaf-like crystals of very similar appearance, and the compound  $\text{CuAl}_2$  in quadrangular crystals. All the alloys containing less than 84% by weight of copper are colourless.

The results of Carpenter and Edwards (*loc. cit.*) are criticised in some respects; in particular, there is no evidence of the existence of the compounds  $\text{Cu}_4\text{Al}$  and  $\text{Cu}_3\text{Al}$  mentioned by these observers.

The tensile strength of the alloys is dealt with in the next abstract.  
G. S.

**Tensile Strengths of the Copper-Aluminium Alloys.** B. E. CURRY and SAMUEL H. WOODS (*J. Physical Chem.*, 1907, 11, 461—491. Compare preceding abstract).—Only those alloys containing up to 25% and over 86% by weight of copper were used; the remaining alloys are too brittle to be of technical value. The test pieces were prepared by the method given by Shepherd and Upton (Abstr., 1905, ii, 587). The tensile strength, the ductility, and the relation between extension and load for chill-cast alloys, for alloys annealed below 500° or above 565° and rapidly cooled, and finally for alloys annealed and allowed to cool at the ordinary temperature are given in tabular form, and the results are also represented by diagrams and curves.

For chill-cast alloys rich in aluminium the tensile strength increases slowly and the ductility diminishes fairly rapidly from 5—20% of copper; annealing these alloys reduces the strength and increases the ductility. The strength of annealed alloys containing 5—20% of copper is practically equal throughout. The most dependable alloy contains about 10% of copper.

Traces of aluminium markedly increase the tensile strength of copper; on further addition of the former metal, the tensile strength increases gradually, attains a maximum at 90% of copper, and beyond that point diminishes. In this case, annealing has comparatively little effect from 100% to 92% of copper, but from 89% to 91% copper the strength of the alloys annealed at 566° and rapidly cooled is considerably increased, but the ductility is lowered. Alloys containing 86% of copper are very brittle. The ductility attains a maximum value between 92% and 95% of copper, and falls very rapidly indeed between 92% and 90% of the same metal, the latter phenomenon being connected with the appearance of  $\beta$ -crystals.

As regards the relationship between crystalline phase present and behaviour of the alloys, the tensile strength of the  $\beta$ -bronzes is higher than that of the  $\gamma$ -bronzes, whilst that of the  $\alpha$ -bronzes increases with decreasing copper content. The ductility of  $\beta$ - and  $\gamma$ -crystals is practically zero, whilst the  $\alpha$ -crystals have a higher ductility the greater the aluminium content.  
G. S.

**Artificial Corundum.** OTTO HÖNIGSCHMID (*Monatsh.*, 1907, 28, 1107—1111).—The product obtained on ignition of a mixture of borax, aluminium turnings, and sulphur consists of crystalline alumina (artificial corundum) together with considerable amounts of amorphous boron and traces of crystalline aluminium boride. Contrary to Kühne's statement (Abstr., 1904, ii, 331), crystalline boron is not formed.  
G. Y.

**Action of Hydrochloric Acid on Manganese Dioxide.** WILLIS B. HOLMES (*J. Amer. Chem. Soc.*, 1907, 29, 1277—1288).—A resume is given of previous work on this subject, and experiments are described which show that when manganese dioxide, suspended in carbon tetrachloride, is treated with dry hydrogen chloride, manganese trichloride and tetrachloride are formed.

On treating the solid product of the reaction with ether, a violet solution of manganese trichloride is obtained, whilst the residue consists of manganous chloride and manganese tetrachloride. It is considered probable that the tetrachloride is the first product formed.

Manganese trichloride is a nearly black solid with a slight green tinge, and is decomposed immediately by water. When the salt is heated, chlorine is evolved, whilst if left in a desiccator it changes into a mixture of manganous chloride and manganese tetrachloride. It dissolves in alcohol with formation of a wine-coloured solution containing the tetrachloride, but if this solution is diluted with ether and kept cold it assumes the violet colour characteristic of the trichloride. When the ethereal solution of the trichloride is poured into water, only half the manganese is precipitated.

Manganese tetrachloride is a reddish-brown solid, stable at the ordinary temperature, but decomposed by moisture. When heated at  $100^{\circ}$ , chlorine is evolved and manganous chloride is produced. On treating the alcoholic solution of the salt with water, all the manganese is precipitated.

E. G.

**Preparation and Properties of the Manganese Borides,  $MnB$  and  $MnB_2$ .** EDGAR WEDEKIND (*Ber.*, 1907, 40, 3851—3854).—A reply to Binet du Jassonneix (this vol., ii, 691).

A. McK.

**Crystallisation and Structure of Steel.** A. A. BAIKOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 399—410).—Beautifully formed octohedral crystals are often formed in the internal cavities of steel ingots. The form of the crystals is really that of the manganous sulphide, these cores then being coated with ferrite, a layer of pearlite being found enclosing the whole. Many such crystals have been investigated, and diagrams are given showing the appearance of their sections with and without etching by various reagents. The most characteristic feature of the crystals is the occurrence of a large amount of manganous sulphide, which, although in small quantities, is also a normal constituent of steel.

Z. K.

**Special Cast-Irons, particularly those containing Nickel.** LEON GUILLET (*Compt. rend.*, 1907, 145, 552—553).—To a white cast-iron containing 3.2% of carbon (total), 0.052% of graphite, 0.2% of silicon, 0.013% of sulphur, and traces of manganese and phosphorus, and to a grey cast-iron containing 2.739% of carbon (total), 1.697% of graphite, 0.16% of manganese, 2.38% of silicon, 0.098% of sulphur, and 1.47% of phosphorus, increasing quantities of nickel were added and the resulting alloys examined chemically and micrographically, care being taken to allow all the products to cool at the same rate. The results show (1) that nickel favours the formation of graphite, and (2) that as the quantity of nickel added increases, first the formation of sorbite is observed (pearlite disappearing in presence of very little nickel), then the cementite assumes the acicular form rarely observed in ordinary cast-irons, then  $\gamma$ -iron and needles of

troosto-sorbite appear, whilst the sorbite disappears, then the  $\gamma$ -iron increases, whilst the troosto-sorbite diminishes, and finally only  $\gamma$ -iron and graphite are observed. In the last case, certain regions of the  $\gamma$ -iron are easily coloured with picric acid, whilst traces of cementite are occasionally found in the centre. The needles of troosto-sorbite often have a cementite nucleus. Similar examination of the manganese cast-irons shows that sorbite, but not  $\gamma$ -iron, is observed. The special cementite formed increases rapidly, and is the more difficultly coloured with sodium picrate as the percentage of manganese present increases. It is confirmed that manganese inhibits the precipitation of graphite. The author concludes that elements which dissolve in iron (nickel, aluminium, silicon) favour the formation of graphite, whilst those (manganese, chromium) which form a double carbide with cementite oppose it.

E. H.

**Corrosion of Iron and Steel.** WILLIAM H. WALKER, ANNA M. CEDERHOLM, and LEAVITT N. BENT (*J. Amer. Chem. Soc.*, 1907, **29**, 1251—1264).—In investigating the question as to whether iron or steel is the more resistant to corrosion, the authors were led to study the conditions which are necessary for rusting to take place and the reactions involved in the process.

It has been stated by Crace Calvert and Crum Brown that water, oxygen, and carbon dioxide are essential to the formation of rust, and this view has been endorsed recently by Moody (*Trans.*, 1906, **89**, 720), who has described experiments which appear to prove that rust is not produced if carbon dioxide is completely excluded. These experiments have now been repeated, and, although similar results have been obtained, it is considered that the retardation or inhibition of the rusting process was due to the presence of alkali, dissolved from the glass, in the water which was in contact with the iron. It has been found that if Jena glass is employed, the iron rusts almost as readily as when left in the open air. Moody's experiments, in which chromic acid was used, are regarded as valueless, since it has been found that this reagent renders iron passive, and that the passivity persists even after the specimen has been washed and dried. It is concluded that the presence of carbon dioxide is not necessary for rusting to occur (compare Dunstan, *Proc.*, 1907, **23**, 63).

Whitney (*Abstr.*, 1903, ii, 430) has described an experiment to show that iron dissolves in water entirely free from oxygen or carbon dioxide, and on this has based a hypothesis that the formation of rust is due to electrolytic action. On repeating this experiment, Dunstan, Jowett, and Goulding (*Trans.*, 1904, **87**, 1556) were unable to detect any trace of iron in the water. It is now found that usually it is not possible to obtain an indication of the presence of iron in the water until it has been concentrated to a few drops. The following experiment has been devised to confirm the view that the corrosion of iron is an electrolytic phenomenon. If a piece of iron is immersed in water containing a little phenolphthalein and a trace of potassium ferricyanide, after a few minutes the surface is seen to be divided into zones of opposite polarity. Those portions on which hydrogen is being liberated, acting as cathodes, become bright red, owing to the

formation of hydroxyl ions, whilst the anodic portions, at which iron is being dissolved, become coated with a blue precipitate.

The amount of iron which can dissolve in water is limited to the quantity which is equivalent to the hydrogen necessary to polarise that portion of the surface which acts as the cathode. Experiments are described which demonstrate that in presence of a depolarising agent, such as hydroxylamine, the solvent action is continuous. It is shown that oxygen also exerts a depolarising action. Hydrogen peroxide, if formed during the rusting process, as suggested by Dunstan, Jowett, and Goulding (*loc. cit.*), can only be produced when hydrogen is being oxidised by the dissolved oxygen. It has been found by experiment that the rapidity with which rusting takes place is a direct function of the partial pressure of the oxygen above the water.

An electric current can pass between bright iron and iron covered with scale if the concentration of the hydrogen ions is increased by the presence of an acid, or if oxygen or some other depolarising agent is present.

In some instances, iron which is easily liable to corrosion bears a much larger number of areas of markedly different potentials on its surface than iron which is resistant to corrosion. E. G.

**Reduction of Ferric and Chromic Chlorides by means of Calcium.** L. HACKSPILL (*Bull. Soc. chim.*, 1907, [iv], 1, 895—897. Compare Abstr., 1906, ii, 161; Watts, Abstr., 1906, ii, 759).—When an intimate mixture of calcium and sublimed, anhydrous ferric chloride is heated to dull redness in a magnesia crucible enclosed in an iron crucible with a screw-lid, the chloride undergoes reduction to metallic iron.

The prolonged action of fused calcium on iron at a temperature above  $1000^{\circ}$  does not yield a calcium-iron alloy, although it is quite possible that iron and calcium unite together with other metals to form ternary alloys.

Calcium reduces chromic chloride at a dull red heat, yielding metallic chromium, but does not alloy with the latter even when kept at about  $1000^{\circ}$  for three hours. T. H. P.

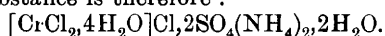
**Ferric Silicates.** EDUARD JORDIS (*J. pr. Chem.*, 1907, [ii], 76, 273—274).—Polemical. A reply to Ulfers (this vol., ii, 776).

G. Y.

[Crystallisation of Inorganic Compounds.] WILLIAM E. GUERTLER (D.R.-P. 182200).—The oxides required to produce the mineral species, olivine, zircon, beryl, and spinelle, were dissolved in fused sodium or potassium metaborate and the temperature of the solution raised to  $1300^{\circ}$  until all the alkali borate had been volatilised; the residue contained the required compounds in a crystalline form. A *nickel-chrome-spinelle*,  $\text{NiO} \cdot \text{Cr}_2\text{O}_3$ , was prepared in this way from its constituent oxides and obtained in the form of small, dark green crystals.

G. T. M.

**Compounds of Salts of the Dichlorochromium Base with Ammonium Salts.** RUDOLF F. WEINLAND and THEODOR SCHUMANN (*Ber.*, 1907, 40, 3767—3771).—A solution of green hydrated chromium chloride (1 mol.) and ammonium sulphate (1 mol.) deposits the *double salt*,  $\text{CrCl}_3 \cdot 2\text{SO}_4(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ , in the form of large, green, four- or six-sided plates when kept a short time in a desiccator. Only one-third of the chlorine is precipitated immediately by silver nitrate from an acidified solution of the salt at  $0^\circ$ , whereas all the sulphate is thrown down immediately by barium chloride. The constitution assigned to the substance is therefore :

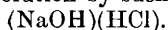


A salt of the formula,  $[\text{CrCl}_2 \cdot 4\text{H}_2\text{O}] \frac{\text{SO}_4}{2} \cdot (\text{SO}_4)_2(\text{NH}_4)_3\text{H}$ , separates in long, slender, green needles from a solution containing green hydrated chromium chloride (1 mol.) and ammonium sulphate (1 mol.) after the addition of sulphuric acid (1—3 mols.). In an acidified solution of the salt at  $0^\circ$ , silver nitrate does not produce an immediate precipitate, but all the sulphate is at once thrown down by barium chloride.

When hydrogen chloride is passed into a solution of either of the above salts, or into a solution containing equal molecular quantities of green hydrated chromium chloride and ammonium chloride, the *double salt*,  $\text{CrCl}_3 \cdot 2\text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ , separates as thick, green, rectangular plates. The salt is deliquescent and turns red when warmed slightly. Silver nitrate added to a solution of the salt acidified with nitric acid precipitates immediately only three-fifths of the chlorine; consequently the constitution assigned to this substance is  $[\text{CrCl}_2 \cdot 4\text{H}_2\text{O}]\text{Cl} \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ .

W. H. G.

**Constitution of Complexes.** ALBERT COLSON (*Bull. Soc. chim.*, 1907, [iv], 1, 889—895).—The author replies to the criticisms of Wyruboff on his work on chromium sulphates (*Abstr.*, 1906, ii, 233). To explain the insensibility of "complexes" towards ordinary reagents, for example, green chromium sulphate towards barium chloride, Wyruboff supposes that these compounds are true ethers formed by the elimination of water contained in ordinary salts, which are regarded as represented in solution by such a formula as



The author urges the following, among other objections, against these views. No difference is established between electrolytes and non-electrolytes. Anhydrous sodium chloride can scarcely be regarded as an ether, since immediately it is dissolved, even in iced-water, it is converted into the salt  $(\text{NaOH})(\text{HCl})$ , whilst ethers are distinguished by the difficulty with which they are hydrolysed. The results already obtained (*loc. cit.*) are confirmed by spectroscopic examination of solutions of chromic salts.

T. H. P.

**Molybdenum Silicide,  $\text{MoSi}_2$ , Tungsten Silicide,  $\text{WSi}_2$ , and Tantalum Silicide,  $\text{TaSi}_2$ .** OTTO HÖNIGSCHMID (*Monatsh.*, 1907, 28, 1017—1028).—Molybdenum, tungsten, and tantalum silicides,  $\text{MSi}_2$ , have been prepared in the same manner as zirconium and titanium silicides (*Abstr.*, 1906, ii, 678). As an excess of silica was

present in each case, the general formula,  $\text{MSi}_2$ , must represent the maximum combining power of silicon with the three metals.

*Molybdenum silicide*,  $\text{MoSi}_2$  (compare Watts, this vol., ii, 31), crystallises in iron-grey prisms with a metallic lustre,  $D^{20} 5.88$ , remains unchanged when heated in air or oxygen, reacts with fluorine at the ordinary temperature with development of heat, and when heated in chlorine yields molybdenum trichloride, but is attacked only very slightly by bromine vapour in a current of hydrogen at a red heat. It dissolves rapidly in a mixture of hydrofluoric and nitric acids, evolving nitrous fumes, and is decomposed by fused sodium hydroxide, but is not attacked by any single inorganic acid, 10–20% aqueous alkalis, or fused potassium hydrogen sulphate at a red heat.

Tungsten silicide,  $\text{WSi}_2$  (Defacqz, this vol., ii, 475), is oxidised slowly when heated in a current of oxygen, and reacts with fluorine only when slightly heated.

*Tantalum silicide*,  $\text{TaSi}_2$ , crystallises in prisms,  $D^{20} 8.83$ , which in colour and metallic lustre resemble molybdenum silicide; it dissolves in hydrofluoric acid, is oxidised when heated in a current of oxygen, reacts with fluorine only when gently heated, and is decomposed readily by fused alkalis. G. Y.

**Uranous Compounds.** A. COLANI (*Ann. Chim. Phys.*, 1907, [viii], 12, 59–143).—Some of the compounds dealt with in this paper have already been described (Abstr., 1903, ii, 652); in the previous paper, the atomic weight of uranium was taken as  $U = 120$ , but in the present one  $U = 240$ . The substances previously formulated as  $\text{USe}$ ,  $\text{U}_4\text{Se}_3$ ,  $\text{U}_4\text{Te}_3$ ,  $\text{U}_3\text{P}_2$ ,  $\text{U}_3\text{As}_2$ ,  $\text{U}_3\text{Sb}_2$ , should therefore be  $\text{USe}_2$ ,  $\text{U}_2\text{Se}_3$ ,  $\text{U}_2\text{Te}_3$ ,  $\text{U}_3\text{P}_4$ ,  $\text{U}_3\text{As}_4$ ,  $\text{U}_3\text{Sb}_4$ .

Improved methods are described for preparing uranium chloride,  $\text{UCl}_4$ , in quantity. One consists in passing a mixture of chlorine and sulphur chloride over the heated green oxide,  $\text{U}_3\text{O}_8$  (compare Matignon and Bourion, Abstr., 1904, ii, 340); the other, in passing carbon tetrachloride over the same oxide at a red heat.

On heating fused uranium chloride in a current of hydrogen bromide, the bromide,  $\text{UBr}_4$ , is formed; hydrogen iodide under similar conditions largely converts the chloride into iodide, but the product always contains about 5% of chloride.

The following are the values of the dissociation pressures in centimetres of the system:  $\text{U}_3\text{O}_8 \rightleftharpoons 3\text{UO}_2 + \text{O}_2$ ;  $625^\circ$ , 1.5;  $685^\circ$ , 2.1;  $745^\circ$ , 2.9;  $800^\circ$ , 6.9;  $850^\circ$ , 10.8;  $880^\circ$ , 12.0;  $940^\circ$ , 15.7;  $965^\circ$ , 16.9;  $990^\circ$ , 20.8;  $1020^\circ$ , 20.1 (?);  $1055^\circ$ , 24.8;  $1090^\circ$ , 25.3;  $1125^\circ$ , 28.1;  $1165^\circ$ , 31.5. There is no evidence to show the existence of any intermediate oxide, such as  $\text{U}_2\text{O}_5$ , this substance probably being a mixture of  $\text{U}_3\text{O}_8$  and  $\text{UO}_2$ . The values given for the dissociation pressures show that in the estimation of uranium the precipitated ammonium uranate can be safely heated at temperatures below  $900^\circ$  without decomposition of the green oxide,  $\text{U}_3\text{O}_8$ , occurring.

Owing to the fact that at a red heat water vapour decomposes uranium sulphide,  $\text{US}_2$ , giving the oxide, hydrogen sulphide, and water, it is not practicable to prepare the sulphide by passing hydrogen sulphide over sodium uranium chloride because of the difficulty of drying the gas

satisfactorily; a mixture of carefully-dried hydrogen and sulphur vapour is used instead, the double chloride being heated at a temperature just short of volatilisation. The sulphide is obtained in small, flattened crystals.

Attempts to prepare uranium antimonide gave only alloys of uranium and antimony of variable composition, not the compound  $\text{U}_3\text{Sb}_4$  as previously stated (*loc. cit.*).

*Uranous metaphosphate*,  $\text{U}(\text{PO}_3)_4$ , is prepared by heating to redness a mixture of uranium oxide and metaphosphoric acid in a gold Rose crucible through which carbon dioxide is passed; the product, after treatment with water and boiling nitric acid to remove unchanged material, forms a green, crystalline powder. This substance only is obtained by the methods described by Hautefeuille and Margottet (*Abstr.*, 1883, 711) as giving the uranic phosphate,  $\text{UO}_3 \cdot 3\text{P}_2\text{O}_5$ , this compound being non-existent; the same is true of the methods described by Johnson (*Abstr.*, 1889, 757) for the preparation of the metaphosphate,  $\text{UO}_3 \cdot 2\text{P}_2\text{O}_5$ , which also does not exist. It is shown that uranic salts when strongly heated with metaphosphoric acid lose oxygen and give uranous metaphosphate.

*Uranous pyrophosphate*,  $\text{UP}_2\text{O}_7$ , can be obtained by calcining the crystalline salt,  $\text{UH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ , in a current of carbon dioxide, but is best prepared by calcining the uranyl salt,  $\text{UO}_2\text{H}_4(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , and reducing the amorphous metaphosphate obtained in hydrogen; the product is amorphous, but becomes crystalline without changing its composition when strongly heated in a current of hydrogen chloride. The crystalline pyrophosphate is also obtained when phosphorus oxychloride vapour is passed over green uranium oxide. The pyrophosphate is distinguished from the metaphosphate by its being far more slowly attacked by acids.

*Uranous orthophosphate*,  $\text{U}_3(\text{PO}_4)_4$ , is obtained as an amorphous precipitate on adding trisodium phosphate to a solution of uranium chloride in an atmosphere of carbon dioxide; it becomes crystalline when heated at a red heat in a current of hydrogen chloride.

On reducing uranic pyrophosphate with hydrogen, a bright green powder consisting of a *basic uranous phosphate*,  $2\text{UO}_2 \cdot \text{P}_2\text{O}_5$ , is obtained; it becomes crystalline when ignited in hydrogen chloride. A substance of the same composition is obtained on reducing uranic orthophosphate with hydrogen.

The *chlorophosphate*,  $3\text{UO}_2 \cdot \text{UCl}_4 \cdot 2\text{P}_2\text{O}_5$ , is obtained on passing the vapour of uranium chloride over metaphosphoric acid, or any one of the uranous phosphates, heated in an atmosphere of dry carbon dioxide; it forms green, orthorhombic crystals [ $a : b : c = 0.8376 : 1 : 0.7473$ ] and is closely related to the wagnerite group.

The following double phosphates are prepared by heating an intimate mixture of the alkali phosphate with an excess of uranous oxide in a platinum Rose crucible through which carbon dioxide is passed; the fused mixture is cooled very slowly, so as to cause the double phosphate to crystallise well and thus become separated from the excess of oxide used.

*Uranium potassium metaphosphate*,  $\text{UO}_2 \cdot \text{K}_2\text{O} \cdot \text{P}_2\text{O}_5$ , prepared by fusing uranium oxide with potassium metaphosphate and potassium



chloride, forms green, orthorhombic crystals [ $a:b:c=0.3711:1:0.3902$ ].

*Uranium potassium pyrophosphate*,  $3\text{UO}_2, 6\text{K}_2\text{O}, 4\text{P}_2\text{O}_5$ , forms green, transparent plates. The *phosphate*,  $4\text{UO}_2, \text{K}_2\text{O}, 3\text{P}_2\text{O}_5$ , is best prepared by heating potassium phosphate with a slight excess of uranium potassium chloride, and forms small, dark green, probably triclinic crystals.

*Uranium sodium metaphosphate*,  $4\text{UO}_2, \text{Na}_2\text{O}, 3\text{P}_2\text{O}_5$ , forms dark green, orthorhombic crystals [ $a:b:c=2.5605:1:1.1918$ ] and is insoluble in boiling nitric acid. When equal weights of sodium metaphosphate (or, better, pyrophosphate) and uranous oxide are heated with an excess of sodium chloride, the *salt*,  $\text{UO}_2, \text{P}_2\text{O}_5, \text{Na}_2\text{O}$ , is obtained; it forms emerald-green, orthorhombic crystals [ $a:b:c=0.6766:1:0.4006$ ] and is easily attacked by acids. *Uranium sodium pyrophosphate*,  $3\text{UO}_2, 6\text{Na}_2\text{O}, 4\text{P}_2\text{O}_5$ , forms green, orthorhombic crystals [ $a:b:c=0.5758:1:0.2157$ ].

*Uranium calcium metaphosphate*,  $\text{UO}_2, \text{CaO}, \text{P}_2\text{O}_5$ , best obtained by fusing uranous metaphosphate with an excess of anhydrous calcium chloride, forms green, monoclinic crystals [ $a:b:c=1.508:1:1.124$ ;  $\gamma=93^\circ 29'$ ]. The analogous *strontium salt*,  $\text{UO}_2, \text{SrO}, \text{P}_2\text{O}_5$ , is orthorhombic [ $a:b:c=1.474:1:1.165$ ]. The *barium salt*,  $\text{UO}_2, \text{BaO}, \text{P}_2\text{O}_5$ , forms very thin, green plates.  
W. A. D.

**Tellurium-Tin Alloys.** HENRY FAY (*J. Amer. Chem. Soc.*, 1907, 29, 1265—1268).—Alloys of tellurium with lead (Fay and Gillson, *Abstr.*, 1902, ii, 260) and with antimony (Fay and Ashley, *Abstr.*, 1902, ii, 266) have already been described. As no compounds of tin with tellurium have been recorded, a study has now been made of a series of alloys of these elements.

The freezing-point diagram resembles that of the lead-tellurium alloys (*loc. cit.*). The curve shows one maximum point indicating the existence of a *compound*,  $\text{SnTe}$ , m. p.  $769^\circ$ , which forms with tellurium a eutectic alloy, m. p.  $399^\circ$ , containing 85% of tellurium. The compound also forms a eutectic alloy with tin of very low concentration.

When examined with the microscope, the alloy containing 48.28% of tin is seen to be quite uniform, but as the proportion of tellurium is increased the eutectic alloy becomes visible, and finally crystals of tellurium appear.  
E. G.

**Alloys of Cobalt and Tin.** F. DUCELLIEZ (*Compt. rend.*, 1907, 145, 502—504. Compare this vol., ii, 693, 779).—Alloys of cobalt and tin containing 59.72, 61.15, and 64.83% of tin were prepared in the manner already described; from these, the compound  $\text{Co}_3\text{Sn}_2$  was isolated by decomposing the finely-powdered material with 15% hydrochloric acid, the compound  $\text{CoSn}$  being separated by similar treatment with concentrated nitric acid. The alloys were thus seen to be mixtures of  $\text{Co}_3\text{Sn}_2$  and  $\text{CoSn}$ . The following table summarises the properties of the whole series of alloys containing from 0—100% of tin:

% of tin.	Composition of alloy.	Definite compounds isolated.	Physical properties.
0	Co and Co <sub>3</sub> Sn <sub>2</sub>	<div> <div>Co<sub>3</sub>Sn<sub>2</sub></div> <div>CoSn</div> </div>	Fragility increases.
57.65			Magnetic alloys.
66.76	Co <sub>3</sub> Sn <sub>2</sub> and CoSn		D=8.862 limit of magnetion.
85	CoSn and Sn		Very fragile.
100			D=8.950.
			Less and less hard and brittle.
			Malleable alloys.

Non-magnetic alloys.

Non-magnetic alloys.

W. A. D.

### Analysis of Certain Alloys containing Tin or Antimony.

ARMAND BERG (*Bull. Soc. chim.*, 1907, [iv], 1, 905—909).—The author studies the changes undergone by metals when heated with a mixture of equal weights of dry sodium carbonate and pure sulphur.

Coarsely-powdered lead or bismuth, or finely-divided silver, copper, or zinc, is converted by this means into sulphide. Tin, even in lumps, is converted into the thioannate, and, if a bright red heat is maintained for some time, finely-divided antimony into thioantimonate. Powdered arsenic is transformed quantitatively into thioarsenate if the mixture is heated cautiously at first, and never beyond dull redness. Cadmium is converted incompletely and with difficulty into sulphide, whilst chromium and aluminium are not sensibly attacked. Nickel undergoes partial transformation, as also does iron; in the latter case, treatment of the mass with water often yields a dark green solution apparently containing colloidal iron. A metal which is only attacked with difficulty is more readily acted on when alloyed with others more easily transformed. These results are utilised in the analysis of certain alloys.

With lead-tin alloys, about 0.5 gram of the coarsely-divided metal is mixed in a porcelain crucible with about six times its weight of sulphur-sodium carbonate, covered with a layer of sulphur, and heated in a muffle furnace, gently at first, and at bright redness for about five minutes. The cold crucible and contents are heated with water, the solution filtered, and the precipitated lead sulphide washed with water containing a little ammonium sulphide. The tin is precipitated from the filtrate by acidifying with hydrochloric acid, and the precipitate washed, dried, calcined, and weighed as dioxide. In absence of metals other than tin and lead, the lead sulphide can be converted into sulphate by heating with ammonium sulphate, and weighed. If iron is present, the mixed lead and iron sulphides are dissolved in concentrated hydrochloric acid, mixed with excess of sulphuric acid, and evaporated to expel hydrochloric acid, the residue being treated with water, and the lead sulphate collected and weighed in the ordinary way.

This treatment of tin with sodium carbonate and sulphur is useful in detecting small proportions of foreign metals, other than antimony or arsenic, which yield insoluble sulphides.

With lead-antimony alloys, the heating is protracted somewhat, and the filtered aqueous extract acidified with hydrochloric acid; the

antimony sulphide thus precipitated is collected in a wide Soxhlet filtering tube, heated in a current of carbon dioxide to remove water and excess of sulphur, and weighed.

Bronzes may be analysed similarly, but they must be finely-divided and heated with sodium carbonate and sulphur for a long time.

T. H. P.

**Crystalline Platinum.** FRITZ LIMMER (*Chem. Zeit.*, 1907, 31, 1025. Compare Moissan, *Abstr.*, 1890, 217).—Platinum is obtained in the form of small octahedra, not only by igniting potassium platinichloride as was shown by Jacquelin (*J. pr. Chem.*, 1841, 22, 22), but also by heating spongy platinum with cupric chloride. In the latter case, part of the metal is also obtained as highly crystalline scales.

W. H. G.

**Radiation from, and Melting Points of, Palladium and Platinum.** CHARLES W. WAIDNER and GEORGE K. BURGESS (*Bull. Bureau Standards*, 1907, 3, 163—208).—The calibration of a Holborn-Kurlbaum optical pyrometer for the radiation from a uniformly heated black body is fully described, the effect of the optical properties of the glasses used with the pyrometer on the temperature measurements being also taken into account. Further, the relation of the radiation of palladium and platinum to that of a black body was investigated for red and green light up to 1250°. The melting points of palladium and platinum were then determined with the pyrometer: (a) when the metals were heated to melting within an iridium furnace; (b) by the surface radiation method, strips of the metals being electrically heated to melting. The melting points were calculated by extrapolation by means of the Wein equation connecting the absolute temperature of a black body with the intensity of any monochromatic radiation, and the corrected values, 1546° and 1753°, were obtained for palladium and platinum respectively.

The melting points in question were also determined by a thermo-electric method, the thermocouples being calibrated by means of the melting points of zinc, antimony, and copper. This method gives lower values than the optical methods, but the actual difference is uncertain, varying with the equation which is employed for the relation between the *E.M.F.* of the thermocouple and the temperature.

G. S.

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### Mineralogical Chemistry.

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**Optical Investigation of the Naphtha from the Holy Isle.**  
M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1907, 566—573).—The coefficient of optical opacity of the moist naphtha in benzene solution, that is, the limiting concentration of solutions transmitting a ray of polarised light through a layer 200 mm. in thickness, is 1/8%. The

naphtha is almost odourless, of a brown colour, and D 0.9438, and of a tarry nature. It has been formed probably by a process of natural fractionation or filtration. The dried naphtha on fractionation is dextrorotatory, with an angle of rotation not exceeding  $6^\circ$ . The last fraction is blackish-brown with a coefficient of opacity  $1/64\%$ , but was far yet from being molecular carbon. The detection of minute particles by means of polarised light is shown to be much more delicate than that by means of ultra-microscopical methods. Z. K.

**Optical Investigation of Berekei Naphtha.** M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1907, 574—578. Compare preceding abstract).—The optical coefficient of the moist naphtha in benzene solution is  $1/4\%$ . The naphtha is normal in character, rich in hydrocarbons, and when dry can be fractionated with hardly any decomposition. It is remarkable that the last fraction obtainable (above  $260^\circ/40$  mm.) from this naphtha, although of a distinctly tarry nature, has an optical coefficient of opacity  $1/8$  in benzene solution. Z. K.

**Optical Investigation of the Bibieibat Naphtha.** M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 802—814. Compare preceding abstract).—The origin of naphtha is a chemical as well as a geological problem. Especially interesting for this purpose is a study of the optical properties of naphtha, the conclusions from which are, in many cases, in agreement with geological data. In calculating the age of a naphtha, the following periods have to be taken into account: (1) the period of formation; (2) of racemisation; (3) of carbonisation; (4) of decomposition: probably but slight in most cases. Thus the coefficient of optical opacity is not by itself a sufficient criterion for estimating the age of a naphtha. Eight different samples of moist Bibieibat naphtha all had a coefficient of optical opacity  $1/4\%$  in benzene solution ( $l=200$  mm.), were closely analogous to natural tar, and belonged to the same geological period: probably the upper Miocene. The naphtha is dextrorotatory, and similar in all respects to the Caucasian naphtha studied previously by the author. The coefficient of opacity of the residue after distillation to  $250^\circ$  was  $1/16\%$ , which shows that but little decomposition occurs during distillation. Z. K.

**Composition of Galician Mineral Oils.** ROMAN ZALOZIECKI and JOACHIM HAUSMANN (*Zeitsch. angew. Chem.*, 1907, 20, 1761—1767. Compare Lachowicz, *Abstr.*, 1884, 166; Pawlowski, *Abstr.*, 1885, 1126; Zaloziecki and Frasch, *Abstr.*, 1902, i, 197).—The high inflammability of the various petroleum fractions obtained from Galician mineral oils is due to the presence of aromatic hydrocarbons. The fraction, b. p.  $20-150^\circ$ , obtained from all the oils examined, contained from 3% to 22% of benzene, toluene, and xylene. W. H. G.

**Roumanian Petroleums. Part IX. Aromatic Hydrocarbons contained in the Petroleums.** PETRUS PONI (*Ann. Sci. Univ. Jassy*, 1907, 4, 192—202. Compare *Abstr.*, 1906, i, 9).—In order to

determine whether the aromatic hydrocarbons, which have been obtained by the distillation of Roumanian petroleums, exist naturally in the oils or are formed in the process of distillation, four samples of petroleum from different wells in the Câmpina district of Prahova have been examined. These were fractionally distilled under a pressure ranging from 29 mm. to 34 mm., and the fractions boiling between 35° and 70° were collected, purified by shaking with sulphuric acid, and each nitrated with its own weight of a mixture of one part of nitric acid (D 1.52) and two parts of sulphuric acid (D 1.8). In this way, nitro-derivatives of toluene, *m*-xylene, mesitylene, and  $\psi$ -cumene were obtained, indicating that these four aromatic hydrocarbons pre-exist in the oils. On recovering the non-nitrated portion of each fraction of oil, it was found that the average loss was 23.6%, and this may be taken to represent the proportion of benzenoid hydrocarbons originally present. The density of the recovered oil was in each case lower than before nitration, and on comparison with the densities of the naphthenes and paraffins of similar boiling point was found to be about halfway between these, so that the non-nitrated portion of the oil appeared to consist of paraffins and naphthenes in approximately equal amounts.

T. A. H.

**Columbates, Tantalates, and Titanates from the Norwegian Pegmatite-Veins.** WALDEMAR C. BRÖGGER (*Vid.-Selsk. Skrifter, Christiania, Math.-Naturv. Kl.*, 1906, No. 6, 1—162).—The granitic pegmatite-veins of the south of Norway are exposed in numerous felspar quarries and are remarkable by reason of the great variety of rare minerals which they have yielded. The first part of a systematic account of the occurrences is devoted to detailed descriptions of the columbates, tantalates, titanates, and titanocolumbates. Several unpublished analyses by the late C. W. Blomstrand are given.

Fergusonite is optically isotropic, owing to alteration and hydration. A crystal, when heated suddenly, shows an incandescent glow and becomes fractured and lighter in colour; after this treatment, the crystal is, in part, optically anisotropic, but it does not possess the tetragonal structure of the original mineral. Analysis of fergusonite from Berg in Råde gave:

Cb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	SnO <sub>2</sub> .	ZrO <sub>2</sub> .	ThO <sub>2</sub> .	UO <sub>2</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	(Di,La) <sub>2</sub> O <sub>3</sub> .	(Y,Er) <sub>2</sub> O <sub>3</sub> .
39.30	6.25	1.44	0.98	trace	2.51	4.68	0.72	2.25	35.03
FeO.	MnO.	MgO.	GfO.	CaO.	H <sub>2</sub> O.	Total.	Sp. gr.		
0.78	0.15	0.05	0.40	1.23	4.00	99.77	4.97		

Neglecting the water and reckoning the dioxides with R<sub>2</sub>O<sub>3</sub>, this corresponds with the formula (Th,U)(Si,Sn)O<sub>4</sub> + 12R'''(Cb,Ta)O<sub>4</sub>.

Ilmenite is found occasionally as rough crystals. An analysis by G. Wallin gave:

TiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	H <sub>2</sub> O.	Total.
48.03	14.88	32.46	3.43	trace	0.10	0.14	99.04

Recalculating the iron as Fe<sub>2</sub>O<sub>3</sub>, 6.92, and FeO, 39.63, this corresponds with Fe<sub>2</sub>O<sub>3</sub> + 14(Fe,Mn,Ca)TiO<sub>3</sub>.

Ilmenorutile is recorded from three localities as black, opaque

crystals with a greyish-black streak and  $D\ 4.71$ ; the crystals are tetragonal with the same habit as tapiolite and mossite, namely, twinned on (101) and elongated in the direction of a polar edge of the pyramid (111). Analyses by O. N. Heidenreich of crystals from Evje and Tvedestrand gave respectively:

TiO <sub>2</sub> .	SiO <sub>2</sub> .	Cb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	FeO.	MnO.	MgO.	CaO.	Total
73.78	0.23	13.74	0.43	11.58	trace	0.04	0.22	100.02
67.68	0.05	20.31	—	11.68	trace	trace	0.28	100.00

Here the ratio of  $R''(\text{CbO}_3)_2$  to  $R''\text{TiO}_3$  is as 1:10 and 3:19 respectively. Ilmenorutile is regarded as a distinct mineral species, consisting of an isomorphous mixture of  $(\text{TiO})\text{TiO}_3$  with  $\text{FeTiO}_3$  and  $\text{Fe}(\text{CbO}_3)_2$ , whilst "nigrine" is a mixture of the first two of these molecules.

Columbite, first discovered in Norway in 1879, is recorded from twenty-five localities. A crystallographic description is given;  $a:b:c = 0.40093:1:0.35867$ . Some of the crystals are of enormous size. The following analyses are of material from Änneröd and Fuglevik respectively:

Cb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	SnO <sub>2</sub> .	SiO <sub>2</sub> .	FeO.	MnO.	CaO.	Loss on ignition.	Total.	Sp. gr.
72.37	5.26	0.67	—	15.04	5.97	0.58	—	99.89	5.32
71.38	5.87	0.51	0.17	15.86	5.33	0.80	0.12	100.04	5.32

A comparison with columbite from other localities indicates that an increase in the amount of tantalum is accompanied by a slight increase in the  $a$ -axis and a decrease in the  $c$ -axis. Crystallographic (homœomorphous) relationships are traced between columbite and potassium nitrate, aragonite, brookite, wolframite, and several other minerals.

Euxenite and polycrase resemble each other very closely; the rather roughly developed orthorhombic crystals have approximately the same angles (which are also near to those of columbite), although they differ somewhat in habit; for both  $a:b:c = 0.3789:1:0.3527$  approximately. A new analysis of euxenite from Alve gives the ratio  $(\text{Cb,Ta})_2\text{O}_5:\text{TiO}_2 = 1:3$ :

Cb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	TiO <sub>2</sub> .	SnO <sub>2</sub> .	ZrO <sub>2</sub> .	ThO <sub>2</sub> .	UO <sub>2</sub> .	(Ce,La,Di) <sub>2</sub> O <sub>3</sub> .	(Y,Er) <sub>2</sub> O <sub>3</sub> .
27.64	1.27	0.17	25.68	0.18	trace	3.58	5.83	2.20	27.73
Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	PbO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
trace	1.13	0.16	0.06	1.08	0.63	0.18	0.09	2.55	100.16

Euxenite and polycrase seem to form a homœomorphous series in which the ratio of  $(\text{Cb,Ta})_2\text{O}_5:\text{TiO}_2$  varies from 1:2 to 1:5. It is proposed to limit the name euxenite to those members of the series in which the ratio is 1:3 or less, and polycrase to those in which it is 1:4 or greater.

*Blomstrandine and Priorite.*—A mineral from Hitterö occurring as large, orthorhombic crystals of tabular habit and with angles near those of æschynite was provisionally, in 1879, referred to this species. The first of the two following analyses proves it to be a titanocolumbate of yttrium earths, whilst æschynite is the corresponding cerium salt. The mineral therefore represents a new species and is called *blomstrandine* (not to be confused with the blomstrandite of

G. Lindström, a hydrous titanocolumbate of uranium); it is recorded from several other Norwegian localities, the second analysis being of material from Arendal:

$\text{Cb}_2\text{O}_5$ .	$\text{Ta}_2\text{O}_5$ .	$\text{TiO}_2$ .	$\text{SnO}_2$ .	$\text{SiO}_2$ .	$\text{ZrO}_2$ .	$\text{UO}_2$ .	$\text{ThO}_2$ .	$(\text{Y}, \text{Er})_2\text{O}_3$ .	$(\text{Ce}, \text{La}, \text{Di})_2\text{O}_3$ .
17.99	0.89	32.91	0.12	0.38	trace	4.01	7.69	28.76	1.97
23.35	1.15	27.39	0.18	0.40	1.33	5.35	4.28	25.62	2.48

$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{ZnO}$ .	$\text{PbO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.	Sp. gr.
1.48	0.27	1.02	—	0.06	0.04	0.22	0.18	1.88	99.88	4.93—4.82
1.43	0.30	1.80	0.09	0.84	0.15	0.90	0.18	2.56	99.78	4.91

In the first analysis, the ratio of metacolumbate to metatitanate is 1 : 3, and in the second 1 : 2. The axial ratios  $a : b : c = 0.4746 : 1 : 0.6673$  of blomstrandine may be converted to correspond closely with those of the chemically related polycrase, and it is considered that the two are dimorphous and related to one another in much the same way as amphibole and pyroxene.

Another mineral of this series is one from Swaziland, South Africa, analysed by G. T. Prior (Abstr., 1899, ii, 433); for this, the name *priorite* is proposed. Blomstrandine and priorite are isomorphous and are respectively dimorphous with polycrase and euxenite. All these minerals are optically isotropic, owing to alteration by hydration. In their brownish-black colour and bright conchoidal fracture, they closely resemble one another in appearance.

The homeomorphous and isomorphous relations of these and of several other minerals and artificial salts are discussed in detail. For example, the formula of rutile is written as  $(\text{TiO})(\text{TiO}_3)$  to express its crystallographic relation to mossaite,  $\text{Fe}(\text{CbO}_3)_2$ , &c.; anatase as  $\text{Ti}_2(\text{TiO}_4)_2$ , showing a relation to fergusonite,  $\text{Y}_2(\text{CbO}_4)_2$ , &c.; and brookite as  $(\text{Ti}_2\text{O}_3)_3(\text{TiO}_3)_2$ , analogous to columbite,  $\text{Fe}_2(\text{CbO}_3)_4$ , &c.

Samarските crystals from two localities were analysed with the following results:

$\text{Cb}_2\text{O}_5$ .	$\text{Ta}_2\text{O}_5$ .	$\text{SiO}_2$ .	$\text{SnO}_2$ .	$\text{ZrO}_2$ .	$\text{ThO}_2$ .	$\text{UO}_2$ .	$\text{UO}_3$ .	$(\text{Ce}, \text{La}, \text{Di})_2\text{O}_3$ .	$(\text{Y}, \text{Er})_2\text{O}_3$ .
38.83	10.70	1.82	0.57	0.62	2.51	9.66	6.78	0.89	9.07
46.44	1.81	2.39	0.15	0.79	2.59	10.82	5.38	1.90	8.33

$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{GaO}$ .	$\text{MgO}$ .	$\text{CaO}$ .	$\text{BaO}$ .	$\text{PbO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
0.36	4.40	0.86	0.30	0.13	4.30	0.38	0.77	0.76	0.08	6.54	100.33
0.45	4.08	0.79	0.64	0.19	3.79	0.38	0.98	0.62	0.08	7.61	100.21

An optical examination of thin sections of these crystals of samarskite shows that the material is not quite homogeneous, and no definite formula can be deduced from the analyses. The analyses, however, indicate a mixture of pyrocolumbates  $(\text{R}''_2[\text{Cb}, \text{Ta}]_2\text{O}_7)$  with a uranate, perhaps  $\text{R}''\text{U}_2\text{O}_7$ .

The so-called *ännerödite* (Brögger, 1881) is now proved to consist of a parallel growth of small crystals of columbite on larger crystals of samarskite; in the original determinations, the smaller crystals of columbite were measured goniometrically, whilst the analysis was made on the inner portion of samarskite.

*Yttrotantalite*, previously known only from Ytterby, in Sweden, is recorded from three Norwegian localities, analyses of material from two of these being given below. The angles of the orthorhombic



crystals are very close to those of samarskite; yttrotantalite and samarskite are isomorphous, tantalum predominating in the former and columbium in the latter:

Cb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	WO <sub>3</sub> .	SiO <sub>2</sub> .	TiO <sub>2</sub> .	SnO <sub>2</sub> .	ZrO <sub>2</sub> .	ThO <sub>2</sub> .	UO <sub>2</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	La <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .
20·38	39·53	0·66	0·96	1·67	1·20	0·57	0·67	3·85	0·42	1·71	12·48
17·75	37·26	2·02	0·61	2·63	2·96	0·46	0·51	4·48	0·51	0·41	12·52

Er <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	GlO.	CaO.	PbO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
3·58	7·48	1·85	0·15	0·35	1·28	—	0·57	trace	0·51	99·87	5·92
3·54	7·61	1·01	0·15	0·58	2·42	0·30	0·81	0·10	1·16	100·25	5·85

Other minerals described are mossite (Abstr., 1898, ii, 387), micro-lite (?), and pyrrhite (?). L. J. S.

**Zeolites from New South Wales.** CHARLES ANDERSON (*Rec. Australian Museum*, 1907, 6, 404—422).—The basalt of Ben Lomond in New South Wales is much decomposed, and the larger cavities contain beautifully crystallised zeolites associated with calcite. Chabazite predominates; the mean of four analyses is given under I; over sulphuric acid there is a loss of 2·0%, and at 100° of 3·43%; formula, CaO, Al<sub>2</sub>O<sub>3</sub>, 4SiO<sub>2</sub>, 6H<sub>2</sub>O. Transparent, glassy crystals of analcite from the same locality gave II; formula, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, 4SiO<sub>2</sub>, 2H<sub>2</sub>O. Mesolite, as slender crystals, also from Ben Lomond, gave III; formula, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, 3SiO<sub>2</sub>, 2H<sub>2</sub>O + 2(CaO, Al<sub>2</sub>O<sub>3</sub>, 3SiO<sub>2</sub>, 3H<sub>2</sub>O). Natrolite and thomsonite, from Inverell, gave IV and V respectively, agreeing with the usual formulæ. Scolecite, from Werris Creek, gave VI, and stilbite, from Jamberoo, VII:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	47·37	19·16	9·52	0·93	1·11	21·84	99·93
II.	54·39	21·76	1·33	trace	13·77	8·71	99·96
III.	43·88	27·14	7·03	trace	10·48	11·86	100·39
IV.	46·38	27·36	0·83	0·13	15·63	9·28	99·61
V.	40·68	29·73	11·66	—	5·74	12·73	100·54
VI.	45·19	25·56	15·39	0·74		13·94	100·82
VII.	57·61	15·56*	8·22	1·19		17·53	100·11

\* Including Fe<sub>2</sub>O<sub>3</sub>.

Crystallographic descriptions are also given of cassiterite, cerussite, barite, monazite, scheelite, vesuvianite, and heulandite from Australian localities. L. J. S.

**Weathering of Natrolite in Phonolites.** FELIX CORNU and C. SCHUSTER (*Tsch. Min. Mitt.*, 1907, 26, 321—326).—A clayey substance, greasy to the touch, and of a red colour, occurs in the crevices in weathered phonolite at Lellowa, Bohemia; it has the composition given under I; D 2·60. A similar substance from amygdaloidal cavities in weathered phonolite at Aussig, Bohemia, gave analysis II. The material completely extracts the colouring matter from a concentrated solution of magenta. The analyses are of air-dried material; about half the water is lost at 110°. These alteration products of natrolite are of indefinite composition and possibly consist of mixtures

of aluminium hydroxide and silicate, although under the microscope they appear to be homogeneous :

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Li <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	44·11	3·28	1·65	26·34	2·62	0·77	1·54	0·28	trace	22·46	100·05
II.	45·21	—	32·55		1·98	—	not det.			19·91	99·65

L. J. S.

**Mode of Formation of Thorianite and Uraninite.** BÉLA SZILÁRD (*Compt. rend.*, 1907, 145, 463—464).—Thorianite contains 65—74% of thorium and 4—11% of uranium, whilst uraninite contains 4—11% of thorium and 65—74% of uranium; the proportions of the two metals thus being the inverse of one another. Just as thorium hydroxide dissolves in a solution of uranium nitrate (this vol., ii, 97), so uranium hydroxide dissolves in a solution of thorium nitrate; in the former case, on evaporation, a substance similar in composition to thorianite is obtained, whilst in the latter a yellow substance similar to uraninite is formed. Salts of thorium and uranium dissolve not only the hydroxides named above, but also the hydroxides of the rare earth metals and of nearly all those metals occurring in thorianite and uraninite; the compounds obtained with yttrium, iron, lead, and zirconium have characteristic properties. All are amorphous. It is suggested that thorianite and uraninite are formed by a process such as that described above.

W. A. D.

**Occurrence of Manganese in a Spring Water in Sweden.** MATS WEIBULL (*Zeitsch. Nahr. Genussm.*, 1907, 14, 403—405).—A sample of water from an estate near Lund in Southern Sweden was found to contain 23 mg. of manganous oxide (MnO) per litre, the quantity of other mineral matters present not being particularly large. *Chrenothrix manganifera* was present in the water and caused the manganese to be deposited in the water-pipes to such an extent as to block them. The formation from which the water came consisted principally of gneiss in which were veins of diorite containing 8·2% of manganous oxide.

W. P. S.

### Physiological Chemistry.

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**The Organic Constituents of Serum.** EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1907, 53, 31—112).—Serum was freed from protein by alcohol, and the protein precipitate extracted with alcohol and ether; the filtrate plus these extracts was evaporated to dryness, and the dry residue extracted with light petroleum or ether, then with alcohol, and finally with water. These extracts were examined separately. The substances found were cholesterol partly free, and partly in the form of esters from which cholesterol was liberated by saponification. Saponification also led to the appearance of choline,

which arises from lecithin and partly from jecorin ; free choline is not present. There appear to be two forms of jecorin with strongly reducing properties ; dextrose and glycuronic acids are also present. A number of imperfectly recognised substances were also separated in the form of silver or copper salts ; some of these are nitrogenous acids, and their empirical formulæ are given. A substance was also found with the composition  $C_{15}H_{15}O_8N_5Ca_2 \cdot 12H_2O$ , which is not altered by boiling with sodium carbonate. Another substance which was identified is creatine. Monoamino-acids, diamino-acids, and xanthine bases were absent.

W. D. H.

**Influence of External Temperature on the Sugar of the Blood.** GUSTAV EMBDEN, HUGO LÜTHJE, and EMIL LIEFMANN (*Beitr. chem. Physiol. Path.*, 1907, 10, 265—272).—In dogs, a low external temperature causes a rise in the amount of sugar in the blood ; a rise in the surrounding temperature causes a fall in the amount. This is evidently related to the maintenance of body temperature, and accords with the fact known previously that cold lessens the hepatic glycogen. In cold weather, there is increased combustion in the body, and sugar is one of the substances burnt ; the increased combustion of sugar does not occur at the seat of sugar formation (the liver) ; the increase in the blood is simply the increased supply on the way to the organs, the muscles where the combustion takes place.

W. D. H.

**The Cleavage of Polypeptides by the Red Corpuscles and Platelets of the Horse.** EMIL ABDERHALDEN and H. DEETJEN (*Zeitsch. physiol. Chem.*, 1907, 53, 280—293. Compare Abstr., this vol., ii, 586).—Red corpuscles were obtained from oxalated horse's blood by filtration ; the early filtrate contains no platelets or colourless corpuscles. Platelets were obtained by centrifugalising off the corpuscles at a slow rate of rotation ; then by rapidly centrifugalising the supernatant plasma, a deposit of pure platelets was obtained. Both red corpuscles and platelets have the property of cleaving dipeptides, glycyl-*l*-tyrosine being the one mainly used. Confirmatory results were obtained with the blood of other animals. The investigation of other tissue cells is in progress, as also is the question whether higher polypeptides and proteins are decomposable in this way. White blood corpuscles have not yet been obtained free from other elements. Lymph cells obtained from the thoracic duct lymph and pus cells have little or no action.

W. D. H.

**The Behaviour of the Blood-plasma and -Serum of the Horse towards certain Polypeptides.** EMIL ABDERHALDEN and BERTHOLD OPPLER (*Zeitsch. physiol. Chem.*, 1907, 53, 294—307).—The plasma and serum of the blood do not produce that cleavage of glycyl-*l*-tyrosine which the red corpuscles and platelets bring about so readily. Any small action observed is probably due to some of the formed elements being still present. A large number of other dipeptides were investigated with the same negative results ; the only case where cleavage occurred was that of *dl*-alanylglycine. Tri- and tetra-peptides were split. This action cannot be due to enzymes absorbed from the

intestine, for both trypsin and erepsin are capable of splitting glycyl-*l*-tyrosine easily. W. D. H.

**The Behaviour of Blood-Serum and Urine towards Glycyl-*l*-tyrosine.** EMIL ABDERHALDEN and PETER RONA (*Zeitsch. physiol. Chem.*, 1907, 53, 308—314).—Human blood-serum was obtained from thirty cases of disease; in eleven, it produced a slight cleavage of glycyl-*l*-tyrosine; in the remainder, it did not. In a few cases, the urine was investigated, but always with negative results. The number of observations is admittedly too small at present for definite conclusions to be drawn. W. D. H.

**The Hæmolytic Action of Isomeric Compounds.** ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1907, 5, 358—364).—From experiments with the isomeric toluic acids and other aromatic acids, it is shown that their hæmolytic and precipitating properties differ, the ortho-compounds being most, and the para-compounds least, active. W. D. H.

**Rate of Hæmolysis under the Influence of Light, Heat, and Hæmolysins.** GEORGES DREYER and OLAV HANSSEN (*Compt. rend.*, 1907, 145, 371—373).—Ultra-violet rays dissolve red corpuscles *in vitro*; the corpuscles are sensibilised by the yellowish green rays. Details of the action of light and heat are given in tables. The hæmolytic effects of megatheriolysin, saponin, and hydrochloric acid can be expressed by the same formula. W. D. H.

**Chemical Inactivation and Regeneration of Complements.** HIDEYO NOGUCHI (*Biochem. Zeitsch.*, 1907, 6, 172—184).—Acids, stronger than carbonic and the higher fatty acids, and alkali hydroxides render the complement inactive when added in *N*/40 solution to an equal bulk of serum. The salts of strong bases with strong acids have no appreciable effect in concentrations below normal, and the salts of weak bases with weak acids are likewise without effect. The salts of weak bases with strong acids, and of strong bases with weak acids, however, inhibit the action of the complement even in comparatively dilute solutions. By neutralisation of the acid or the alkali, or by removal of the salt, the activity of the complement can be wholly or partially restored.

Complements are in some way comparable with the oleates of organic bases, especially as certain oil soaps are found to increase the activity of the complement (compare following abstract). G. B.

**A Lipolytic Form of Hæmolysis.** HIDEYO NOGUCHI (*Biochem. Zeitsch.*, 1907, 6, 185—191. Compare preceding abstract).—Fat-free lipase (from pancreas emulsion) becomes hæmolytic in the presence of a neutral fat (triolein, butter, &c.). Neither the fat nor the lipase contains lecithin in appreciable quantity. The lipase can also be activated by the serum of dogs and guinea-pigs, but ox-serum seems to contain too little olein to act as complement in lipolytic hæmolysis (compare also Neuberg and Reicher, this vol., ii, 570, and von Liebermann, *Biochem. Zeitsch.*, 1907, 4, 25). G. B.

**The Blood Supply of the Salivary Glands and Character of Saliva in Dog and Cat.** A. J. CARLSON, J. R. GREER, and F. C. BECHT (*Amer. J. Physiol.*, 1907, 20, 180—205).—Diminution of oxygen supply lessens the amount of saliva obtained by stimulation of nerves; but the saliva formed is more concentrated. The secretion of water and inorganic salts is dependent more directly on free oxygen than that of organic substances. Heidenhain's theory of trophic secretory fibres is considered superfluous. W. D. H.

**Influence of Therapeutic Agents in the Gastric Secretion.** JOHANN FEIGL (*Biochem. Zeitsch.*, 1907, 6, 17—46, 47—60).—The experiments were made on dogs with a Pawloff fistula, and were mainly undertaken with a view to understanding the value of mineral waters. The first paper relates mainly to the favouring action of iron and its compounds on the formation of the juice. The second deals with other metals in the metallic state, and an important factor in their action is shown to be their solubility in dilute hydrochloric acid. W. D. H.

**Inhibition of Tryptic Digestion.** SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1907, 52, 412—424).—The antitryptic action of serum-albumin is due to the trypsin being taken up by the protein itself, or by some substance attached to it. The action is not reversible, or only slightly so, and has much in common with what is seen in the neutralisation of a toxin by an antitoxin. After treatment with dilute acetic acid, serum-albumin loses this property. In large quantities, serum-albumin inhibits the digestion of easily digestible proteins, and egg-white has a similar action. W. D. H.

**Digestion of Fat.** II. S. LEVITES (*Zeitsch. physiol. Chem.*, 1907, 53, 349—355).—Fats are split into their constituents during digestion, and it is these which are absorbed. The present research, carried out on some of London's dogs, deals with the relative absorption of fatty acids and their sodium salts. If stearic, palmitic, and oleic acids are given, the quantities absorbed bear the relationship 1 : 3 : 4 respectively. Under ordinary circumstances, most of the acids are saponified; the absorbability of the sodium salts has the same relationship as, and is two and a half times greater than, that of the acids. All the glycerol is absorbed before the ileum is reached. W. D. H.

**The Behaviour of *d*-Alanine in the Organism of the Dog.** EMIL ABDERHALDEN, ALFRED GIGON, and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 53, 113—118).—An important question is now at issue as to the form in which the digestive products of proteins enter the general circulation, and the authors' efforts to find the simplest cleavage products there have been fruitless. A preliminary question to settle is whether amino-acids introduced into the circulating blood are detectable there after a certain length of time, and the present work deals only with one of these acids, namely, *d*-alanine. Mixed with blood *in vitro*, 3.43 out of 4 grams were recovered by the ester method. The experiments were made on dogs,

and in each case 8 grams were injected into the blood stream. The animal was killed about twenty minutes later, and the blood collected, as well as any urine passed. Very little of the *d*-alanine was recovered. In some of the animals, the liver was excluded from the circulation by Eck's or a similar operation; in these cases, the amounts of amino-acid recovered from the blood were respectively: (1) 0.6; (2) 0.45, and (3) 0.13 gram. In one case, the amino-acid was given by the stomach; examination of the gastro-intestinal contents showed that most of it was absorbed, but only 0.21 gram was isolated from the blood. In two normal dogs, the amount recovered after intravenous injection was larger than in the others, namely, 2.36 and 1.4 grams. This was not expected. In cases where urine was passed, the amount recovered from the urine was usually less than that found in the blood, and none at all was found in the urine of the normal dogs. Dogs having an Eck's fistula and fed on the cleavage products of casein passed amino-acids in their urine; normal dogs did not.

W. D. H.

**Fermentative Cleavage of Polypeptides.** EMIL ABDERHALDEN and ALFRED GIGON (*Zeitsch. physiol. Chem.*, 1907, 53, 251—279. Compare this vol., ii, 677).—Glycine has little or no influence on the fermentative cleavage of glycyl-*l*-tyrosine which is brought about by expressed yeast juice. As a general rule, the optically-active amino-acids which occur in natural digestion (for example, *l*-leucine) inhibit this action; the opposite amino-acids (in the optical sense) have little or no influence, whilst the racemic substances have a variable action, but usually a less powerful one.

W. D. H.

**Absorption of Monoamino-acids in the Alimentary Canal.** EMIL ABDERHALDEN, O. PRYM, and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 53, 326—333).—Experiments were made on London's dogs with glycine, *d*-alanine, and *dl*-leucine. If given by the mouth, they are recognisable in the stomach for a long time. By far the greatest amount of them, probably all, pass through the pylorus, and in the duodenum absorption begins rapidly. In the lower segments of the intestines, they have disappeared.

W. D. H.

**Cleavage of Diglycyl-glycine and the Biuret Base in the Dog's Alimentary Canal.** EMIL ABDERHALDEN, E. S. LONDON, and CARL VOEGTLIN (*Zeitsch. physiol. Chem.*, 1907, 53, 334—339).—Diglycyl-glycine and triglycyl-glycine ethyl ester are not decomposed in the dog's stomach, or only in minimal quantity; whereas in the intestine, cleavage and, with it, absorption occurs rapidly.

W. D. H.

**The Value in the Dog of Protein Cleavage Products.** EMIL ABDERHALDEN and PETER RONA (*Zeitsch. physiol. Chem.*, 1907, 52, 507—514. Compare Abstr., this vol., ii, 339).—A growing dog was fed on the ultimate cleavage products of protein for three weeks with good results. Although the difficulty of detecting such substances in the blood is admitted, and the possibility that the tissue cells generally

can synthesise their protein from such substances is not denied, the general conclusion is reached that the main place where protein synthesis occurs is in the intestinal wall. W. D. H.

**Normal Digestion of Protein in the Alimentary Tract of Dogs.** III. EMIL ABDERHALDEN, KORNEL VON KÖRÖSY, and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 53, 148—163. Compare Abstr., 1907, ii, 489).—As in former experiments, a series of dogs was taken, each with a fistula in a different part of the alimentary tract. They were fed on a definite protein (gliadin), and the issuing chyme collected and analysed, so as to follow the course of digestion and absorption. The results coincide with those previously published. Amino-acids are rapidly absorbed. Leucine was found in all cases; glycine in none. Alanine, glutamic and aspartic acids were also always found. Dipeptides were also found, although it is doubtful whether these were precursors of the amino-acids or formed from them. Some feeding experiments with various dipeptides were performed, and the methods of examination of the chyme are described in full. The results are not wholly conclusive, but further experiments with larger amounts are in progress. W. D. H.

**The Cleavage of Edestin (from Hemp Seed) by Pancreatic Juice Alone, and by Gastric and Pancreatic Juices.** EMIL ABDERHALDEN and ALFRED GIGON (*Zeitsch. physiol. Chem.*, 1907, 53, 119—125).—In the body, protein is successively acted on by gastric juice, pancreatic juice, and erepsin, and so is broken down in stages to its simplest cleavage products. The importance of gastric digestion is far from clear, except in the case of a few proteins which are not readily attacked by pancreatic juice. An attempt to elucidate this point was made in the present experiments, although it is confessed that the result throws but little light on the problem. Edestin was *in vitro* subjected to the action of gastric juice for a certain time (four days), then the mixture was neutralised and pancreatic juice activated by intestinal juice added, and digestion allowed to continue for another four days, putrefaction being prevented by toluene. Another and equal quantity of edestin was subjected to the action of activated pancreatic juice for eight days, and a third portion for four days. The amount of tyrosine and glutamic acid in each digest was then determined. The amounts of these two substances in the original edestin was 2·3 and 16·5% respectively. In all experiments (five in number), the yield of tyrosine was 2·2 to 2·3 in all digests. The yield of glutamic acid was never so high as 16·5; it was as low as 3 and as high as 11·5. But the lowest yield was always from the digest where pancreatic juice alone was used for four hours, and the highest where the pancreatic juice was used for eight hours; an intermediate number was obtained from the cases where pancreatic followed gastric digestion. An unknown factor, however, was the amount of erepsin in the intestinal juice used for activation. W. D. H.

**The Cleavage of Casein by Pancreatic Juice.** EMIL ABDERHALDEN and CARL VOEGTLIN (*Zeitsch. physiol. Chem.*, 1907, 53, 315—319).—A former research with edestin (Abstr., 1905, i, 620;



ii, 838) showed that the whole of the tyrosine and the tryptophan in it is rapidly set free by activated pancreatic juice, whereas other amino-acids, such as glutamic acid, are more slowly liberated. A similar piece of work with casein now recorded gives similar results, except that glutamic acid is set free rather more readily.

W. D. H.

**Animal Digestion. XI. Gastric Digestion of Mixed Diets.** E. S. LONDON and A. SAGELMANN (*Zeitsch. physiol. Chem.*, 1907, 52, 482—484).—An experiment is recorded on one of the authors' dogs with a fistula, showing a comparison between what occurs when a pure protein (gliadin) diet is given, and one mixed with fat. The gliadin disappears from the stomach into the intestine either with or without fat admixture four hours after the meal, whereas at the same time only 41% of the fat has passed on. Delay in the passing out of the protein occurred in the first three hours of the experiment when fat was given. The "sorting action" of the stomach is to be still further studied.

W. D. H.

**Animal Digestion. XII. Influence of Quantity on Digestion in the Stomach.** E. S. LONDON and W. W. POLOWZOWA (*Zeitsch. physiol. Chem.*, 1907, 53, 240—245. Compare preceding abstract).—Increase in the amount of protein given leads to an increase in the amount of nitrogen remaining in the stomach at any given moment; the amount which leaves the stomach increases up to a certain maximum (600 grams in the case of dogs); it then remains constant (up to 800—1000 grams), but beyond this diminishes. Maximal feeding delays both the motor and digestive activity in the stomach. Digestion proceeds most rapidly in the periphery of the stomach contents.

W. D. H.

**Animal Digestion. XIII. Further Methods.** E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 53, 246—250).—A description is given of the preparation of more dogs for the study of digestion. The main new operation is a transplantation of the first duodenal papilla.

W. D. H.

**Animal Digestion. XIV. Behaviour of Alcohol in the Digestive Tract.** M. H. NEMSER (*Zeitsch. physiol. Chem.*, 1907, 53, 356—364).—The experiments were made on the dogs rendered familiar by London's publications. Alcohol is absorbed throughout the alimentary tract. In the mouth, naturally, the absorption is minimal; about 20% was absorbed from the stomach, in the duodenum 8·7%, in the jejunum 52·7%, and in the ileum 17·8%.

W. D. H.

**Animal Digestion. XV. The Behaviour of Meat in the Stomach.** E. S. LONDON and W. W. POLOWZOWA (*Zeitsch. physiol. Chem.*, 1907, 53, 403—410).—No absorption of nitrogen occurs in the stomach when meat is given. This confirms previous researches in which egg-white and bread were given.

W. D. H.

**Chemical Studies on Growth. I. Inverting Enzymes.** LAFAYETTE B. MENDEL and PHILIP H. MITCHELL. **II. Purine Metabolism.** L. B. MENDEL and P. H. MITCHELL. **III. Glycogen.** L. B. MENDEL and CHARLES S. LEAVENWORTH (*Amer. J. Physiol.*, 1907, 20, 81—96; 97—116; 117—126).—Inverting enzymes appear early in the embryonic intestine, so contrasting with proteolytic enzymes. In the embryo pig, maltase and lactase are present, but sucrase is absent, although present after birth. Lactase is found in some portions only of the intestine. In birds, lactase is never found, but sucrase is present in the newly-hatched chick and in the adult hen.

The nucleic acid of the embryo pig's liver yields only two purine substances, adenine and guanine. Nuclease and adenase are present. Guanase is absent as in the adult pig, but the other viscera yield it at an early age. Oxydases and the uricolytic ferment are not developed until after birth.

A high percentage of glycogen is not characteristic of embryonic tissues. The liver, however, does not assume its glycogenic function early in the pig. Glycogen is regarded simply as a store of nutrient energy, rather than, as Creighton thought, a peculiar mark of histogenesis.

W. D. H.

**Nutritive Value of Non-Protein Nitrogenous Substances.** MAX MÜLLER (*Pflüger's Archiv*, 1907, 119, 339—349).—A final contribution to the polemical literature which has arisen on this subject. The present article is directed against Kellner (compare this vol., ii, 491, 794).

W. D. H.

**Substitution of Protein by Amides.** KONRAD FRIEDLÄNDER (*Landw. Versuchs-Stat.*, 1907, 67, 283—312).—The nitrogen of molasses fed in conjunction with food deficient in protein is unable to prevent loss of nitrogen, although most of the amide nitrogen of the molasses is converted by bacteria into protein compounds. Asparagine showed a slight sparing action, but its effect is not at all comparable with that of actual protein (aleuronate).

N. H. J. M.

**Nutritive Value of Gelatin. II.** JOHN R. MURLIN (*Amer. J. Physiol.*, 1907, 20, 234—258).—Carbohydrate not needed for combustion is far more efficacious in reducing the nitrogen output than carbohydrate coming within the requirements of potential energy. It is this that renders it so important in convalescence and growth, and may explain the craving for sweets in the young. The sparing action of gelatin is, however, not due to any dextrose it may give rise to, but owing to its containing substances which are nitrogenous. Its chief amino-acid (glycine) can be retained temporarily in the body, and so may serve to explain the high replacement of other proteins by gelatin described previously; but even with abundance of carbohydrate it is not retained permanently.

W. D. H.

**Increased Assimilation of Lecithin and its Behaviour in the Organism.** GIUSEPPE FRANCHINI (*Biochem. Zeitsch.*, 1907, 6, 210—225).—The livers of rabbits, fed exclusively on lecithin, had a

lecithin content of 2.3%, as compared with 1.5% in the starved control animals. There was no increase of lecithin in the brain, and but little increase in the muscles. The increment in the liver persisted for at least a fortnight. In the urine, there was an increase of glycerophosphoric acid, but not of choline; the latter substance is represented by an increase in the amount of formic acid. The lecithin content of the faeces was but slightly greater; in the muscles and in the liver there was an increased amount of glycerophosphoric acid.

G. B.

**The Sense of Taste. I.** C. TH. BECKER and REGINALD O. HERZOG (*Zeitsch. physiol. Chem.*, 1907, 52, 496—505).—Experiments are recorded with the object of correlating taste and chemical composition. From the results, it is found, in relation to acid tastes, that nitric acid is less intense than hydrochloric. If the intensity of the latter is taken as 100, trichloroacetic acid is 76, formic acid 84, lactic acid 65, acetic acid 45, and butyric acid 32. These figures run fairly parallel with those of the diffusion coefficients of the acids. Similar experiments with alkalis were inconclusive, for in low concentrations alkalis taste sweet. Carbohydrates are arranged in the following order of sweetness: sucrose, levulose, lactose and dextrose equal, maltose, galactose.

W. D. H.

**Phosphatides of Egg-Yolk. I.** M. STERN and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1907, 53, 370—385).—In the investigation of this subject, three phosphatides were separated, one only slightly soluble in alcohol, one slightly soluble in ether, and one easily soluble in both reagents. The bulk of the paper deals with methods of isolation, and a preliminary study of the properties of the three substances.

W. D. H.

**Tyrosine, Glycine, and Glutamic Acid in Different Developmental Periods in the Fertilised Hen's Egg.** EMIL ABDERHALDEN and MARTIN KEMPE (*Zeitsch. physiol. Chem.*, 1907, 53, 398—402).—Before incubation, the eggs yielded per 100 grams of egg-white, 1.82 tyrosine, 12.8 glutamic acid, and 1.2 glycine. Ten days later, another lot of eggs of the same set gave the following numbers: 2.11 tyrosine, 13.5 glutamic acid, and 1.15 glycine. After another ten days (end of incubation), the finely-divided young chickens gave 2.25 tyrosine, 12.52 glutamic acid, and 1.35 glycine. The changes are so slight that inferences as to the possibility of one amino-acid being changed into others cannot be drawn.

W. D. H.

**The Anticytolytic Action of the Salts of Bivalent Metals.** JACQUES LOEB (*Biochem. Zeitsch.*, 1907, 5, 351—357).—A further contribution on the lines of the author's previous work on the antagonism of various salts on the development, &c., of cells.

W. D. H.

**Effect of Narcotics on the Detachment of Electrolytes from Cell-proteins.** HERBERT E. ROAF and E. ALDERSON (*Bio-Chem. J.*, 1907, 2, 412—430).—Chloroform, ether, carbon dioxide, and

heat-coagulation change the physical condition of the inorganic constituents of tissues, so that ions are liberated, and an increase of diffusion through parchment takes place. This is not due to the reagents acting on an impermeable membrane around cells, but is the result of an alteration in the relationship of the salts to the proteins. The theoretical bearing of these changes on the activity of cells, especially when anæsthetised, is discussed. W. D. H.

**Physico-pathological Action of Colloidal Metals on Man.** M. ASCOLI and G. IZAR (*Biochem. Zeitsch.*, 1907, 5, 394—409).—The colloidal metals in small quantity accelerate autolytic processes. The present experiments consist in administering them to human beings. After being given hypodermically and intravenously, there is an increase in nitrogenous output. If given by the mouth, the effect is less. Full details of the amount of the various nitrogenous compounds are given in tables. After being heated to 120°, this action of the colloidal metals is lost. W. D. H.

**Influence of Inorganic Colloids on Autolysis. Part II.** M. ASCOLI and G. IZAR (*Biochem. Zeitsch.*, 1907, 6, 192—209. Compare preceding abstract).—The rate of autolysis of liver substance (as measured by the nitrogen content of the filtrate after coagulation) is considerably accelerated by small quantities of (positively charged) colloidal ferric and aluminium hydroxides; for example, by traces corresponding with 0.1 mg. Fe. With larger quantities, the acceleration is less marked, whilst still larger quantities inhibit. Similar results were obtained with colloidal arsenious sulphide, manganese dioxide, and palladium. When heated previously, ferric hydroxide is much less active. G. B.

**The Influence of Inorganic and Organic Acids on Liver Autolysis.** M. ARINKIN (*Zeitsch. physiol. Chem.*, 1907, 53, 192—214).—Up to a certain optimum, which varies with different acids, increase of acidity hastens autolysis; this action is especially seen in the first stages of proteolytic cleavage. On the other hand, acid hinders the cleavage of nuclein compounds. W. D. H.

**Autolysis.** LUIGI PRETI (*Zeitsch. physiol. Chem.*, 1907, 52, 485—495).—The question of the influence of alkalinity on the autolysis of the liver was investigated; the optimum varied in different experiments. The presence of blood lessens the formation of proteoses and purine bases in liver autolysis, but the autolysis occurring in the blood itself has to be allowed for. This action of blood is found when blood is added to the organ during autolysis. If the liver contains blood in its vessels, the same is true; autolysis is more rapid in the blood-free organ. Numerical details are given. W. D. H.

**Liver Autolysis.** EMIL ABDERHALDEN and O. PRYM (*Zeitsch. physiol. Chem.*, 1907, 53, 320—325).—Protein-cleavage occurs very slowly in autolysis. Even after fifty days, in the case of the liver, complexes are still present which give the biuret reaction, and only a

little more than half the quantity of cleavage products are obtained, which are formed by hydrolysis with hydrochloric acid. W. D. H.

**The Glycogen of the Rabbit's Liver.** III. IVAR BANG, MALTE LJUNGDAHL, and VERNER BOHM (*Beitr. chem. Physiol. Path.*, 1907, 10, 312—319. Compare Abstr., 1907, ii, 487, 634).—In morphine and strychnine poisoning there is an increase in the quantity of the ferment in the liver; this is more marked and comes on sooner in the case of strychnine. In phloridzin-diabetes there is no such increase, or it is very small. A combination of puncture-diabetes and phloridzin-diabetes causes less rise in the sugar of the blood than occurs in simple puncture-diabetes. In phloretin-diabetes, on the other hand, there is an undoubted increase in the ferment. W. D. H.

**The Formation of Dextrorotatory Lactic Acid in the Autolysis of Animal Organs.** II. T. KIKKŌJI (*Zeitsch. physiol. Chem.*, 1907, 53, 415—419. Compare Abstr., 1906, ii, 873).—By autolysis of ox spleen, *d*-lactic acid, which was identified by the examination of its zinc salt, was found in large amount. Its origin is obscure. By continuing the digestion, it is destroyed to a variable extent.

W. D. H.

**Physico-chemical Changes in Muscle during Fatigue.** GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1907, 6, 158—171).—Faradisation *in situ* of the muscles of dogs produces a decrease in the electrical conductivity and osmotic pressure of the plasma, provided the fatigue lasts long enough. At the same time, the osmotic pressure of the blood-serum increases slightly; its electrical conductivity remains constant.

G. B.

**Action of Normal Fatigue Substances on Muscle.** FREDERIC S. LEE (*Amer. J. Physiol.*, 1907, 20, 170—179).—A full account of experiments previously published.

W. D. H.

**Variations in Muscular Glycogen.** F. MAIGNON (*Compt. rend.*, 1907, 145, 334—337).—Different muscles of the dog, and even different parts of the same muscle, show great differences in glycogen percentage. These differences, as well as the total amount of glycogen, diminish on inanition. Glycogen varies also with the season of the year, being most abundant in February and least in July.

W. D. H.

**Glycogen in the Human Placenta.** GIUSEPPE MOSCATI (*Zeitsch. physiol. Chem.*, 1907, 53, 386—397).—The amount of glycogen in the placenta averages 3 grams (0.5%). After delivery, it diminishes, and twenty-three hours later has practically disappeared; this is not modified by antiseptics. In the placenta of the unripe foetus, glycogen is relatively more abundant.

W. D. H.

**Nucleic Acid from the Human Placenta.** T. KIKKŌJI (*Zeitsch. physiol. Chem.*, 1907, 53, 411—414).—The nucleic acid obtained from

the human placenta resembles that obtained from the thymus in properties and composition. By boiling it with dilute sulphuric acid, the resulting products are : humin substances, lævulic acid, guanine, xanthine, adenine, hypoxanthine, cytosine, and thymine. W. D. H.

**Oxidation Products of Cholesterol in Animal Organs. II.** ISAAC LIFSCHUTZ (*Zeitsch. physiol. Chem.*, 1907, 53, 140—147).—The oxidation products of cholesterol previously described (this vol., i, 315), namely, oxycholesterol,  $C_{26}H_{42}(OH_2)$ , and its ether-like precursor,  $(C_{26}H_{43}O)_2O$ , can be easily recognised spectroscopically after the addition of glacial acetic and concentrated sulphuric acids. The present research shows them to be found in bone-fat and in blood. The examination of other tissues is in progress. W. D. H.

**Uric Acid Synthesis in Men and Mammals.** WILHELM PFEIFFER (*Beitr. chem. Physiol. Path.*, 1907, 10, 324—336).—Feeding experiments on men and apes show that the administration of malonamide, tartronamide, and tartronic acid cause no increase of uric acid formation. Even feeding on uric acid itself has but little effect. In allantoin feeding, there was on one day an increase, which was followed the next day by an abnormally low output. Uric acid synthesis does not occur in men or mammals, and Wiener's positive results with dialuric acid, lactic acid, &c., are criticised. Pathological increase of uric acid formation, as in gout, is attributed to increase of oxidative formation from purine bases. No doubt a factor to be considered in such cases is diminished excretion due to kidney trouble. W. D. H.

**Spontaneous Separation of Casein Compound from Milk.** LUIGI PRETI (*Zeitsch. physiol. Chem.*, 1907, 53, 419—426).—Some milk which had been kept for a year with the addition of chloroform, and of which the reaction remained unchanged, had deposited an abundant precipitate, the supernatant liquid giving only a slight cloud on the addition of acetic acid. On examination, it proved to be a compound of calcium phosphate and calcium caseinate, but whether the caseinogen had been changed into casein was uncertain. In view of opinions recently expressed that the differences between caseinogen and casein are only those of aggregation, it is pointed out that the two substances differ greatly, not only in solubility, but in percentage composition, casein being the richer in calcium and in phosphorus. W. D. H.

**Relation of Phenols to Sulphuric Acid Excretion.** LEOPOLD SPIEGEL (*Arch. exp. Path. Pharm.*, 1907, 57, 270—278).—Phenols are excreted as ethereal sulphates, and, on the assumption that the sulphuric acid originates from a protein side-chain, administration of a phenol should on Ehrlich's hypothesis stimulate an increase in this side-chain, and ultimately lead to an increase of total sulphuric acid in the urine. A phenol was given in the form of an innocuous compound, namely, euguform (a partially acetylated condensation product of guaiacol and formaldehyde, from which guaiacol is liberated in the organism), and the sulphuric acid in the urine was found to be diminished. This is so both for total sulphates and ethereal sulphates, so that the relationship between the two remains much the same. W. D. H.

**Excretion of Alanine by the Urine.** SIEGFRIED OPPENHEIMER (*Beitr. chem. Physiol. Path.*, 1907, 10, 273—276).—R. Hirsch stated that *dl*-alanine in quantities, which in a well-nourished dog is completely assimilated, finds its way partly into the urine when the animal is in a state of inanition. This statement is attributed to the fallacies of the method used. By the use of the naphthalenesulphonic chloride method, alanine can always be detected in the urine if given in sufficient amount. In men, doses of 10 grams were given with a full meal, and from 1 to 2.6 grams were recovered within the next few hours in the urine. W. D. H.

**Nitrogenous Constituents of the Urine.** ADOLF JOLLES (*Biochem. Zeitsch.*, 1907, 5, 419—421).—If urine is treated with sodium hypobromite, the nitrogen evolved is mainly from urea and ammonia, but partly from uric acid and allied substances. If the urine is previously oxidised by potassium permanganate in a sulphuric acid solution, the yield from these other substances is increased. Uric acid itself, however, accounts for only a small proportion of the increase. Illustrative analyses are given. W. D. H.

**Urinary Chromogen following the Administration of Indolecarboxylic Acid.** CH. PORCHER and CH. HERVIEUX (*Compt. rend.*, 1907, 145, 345—347).—If indole is given to a dog, indigotin is obtained from the urine. Scatole and other derivatives of indole do not necessarily give the same result. Indolecarboxylic acid behaves, however, in the same way as indole. W. D. H.

**Abnormal Fat Assimilation in Disease.** OWEN T. WILLIAMS (*Bio-Chem. J.*, 1907, 2, 395—407).—There are conditions in the intestines in which certain soaps or other insoluble compounds of fatty acids are not absorbed. True intestinal sand, appendix concretions, and other deposits are often formed largely of fats and soaps, which are compounds of saturated fatty acids. Clinical and chemical details of cases are given. W. D. H.

**Electrolytes in Pathological Effusions.** OSKAR C. GRUNER (*Bio-Chem. J.*, 1907, 2, 383—394).—An investigation of pathological fluids on the lines of physical chemistry, the chief method employed being that of conductivity. Transudations (that is, non-inflammatory effusions) contain an excess of sodium chloride over achloride electrolytes (Bugarsky and Tangl's classification). Inflammatory effusions or exudations contain a relatively smaller number of chlorides; the increase of achlorides is probably due to the cells these fluids contain. The conductivity of both sets of fluids is remarkably constant. Ovarian cyst fluid usually contains more achlorides than chlorides. W. D. H.

**Liver Diastase in Pancreatic Diabetes.** IVAR BANG (*Beitr. chem. Physiol. Path.*, 1907, 10, 320—323).—These observations on dogs show that the amount of ferment in the liver during pancreatic diabetes is not much greater than in normal rabbits. Pancreatic

diabetes does not appear to be due to increased change of glycogen. Glycogen formation is probably either prevented or greatly lessened. This form of diabetes therefore contrasts with that produced by puncture and by other nervous agencies.

W. D. H.

**Gout and Contracted Kidney.** TOLLENS (*Zeitsch. physiol. Chem.*, 1907, 53, 164—180).—Observations on patients, and on their excretion of uric acid and purine substances, show that alterations in the kidneys, especially those which produce a contracted condition, diminish the excretion of uric acid in gouty people, and this forms a determining factor in the production of gouty deposits in the tissues.

W. D. H.

**The Occurrence of Glyoxylic Acid in the Puerperal Period.** J. HOFBAUER (*Zeitsch. physiol. Chem.*, 1907, 52, 425—431).—Glyoxylic acid was tested for in the urine by the preparation of its calcium salt, by the crystals it forms with phenylhydrazine, and by the addition of peptone (Hopkins-Cole reaction). It is present in numerous cases of pregnancy; this is most marked during the early months, and still more so during the last few days of pregnancy when "pains" are coming on. The relationship of this to allantoin formation during the same period is pointed out.

W. D. H.

**Chemical Alterations of the Blood-Serum in Infections with Pyogenes communis.** GIUSEPPE BOLOGNESI (*Biochem. Zeitsch.*, 1907, 6, 149—157).—Toxic albumoses could not be detected in ox serum which had been infected with *Streptococcus* and with *Staphylococcus*. Sera, infected both *in vivo* and *in vitro*, gave a greater "globulin" precipitate than normal sera; the precipitation was carried out by adding to serum 5 volumes of 1:2000 salicylic acid solution (instead of passing carbon dioxide). A similar increase in the globulin precipitate is brought about even in normal serum by mere exposure to 37° (compare Starke, Abstr., 1901, i, 242; 1902, i, 192; and Moll, Abstr., 1904, i, 356, and 1906, i, 53, on the artificial change of albumin into globulin).

G. B.

**Action of Drugs on Cerebral Vessels.** CARL J. WIGGERS (*Amer. J. Physiol.*, 1907, 20, 206—234).—The influence of a number of drugs is described, such as adrenaline, chloroform, digitalis, &c. No drug possesses an action exclusively confined to nerve terminal or muscle substance, but the graded affinity which exists affords a proof of the existence of nerve fibres in blood vessels. The reactions of the cerebral vessels to adrenaline and apocodeine are such that functional nerve terminals must be assumed to exist there.

W. D. H.

**Action of Organic Ions; Particularly of Guanidine.** HERMANN FÜHNER (*Chem. Zentr.*, 1907, ii, 551; from *Zentr. Physiol.*, 20, 838—839).—The conductivity of the quaternary ammonium hydroxide bases is very nearly the same as that of potassium and sodium hydroxides, and guanidine is almost as strong a base. Since these compounds are dissociated in solution, their pharmacological action



must be caused by ions. The curare and muscarine-like action of quaternary ammonium compounds and the physiological effect of guanidine must be due therefore to organic univalent cations. The action of guanidine and muscarine is affected by calcium chloride in the same way as that of alkali salts. With frogs, large doses of guanidine have a curare-like effect. E. W. W.

**The Behaviour of Urobilin in the Rabbit.** G. FROMHOLDT (*Zeitsch. physiol. Chem.*, 1907, 53, 340—348).—Rabbits' urine is normally free from urobilin. If urobilin prepared from human faeces is given, either pure or in the form of its zinc compound, to rabbits by the mouth, none appears in the urine. If given subcutaneously or intravenously, it rapidly passes into the urine, and from a half to three-quarters of that given is recoverable there. If bilirubin is given by either method, neither it nor urobilin is found in the urine. W. D. H.

**Quantitative Changes in the Composition of the Inorganic Constituents of Tissues in Phosphorus Poisoning.** MARTIN KOCHMANN (*Pflüger's Archiv*, 1907, 119, 417—442).—Phosphorus has a specific influence on calcium metabolism, and its therapeutic use for the improvement of the metabolism of bone rests on a rational basis. It often occurs that as calcium increases in a tissue, potassium and sodium diminish, and vice versa. The analyses given of the tissues in animals treated with phosphorus show also that magnesium alters quantitatively, but the explanation of the change is not evident. The phosphorus in the tissues changes like the calcium. The effects are most marked in the bones, least in the muscles. W. D. H.

**Relative Toxicity of Salts of Chromium, Aluminium, Magnesium, and Rare Metals.** ALEXANDRE HÉBERT (*Compt. rend.*, 1907, 145, 337—340; *Bull. Soc. chim.*, 1907, [iv], 1, 1026—1032).—Zirconium, thorium, aluminium, and chromium salts are toxic to animals and lower organisms, but this is, in part, due to the acidity of the solutions used. Cerium, lanthanum, and magnesium salts are relatively innocuous. No relationship between toxicity and antiseptic power was found, neither does atomic weight or valency form a factor in the toxicity. W. D. H.

**Experimental Treatment of Trypanosomiasis in Rats.** H. G. PLIMMER and J. D. THOMSON (*Proc. Roy. Soc.*, 1907, B, 79, 505—516. Compare Abstr., 1906, ii, 787).—The bisazo-compound, prepared from *o*-dichlorobenzidine and H-acid, and trypan-red were found to have a slight inhibiting effect. Atoxyl caused the entire disappearance of the trypanosomes, but they invariably recurred, in the authors' experience, and death was only delayed.

*p*-Tolylarsonic acid caused an effective temporary disappearance of the trypanosomes even in a recurrent case after the use of atoxyl. Dimethyl sodium arsenate and sodium cacodylate have no effect on the development of the disease, neither have fluorescein nor sodium cinnamate. G. S. W.

## Chemistry of Vegetable Physiology and Agriculture.

**The Products of *Bacillus coli communis* in Symbiosis with Lactic Acid Bacilli.** G. BELONOWSKI (*Biochem. Zeitsch.*, 1907, 6, 251—271).—The lactic acid bacillus, and especially a bacillus of Bulgarian sour milk (*B. bulgaricus*), when grown in broth with *B. coli*, diminish the proteolysis due to the latter organism. No mercaptan or hydrogen sulphide was produced, and the amount of indole was much less than that produced by *B. coli* grown separately. The presence of calcium carbonate in excess increases, and that of milk-sugar decreases, the extent of proteid decomposition. G. B.

**Endotoxins of *Vibrio*'s.** M. ARINKIN (*Biochem. Zeitsch.*, 1907, 6, 226—250). The hæmolysin of *Vibrio Naskin* is an endotoxin, and can be extracted from agar cultures by *N*/200 alkali hydroxide or *N*/10 alkali carbonate; best, however, by physiological saline solution after grinding with sand. It resembles a true toxin in every respect. G. B.

**Influence of Manganese Salts on Alcoholic Yeasts.** E. KAYSER and H. MARCHAND (*Compt. rend.*, 1907, 145, 343—346. Compare this vol., ii, 383).—The suggestion that more complete fermentation might be obtained by yeasts accustomed to the presence of manganese is now shown to be correct. It would probably be advantageous to employ such yeasts in hot climates where fermentation is sometimes slow. N. H. J. M.

**Malic Acid in Musts and Wines. Its Consumption in Fermentation.** W. MESTRESAT (*Compt. rend.*, 1907, 145, 260—261; *Ann. Chim. anal.*, 1907, 12, 347—349).—The amount of malic acid in musts and wines sometimes exceeds that of tartaric acid. During alcoholic fermentation, the amount of malic acid diminishes considerably; its consumption seems to be closely connected with fermentation and the presence of yeast. N. H. J. M.

**Acetylmethylcarbinol in Certain Italian Wines.** GIOVANNI SALOMONE (*Boll. chim. farm.*, 1907, 46, 685—688).—The author has detected acetylmethylcarbinol in two Italian wines. The amount present was estimated (1) by preparing the osazone, crystallising it from acetic acid, and weighing, and (2) by weighing the silver obtained by heating the distillate from the neutralised wine with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), the results being:

	Osazone.	Tollens' reagent.
Wine from S. Venanzo .....	0.2196 %	0.2237 %
„ „ Petrara .....	0.1880	0.2012

The formation of acetylmethylcarbinol in these wines is found to be due to *Bacillus tartricus* (see Grimbert, *Abstr.*, 1901, ii, 328). Results are given of the complete analyses of the two wines. T. H. P.

**Origin of the Deposits of the Colouring Matter of Red Wines.** V. MARTINAND (*Compt. rend.*, 1907, 145, 258—259).—The chief cause of the deposits is the direct oxidation of the polyphenols present in the wines. Deposits are also formed, as shown previously, by the action of aldehydes on the colouring matter. N. H. J. M.

**Accumulation of Radioactive Substances in Vegetable Organisms.** CAMILLO ACQUA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 357—360).—Tarchanoff and Moldenhauer (*Bull. Acad. Sci. Cracow*, 1905) found that, although the whole seeds of wheat, barley, oats, and rye exhibit only very slight radioactivity, the same seeds from which the paleæ have been removed caused rapid discharge of an electroscope, and affect a photographic plate. When the seeds germinate, even in water alone, the radioactive substance passes into the roots, and gradually diminishes from the latter to the stems and leaves. The author has been unable to confirm these results, the only instance in which a slight accumulation of active material was apparent being with seeds germinated in a 0.05% solution of thorium nitrate.

T. H. P.

**Decomposition of Nucleic Acid in Germinating Seeds.** W. ZALESKI (*Ber. deut. bot. Ges.*, 1907, 25, 349—356).—During the germination of seeds of *Vicia Faba*, the protein phosphorus increases in the growing parts, and there is also an increase in the amount of purine bases and protein nitrogen in the axial organs. These results indicate that nucleoproteins are probably formed.

It remains undecided whether nucleic acid is formed in the axial portions of the germinating plant or whether it migrates from the cotyledons. Probably the purine bases and phosphates enter the growing parts of the plant and these unite with other compounds to form nucleic acid. This view is supported by the fact that an enzyme which decomposes nucleic acid is present in the axial organs and that, notwithstanding the enzyme, the nucleic acid increases.

N. H. J. M.

**Autolytic Production of Ammonia in Plants.** W. ZALESKI (*Ber. deut. bot. Ges.*, 1907, 25, 357—360).—Experiments with etiolated *Vicia Faba* seedlings and asparagus juice showed that the amount of ammonia increased during autodigestion. The ammonia may be produced directly from protein or else from the decomposition products of protein.

In a similar experiment with the expressed juice from bulbs of *Allium Cepa*, there was a loss of ammonia, due either to the synthesis of amides or phosphatides, or, perhaps, to direct precipitation as ammonium magnesium phosphate.

N. H. J. M.

**Synthesis of Proteins in Plants.** W. ZALESKI (*Ber. deut. bot. Ges.*, 1907, 25, 360—367).—Experiments in which mutilated potato tubers were kept three or four days in darkness showed that, whilst the protein nitrogen increased, the phosphorus in the form of protein did not, indicating a production of protein free from phosphorus. A similar result was obtained with bulbs of *Dahlia variabilis*. In the case of

*Allium Cepa*, the results indicated an increase both of protein and of phosphorus in the form of nucleic acid.

Notwithstanding the building up of protein, it is shown that *Dahlia* and *Allium* bulbs both contain proteolytic enzymes which break down proteins. The proteolysis is weaker in mutilated than in uninjured bulbs.

N. H. J. M.

**Vegetation of Odoriferous Plants. Successive Conditions of Vegetable Substances.** ROURE-BERTRAND, JUN. (*Chem. Zentr.*, 1907, ii, 474—476; from *Wiss. indust. Ber.*, Roure-Bertrand, jun., [2], 5, 6—29).—The total and water-soluble dry matter and mineral matter were determined in the different parts of *Basilicum* plants at different periods of growth.

N. H. J. M.

**Physical and Chemical Properties of the Fat of the Common Chestnut.** RAFFAELE PALADINO (*Rend. Accad. Sci. Fis. Nat. Napoli*, 1907, [iii], 13, 89—93. Compare Abstr., 1906, ii, 624).—The fat of the common chestnut is not homogeneous, and can be separated by filtration under pressure into an oily portion and one more solid. The former, which has a characteristic penetrating odour, has  $D_{15}^{20}$  0.9045, m. p. 50°, solidifying point 20°, acidity 2.20%, expressed as oleic acid, and saponification index 194.0, and contains volatile acids corresponding with 20 c.c. of *N*/10 alkali per 100 grams. Its spectrum exhibits two absorption bands between lines *C* and *D*. Microscopic examination reveals radiating aggregates of crystals of stearic and palmitic acids, and the elaidic test yields a pale yellow, pasty product. With sulphuric acid, it gives a red coloration which changes to an intense reddish-brown, especially after agitation of the liquid; with nitric acid, it yields a yellow coloration which becomes orange-yellow after shaking, and especially after heating on the water-bath; with Hauchecorne's reagent (3 parts of nitric acid of 40° B. and 1 part of water), it gives an intense red coloration after heating on the water-bath. It absorbs oxygen from the air, undergoing a change in consistency.

T. H. P.

**The Occurrence of Nitrous Acid in Erythrina.** F. WEEHUIZEN (*Pharm. Weekblad*, 1907, 44, 1229—1232).—The author has detected nitrous acid in the leaves of *Erythrina* which had been macerated and put aside for a short time. If the enzyme were killed prior to maceration by immersion of the leaves in boiling water for half a minute, nitrous acid was not found. From this, it is inferred that the nitrous acid is liberated from a glucoside by the action of an enzyme.

A. J. W.

**Formation of Nitric Acid in Soils.** ERNST MURMANN (*Chem. Zentr.*, 1907, ii, 624; from *Oesterr. Chem. Zeit.*, 1907, [2], 10, 181).—Addition of a 0.1% of calcium carbonate accelerated nitrification; with 2%, there was a slight decrease.

N. H. J. M.

**Action of [Furnace] Dust on Soil and Plants.** EMIL HASELHOFF (*Landw. Versuchs-Stat.*, 1907, 67, 157—206).—The com-

position of the dust varies even when similar substances are burnt. The injurious constituents are mainly chlorides, sulphides, and, perhaps, sulphates. When the dust falls on the soil, the sodium it contains is highly injurious to vegetation, especially when the soil is of a kind favourable to the production of hydrogen sulphide. The direct contact of the dust with leaves may result in the leaves being more or less destroyed. In this case, sodium sulphide is the most injurious constituent, then sodium sulphate, and, last, calcium sulphide. The extent of the absorption by the plant of the constituents of the dust will depend on the period of growth at the time. Analysis of unhealthy plants will give indications of the nature of the injurious substance.

N. H. J. M.

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## Analytical Chemistry.

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**Retention of Chemical Substances by Filter Paper.** MANSIER (*Amer. Chim. anal.*, 1907, 12, 397—400. Compare Abstr., 1902, ii, 690).—Further experiments on the retention and uneven distribution of mercuric chloride, quinine sulphate, morphine, hydrochloride, &c., in filter papers. L. DE K.

**Gasometric Estimation of Hydrogen Peroxide.** WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1907, 29, 1315—1319).—The author's ureometer (Abstr., 1906, ii, 816) may be used also for the estimation of hydrogen peroxide. When hydrogen peroxide is treated with sodium hypobromite solution, oxygen is liberated, the volume of which may be accurately measured, and the corresponding weight calculated by aid of a table. L. DE K.

**Reaction of Silver Nitrate and Iodine. Standardisation of Solutions by Saturation. Iodometry by Means of Silver Nitrate.** WLADIMIR E. PAWLOFF and S. D. SCHEIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 943—947).—The reaction of silver nitrate with iodine proceeds according to the equation,  $5\text{AgNO}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} = 5\text{AgI} + 5\text{HNO}_3 + \text{HIO}_3$ , which can be employed: (1) for iodometric purposes; (2) to determine or to verify the strength of alkali hydroxides and of barium hydroxide, and (3) for the titration of silver nitrate. The acidic hydrogen in the reaction mixture of iodine and silver nitrate is invariably found to be 99.71 of the theoretical value; this is due probably, either to the reaction not proceeding to a finish, or to the formation of double compounds of silver iodide with hydrogen iodide or with silver nitrate. Z. K.

**Use of Calcium Nitrate in Oxidising Fusions.** ALBERT STUTZER (*Zeitsch. angew. Chem.*, 1907, 20, 1637).—If vegetable matter is incinerated, the phosphorus and sulphur in organic com-

bination may be lost partially unless the ash is strongly alkaline ; hence, in the estimation of the total phosphorus and sulphur, it is necessary to fuse with an oxidising agent. Basic calcium nitrate is recommended for this purpose, as it melts below  $100^{\circ}$ , and no loss by detonation or spirting is to be feared. G. Y.

**The Use of Titanium Trichloride in Volumetric Analysis. III.** EDMUND KNECHT and EVA HIBBERT (*Ber.*, 1907, 40, 3819—3827).—An account of various modifications which have been made in the methods described previously for estimating nitro-compounds, indigotin, thioindigotin, azo-dyes, and iron by means of titanium trichloride (*Abstr.*, 1903, ii, 509 ; 1905, ii, 872, 910). Sodium hyposulphite may be readily estimated by adding the solid salt to a solution of methylene-blue, and determining the excess of unreduced dye by means of titanium trichloride. It is also shown that *o*-nitrobenzeneazophenol (compare Grandmougin, this vol., i, 166) and *p*-nitro-*p'*-methoxyazobenzene (compare Schmidt, *Abstr.*, 1905, i, 951) are completely reduced by titanium trichloride. W. H. G.

**The "Nitron" Method for the Estimation of Nitric Acid.** STANLEY W. COLLINS (*Analyst*, 1907, 32, 349—357).—This method was found to be trustworthy for the estimation of nitric acid in potassium nitrate, calcium nitrate, magnesium nitrate, in mixtures of potassium nitrate with magnesium and potassium sulphates, and in fertilisers containing potassium nitrate, ammonium sulphate, and calcium phosphates. The method as described originally by Busch (*Abstr.*, 1905, ii, 282) was employed without modification. The method was also found to be useful for the estimation of nitric acid in water (compare *Abstr.*, 1905, ii, 418). W. P. S.

**Estimation of Phosphoric Acid by the Pemberton and Pemberton-Sulphuric Acid Methods.** G. H. G. LAGERS (*Chem. Weekblad*, 1907, 4, 632—634. Compare Pemberton, *Abstr.*, 1894, ii, 254 ; 1895, ii, 415 ; Hissink and van der Waarden, *Abstr.*, 1905, ii, 419).—The author criticises unfavourably the Pemberton and Pemberton-sulphuric acid methods for the estimation of phosphoric acid. A. J. W.

**Volumetric Estimation of Phosphoric Acid.** W. D. RICHARDSON (*J. Amer. Chem. Soc.*, 1907, 29, 1314—1315).—Two grams of the fertiliser are heated with 30 c.c. of strong nitric and 5 c.c. of hydrochloric acid, and then boiled with addition of 10 c.c. of water for five minutes ; 25—30 c.c. of 10% barium chloride solution are added, and, when cold, the whole is diluted to 250 c.c. The liquid is then filtered through a dry filter, the first portion of the filtrate is rejected, and 25 c.c. are titrated by the A.O.A.C. modification of the Pemberton method, which will now give satisfactory results owing to the absence of sulphates. L. DE K.

**Estimation of Small Quantities of Arsenic in Foods, &c.** BOUWE SJOLLEMA and M. J. VAN'T KRUY ( *Chem. Weekblad*, 1907, 4, 547—552).—A combination of the process devised by Thorpe (*Trans.*,

1906, 408) and that of Berntrop (Abstr., 1906, ii, 706). The organic matter is destroyed by moistening 2 grams of the cut-up material with hot water and then adding 20 c.c. of lime water and 0.5 gram of magnesium oxide. The whole is well mixed with a glass rod and heated until the mass has charred completely. The carbon is then burnt off in a muffle. The ash is dissolved in 20 c.c. of dilute sulphuric acid and boiled in a flask with 0.5 gram of potassium metarsulphite. When the free sulphur dioxide has completely evaporated, the liquid is allowed to cool and diluted to 50 c.c. An aliquot portion is then treated as directed by Berntrop. The authors advise the use of a second mirror tube to retain traces of arsenic which would otherwise be lost. When it is thought that all the arsenic has deposited, the experiment should still be continued for another half-hour to make certain. The estimation of the arsenic by means of standard mirrors is not safe, but the iodine titration of the arsenical mirrors gives very satisfactory results.

The process is not applicable to organic arsenical compounds.

L. DE K.

**Filippi's Method for Separating the Acids of Arsenic from Urine.** M. TONEGUTTI (*Boll. Chim. Farm.*, 1907, 46, 681—685).—In his thesis on "Toxicology of Arsenical Compounds" (Florence, 1904), Filippi states that alkali arsenites and arsenates are precipitated quantitatively from solution by a reagent composed of 15 grams of barium chloride, 20 c.c. of concentrated ammonia solution, and 80 c.c. of distilled water, and that this method may be used for the separation of arsenites and arsenates from urine. The author finds that the above ammoniacal barium chloride solution precipitates arsenic trioxide or arsenites only to a small degree; arsenates are well precipitated by excess of barium chloride and ammonia, but in proportions different from those given by Filippi.

T. H. P.

**Estimation of Carbon Dioxide in Electrolytic Chlorine, Bleaching Powder, or Bleaching Fluids.** PETER PHILOSOPHOFF (*Chem. Zeit.*, 1907, 31, 959—960).—A slight modification of Ferchland's process (compare Abstr., 1906, ii, 842). The electrolytic chlorine or that evolved by acting on bleaching powder, &c., with hydrochloric acid is collected in a Bunte burette and the chlorine is absorbed by metallic mercury, the contents being finally well shaken. The coating of mercurous chloride is removed by shaking with a few c.c. of brine, and a reading of the residual gas is taken with the usual precautions. The amount of carbon dioxide is then found as usual by absorption with aqueous potassium hydroxide.

L. DE K.

**Rapid Estimation of Carbon and Hydrogen in Organic Substances.** PIERRE BRETEAU and HENRI LEROUX (*Compt. rend.*, 1907, 145, 524—526 \*).—A combination of the methods of Morse and Taylor (Abstr., 1905, ii, 480), Carrasco and Plancher (Abstr., 1906, ii, 201), and Dennstedt (Abstr., 1905, ii, 202).

About 0.15 gram of the substance is placed in a boat and heated slowly at intervals in a current of purified oxygen. The products

\* And *J. Pharm. Chim.*, 1907, 26, 385—392.



are then passed over a spiral of platinum heated to redness by electricity, so as to ensure perfect combustion. Towards the end, the boat is heated to intense redness to burn the residual carbon. The operation takes from fifteen to forty minutes.

If the substance contains nitrogen, sulphur, or halogens, the products of combustion are passed through a U-tube containing lead peroxide heated at  $170^{\circ}$  before being absorbed in the usual apparatus.

L. DE K.

#### Simplification of Dennstedt's Method of Combustion.

R. BAUMERT (*Ber.*, 1907, 40, 3475—3477).—In using Dennstedt's method for the estimation of carbon and hydrogen, the author found that the method occasionally gave bad results when the substance burned with difficulty. Various modifications of the method were accordingly devised. The Dennstedt oven was used, but the tubes were 18 mm. in diameter. Copper oxide asbestos was used in place of platinised quartz when the substance did not contain halogen; when halogen was present, platinised asbestos was used. Lead peroxide asbestos was substituted for lead peroxide, and silver asbestos for molecular silver. The Dennstedt absorption apparatus was employed. Details are given regarding the preparation of the materials in question, and the method of conducting the combustion is also described.

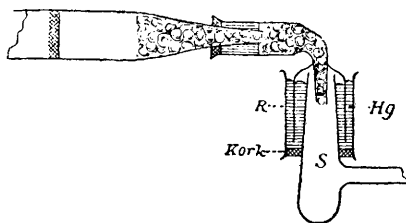
A. McK.

**The Use of Palladium as a Contact Substance in Elementary Analysis.** MAX DENNSTEDT (*Ber.*, 1907, 40, 3677—3681).—A criticism of Jacobsen and Landesen's work (this vol., ii, 718). Palladium is in no wise superior to platinum as a contact substance.

W. R.

**Mercury Seal instead of Cork or Indiarubber in Organic Analysis.** J. MAREK (*J. pr. Chem.*, 1907, [ii], 76, 180—184).—The arrangement shown in the annexed figure is recommended instead of a cork or rubber stopper for

connecting the absorption apparatus with the combustion tube in elementary analysis. The joint of the combustion tube with the adapter, which may be of soft glass, is luted with asbestos covered with fused silver chloride; the end of the combustion tube and the adapter are filled with silver



lace, which conducts heat sufficiently to prevent condensation of water. On completion of the combustion, the mercury seal is removed and *S*, which is the side-tube of the water absorption apparatus, is covered with a glass cap. The horizontal part of the adapter may be lengthened and filled with lead dioxide for the absorption of halogens or oxides of sulphur and nitrogen, when it must be heated in an air-bath.

G. Y.

**Estimation of Potassium by the Perchloric Acid Method in Manures, Soils, Crops, &c.** VINCENT SCHENKE and PAUL KRUGER (*Landw. Versuchs.-Stat.*, 1907, **67**, 145—156).—When the perchloric acid method is employed, it is important first to completely precipitate the sulphuric acid, avoiding the addition of more than a slight excess of barium chloride. Phosphoric acid must also be removed, and, after addition of perchloric acid, the hydrochloric acid must be completely expelled.

Results of a considerable number of analyses are given showing agreement with the platinic chloride method. N. H. J. M.

**Eosin Reaction of Glass at Fractured Surfaces.** FRANZ MYLIUS (*Zeitsch. anorg. Chem.*, 1907, **55**, 233—260).—The eosin test described in a previous paper (Abstr., 1889, 549) has now been developed into a quantitative method for the rapid estimation of the quality of glass. It is pointed out that the test should be applied to a freshly-broken surface, and a method for obtaining such a surface, which should be smooth and 100—200 sq. mm. in section, is described. The preparation and storage of the eosin solution are also fully discussed.

In the majority of the experiments, the prepared surface was subjected to the direct action of the ethereal solution of eosin, which was saturated with water, and the amount of action was estimated by the depth of colour produced when the surface was pressed on filter paper, or, more accurately, by dissolving the deposited alkali salt of eosin in water and estimating it colorimetrically.

The amount of eosin deposited per unit area in one minute, resulting from a rapid hydrolytic decomposition of the glass, is taken as a measure of the "hygroscopic character" of the glass. In the case of certain resistant glasses, the amount deposited after prolonged contact is not much greater than after one minute, owing to the production of practically impermeable surface layers, but in inferior glasses the amount of action increases regularly with the time of contact.

The "weathering" of a glass (measure of its resistance to the disintegrating effect of the moisture and carbon dioxide of the atmosphere) is best judged from the ratio of the amount of eosin deposited in one minute to that on prolonged contact (one day).

In the case of the light optical glasses, the eosin values determined as above with fresh surfaces can be taken as a measure of the resistant character of the cut and polished article, but the behaviour of heavy glass containing lead and barium has not yet been investigated adequately in this respect. G. S.

**Indicator for the Estimation of Free Acidity in Zinc Chloride Solutions, &c.** CARL KIRSCHNICK (*Chem. Zeit.*, 1907, **31**, 960).—One gram of methyl-orange and one gram of indigo-carmin are dissolved separately in one litre of water. To prepare the indicator, 20 c.c. of the methyl-orange and 60 c.c. of the indigo-carmin are mixed and made up to a litre.

When applying the test, 10 c.c. of the indicator are diluted to 100 c.c., and 10 c.c. of undiluted (25% Zn) zinc chloride solution are

added. A permanent green coloration shows alkalinity; a rose coloration shows acidity. The liquid is then titrated either with standard acid or alkali. The process also serves for the estimation of free acid in superphosphates.

L. DE K.

#### Certain Methods of Estimating Lead Peroxide in Minium.

CARMELO MARCHESE (*Gazzetta*, 1907, 37, ii, 289—296).—The author has examined the following methods of estimating lead peroxide in red lead: (1) that of Forestier (*Annal. Lab. Chim. R. Gabelle*, 5, ii, 486), in which the red lead is heated for half an hour on the water-bath with 10 c.c. of 10% acetic acid solution and 20 c.c. of water, the insoluble residue, after washing, representing lead peroxide and other insoluble matter; (2) Szterkher's method (*Abstr.*, 1902, ii, 531), depending on the insolubility of lead peroxide in nitric acid (2 c.c. of D 1.18 and 30 c.c. of water) free from nitrous acid; (3) Topf's method (*Abstr.*, 1887, ii, 997) and Fresenius and Will's method.

Forestier's method does not give good results unless the heating is prolonged and a greater proportion of acetic acid used—greater than that indicated by this author. Fresenius and Will's method gives good results, but an error of a few tenths of 1 mg. in the weight of the carbon dioxide makes a comparatively large error in the result. The best methods are those of Szterkher and Topf, the latter in a slightly modified form.

T. H. P.

**Acidimetric Titration of Mercuric Cyanide.** S. GOY (*Chem. Zentr.*, 1907, ii, 560—561: from *Apoth. Zeit.*, 22, 532—533).—0.25 Gram of the sample is dissolved in 200 c.c. of water, 2 grams of potassium iodide and one drop of 0.2% methyl-orange solution are added, and the liquid is titrated with *N*/10 hydrochloric acid; 2 mols. of hydrogen chloride = 1 mol. of mercuric cyanide. After titration, the liquid contains the mercury as the double mercuric potassium iodide compound. The liberated hydrogen cyanide does not interfere.

In basic mercuric cyanide, the oxide may be titrated directly with hydrochloric acid; another portion is then titrated with addition of potassium iodide.

L. DE K.

**Normal Proportion of Manganese in Mistelles [Fortified Musts].** GUSTAVE MASSOL (*Bull. Soc. chim.*, 1907, [iv], 1, 953—956).—In order to prevent insufficiently fortified musts from undergoing fermentation, sulphurous acid or sodium hydrogen sulphite is sometimes added, excess of this agent being in some cases destroyed by means of potassium permanganate. The latter may be detected by estimating the manganese present in the wine.

The author has estimated the proportion of manganese normally present in various fortified musts and wines to which no permanganate has been added, the procedure being as follows. The sulphated ash of 25 c.c. of the wine is dissolved in 5 c.c. of concentrated nitric acid, the solution mixed with 20 c.c. of water and 2 grams of lead peroxide, and boiled for two minutes. The coloured liquid thus obtained is

compared with a series of control tubes, prepared, under the same conditions, from standard manganese sulphate solutions containing from 0.1 to 4.0 milligrams of MnO per litre. No relation exists between the intensity of colour and the manganese content of the unfermented fortified musts, which contain from 0—0.010 gram MnO per litre (compare Maumené, *Abstr.*, 1884, 879). T. H. P.

**The Behaviour of Molybdic Acid in the Zinc Reductor.** D. L. RANDALL (*Amer. J. Sci.*, 1907, [iv], 24, 313—316. Compare Miller and Frank, *Abstr.*, 1903, ii, 761).—The reducing action of zinc on molybdenum trioxide in sulphuric acid solution has been examined. To prevent oxidation by the air, the reduced molybdenum solution was brought into contact immediately with excess of an oxidising agent. Potassium permanganate cannot be used as the oxidising agent, for this is sensibly reduced by the hydrogen evolved, as was shown by blank experiments. By using a solution of iron alum, the molybdic acid is found to be accurately reduced to the sesquioxide,  $\text{Mo}_2\text{O}_3$ . Addition of phosphoric acid to the ferric solution makes the end point in the titration of the reduced iron with permanganate quite easy to recognise.

It is shown that the method may be applied to the estimation of phosphorus after precipitation as ammonium phosphomolybdate.

H. M. D.

**Detection of Sugar in Urine.** N. RUSTING (*Pharm. Weekblad*, 1907, 44, 1178—1184).—The author discusses the methods employed in the detection of sugar in urine, and recommends the following procedure. Dilute a small quantity of urine with about four times its volume of water, add two drops of platinic chloride solution, and a small proportion of Nylander's reagent. Heat the mixture to incipient ebullition, and set it aside. If a distinct darkening in colour does not develop within one minute, the percentage of sugar present is negligible.

A. J. W.

**Estimation of Lævulose and Dextrose.** LÉON PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1907, 25, 125—127).—The following formulæ are given for the estimation of dextrose and lævulose in mixtures of the same, the reducing power of invert sugar being taken as the basis of the calculation. In 100 grams of the mixture, let there be  $x$  grams of dextrose and  $y$  grams of lævulose, and let  $p$  and  $p'$  be the polarisation values compared with sucrose, whilst  $r$  and  $r'$  are the reducing powers compared with that of invert sugar, then  $P$  (the specific rotation of the mixture) will equal  $px + p'y$ , and  $R$  (the quantity of the reducing sugars) will equal  $rx + r'y$ . Now  $p = 0.793$ ,  $p' = 1.356$ ,  $r = 0.960$ , and  $r' = 1.040$ , whence  $P = 0.793x - 1.356y$  and  $R = 0.960x + 1.040y$ .

Therefore  $x = \frac{1.356R + 1.040P}{2.126}$  and  $y = \frac{0.793R - 0.960P}{2.126}$

W. P. S.

**Toxic Hungarian Haricots.** EVESQUE, VERDIER, and BRETIN (*J. Pharm. Chim.*, 1907, 8, 348—349).—Morphologic and histologic

characters are insufficient to pronounce haricots non-toxic; they should be tested chemically for cyanogenetic principles. These may be detected by macerating the beans with water and a little tartaric acid, and testing the vapours for hydrocyanic acid by the odour or with paper soaked in sodium picrate, which turns a garnet colour. Quantitatively, the amount of hydrogen cyanide given off is estimated as follows: 25 grams of the coarsely-powdered beans are digested for twelve hours in a distilling flask with 250 c.c. of water and 1 gram of tartaric acid. The flask is connected with a Cloez condenser, the end of which dips into a beaker containing 20 c.c. of water and 10 c.c. of ammonia to prevent any loss of hydrocyanic acid. Distillation is continued until 20—40 c.c. of liquid have passed over, and until the last portion of the distillate shows freedom from hydrocyanic acid by not bleaching water coloured with iodine. The ammoniacal liquid is then mixed with 10 drops of 20% potassium iodide and titrated with *N*/100 silver nitrate until a permanent turbidity is formed. One c.c. of silver solution = 0.0216 gram of hydrogen cyanide. Hungarian beans may yield as much as 0.342 gram of the acid per kilo.

L. DE K.

#### Pettenkofer's Reaction for the Detection of Bile Acids

JULES VILLE (*Bull. Soc. chim.*, 1907, [iv], 1, 965—968).—The violet-purple coloration obtained by the addition of sulphuric acid to bile acids in presence of traces of sucrose has been attributed by Mylius (*Abstr.*, 1887, 1149) to the furfuraldehyde formed from the sugar under these conditions. On using furfuraldehyde in place of sucrose, the author finds that the colour obtained is different, and that the spectrum exhibits two absorption bands with mean wave-lengths of  $\lambda = 510$  and 546, whilst, when sucrose is used, the mean wave-lengths of the two absorption bands are 528 and 576. If rise of temperature is avoided by adding the bile and sucrose or furfuraldehyde to a cooled mixture of equal volumes of sulphuric acid and water, the distinctive characters of the colorations do not appear so quickly; the author recommends this manner of applying the test. Further experiments show that the coloration produced when sucrose is employed is due to the products of hydrolysis of the sugar, especially to the levulose.

T. H. P.

**Detection of "Saccharin" in Wines.** ACHILLE TAGLIAVINI (*Boll. chim. farm.*, 1907, 46, 645—646).—Twenty c.c. of wine containing 0.0002 gram of saccharin was acidified with 2 drops of hydrochloric acid, evaporated to one-half its volume, and agitated with 40 c.c. of pure toluene. The residue obtained on evaporating the filtered toluene extract had a sweet taste, and, when dissolved in water, filtered, and mixed in the cold with mercurous nitrate solution, gave a faintly turbid liquid which gradually precipitated a white mercury compound of "saccharin" (Vitali, *Abstr.*, 1900, ii, 57). Toluene also extracts salicylic acid from wines which contain it; in this case, the residue from the toluene gives a violet coloration when dissolved in water and treated with ferric chloride. When salicylic acid is present, the sweet taste of the toluene residue must be depended on for the detection of saccharin.

T. H. P.

**Detection of Glutamine.** EUGENE SELLIER (*Bull. Assoc. chim. Sucr. Dist.*, 1907, 25, 124—125).—Having been quoted by Schulze as finding that magnesia has no action on glutamine in aqueous solution, even at a boiling temperature, the author wishes to contradict this statement. Glutamine is decomposed when its aqueous solution is boiled with magnesia at the ordinary pressure of the atmosphere, but, if the pressure be reduced sufficiently to cause the solution to boil at a temperature of from 35—40°, reaction does not take place. Under these conditions, ammonium salts may be removed completely from glutamine without injury to the latter.

W. P. S.

**Estimation of Acetanilide in Headache Powders.** ATHERTON SEIDELL (*J. Amer. Soc. Chem.*, 1907, 29, 1091—1093).—The acetanilide is extracted by means of chloroform and the residue heated for an hour on the steam-bath with dilute hydrochloric acid (1:4), or else boiled vigorously for five minutes. Or the powder may be extracted with a small quantity of water to remove soluble matter and the residue then submitted to the acid treatment. In either case, the acetanilide is decomposed, yielding aniline, which is then estimated by the well-known bromine titration.

Caffeine and salol do not interfere with the process, but phenacetin and antipyrin prevent its application.

L. DE K.

**Fluorescence of Cocaine and Tropacocaine.** C. REICHARD (*Pharm. Zeit.*, 1907, 52, 698—699).—When crystals of cocaine hydrochloride are examined with the microscope, they exhibit, when viewed at certain angles, a striking coloration, due to refraction and dispersion. As the microscope stage is turned, the colour changes from blue to emerald-green. The same phenomena are shown by tropacocaine hydrochloride. Small quantities of cocaine can be detected by placing a drop of the solution of the hydrochloride on a slide, allowing it to evaporate spontaneously, and examining the crystalline residue. By means of the colour phenomena, 0.000001 gram of the alkaloid can be detected. This "fluorescence" is considered to be due chiefly to the presence of the benzoyl group in the compounds. Benzoic acid exhibits similar changes of colour when treated in the same way.

E. G.

**Estimation of Ecgonine in Java-Coca.** MAURITS GRESHOFF (*Pharm. Weekblad*, 1907, 44, 961—963).—The total alkaloids obtained from 15 grams of powdered coca-leaves in the manner previously described by the author (*ibid.*, 1905, 286—290) are boiled for an hour in a reflux apparatus with thirty times the weight of dilute hydrochloric acid (Dutch Pharmacopœa) and an equal volume of water. The total alkaloids need not be dried for three hours at 95° as directed previously. When cold, the solution is filtered and extracted twice in succession with an equal volume of ether. The aqueous solution is then evaporated to dryness on the water-bath, and the residual ecgonine hydrochloride, after being dried at 90—95°, is weighed. The percentage of the crystalline ecgonine (which contains 1 mol. of water)

is then found by multiplying with the factor 6.11, namely,  
 $(100/15) \times (203/221.5)$ .  
L. DE K.

**Reactions of Scopolamine.** C. REICHARD (*Pharm. Zentr.-h.*, 1907, 48, 659—664).—If a small quantity of the alkaloid is treated with a drop of concentrated sulphuric acid, the crystals are blackened, but no other change takes place in the cold. On warming the mixture, a bright blue coloration is produced. A mixture of scopolamine and potassium dichromate is coloured deep blue on the addition of a little concentrated sulphuric acid. Nitric acid gives no colour reaction with the alkaloid, but the latter reduces mercuric and copper salts. On evaporating an aqueous solution of the alkaloid with the addition of  $\alpha$ -naphthol, moistening the residue with hydrochloric acid, again evaporating and treating the residue with a drop of concentrated potassium hydroxide solution, a bright yellow coloration is obtained; the colour changes to green when the moist mass is heated. A bright blue coloration is produced when a mixture of scopolamine and potassium ferrocyanide solution is evaporated to dryness and treated with a drop of hydrochloric acid. The author employed scopolamine hydrobromide in investigating the above reactions. W. P. S.

**Alkaloid Reactions (Yohimbine).** C. REICHARD (*Pharm. Zentr.-h.*, 1907, 48, 755—761).—Yohimbine, m. p. about  $234^{\circ}$ , becomes yellow on exposure to light and air, and is dextrorotatory (compare Spiegel, *Abstr.*, 1899, i, 966). If a small amount of the hydrochloride, m. p. about  $300^{\circ}$ , is rubbed with a drop of concentrated sulphuric acid, each particle appears to swell to a transparent, granular mass, whilst a white, crystalline rim is formed at the edge of the liquid; the residue obtained on removal of the excess of acid forms a transparent, colourless varnish with a brilliant light blue and yellowish-brown fluorescence. When heated with concentrated sulphuric acid, the hydrochloride gives a blue coloration, becoming again colourless, or a dirty, greyish-blue on cooling. A highly characteristic reaction for yohimbine is obtained with 25% colourless nitric acid, which gives an intense yellow coloration, and on evaporation leaves a residue of yellow, microscopic needles; when gently heated, this residue partially disappears, the remainder becoming greenish-yellow and resuming the original shade on cooling. With dilute aqueous potassium hydroxide, yohimbine hydrochloride forms small prisms similar to those obtained from solutions of morphine salts; the alkaline solution and crystals have a blue fluorescence. When treated with aqueous potassium dichromate and allowed to evaporate, the hydrochloride forms a yellow residue, which gradually becomes blue in the centre. A similar, but darker, blue is obtained in the same manner with dilute ammonium molybdate. The blue residues dissolve in concentrated sulphuric acid forming colourless solutions, becoming in the dichromate mixture brown, or with the molybdate mixture blue, when diluted and dried on filter paper. On evaporation with aqueous potassium ferrocyanide, yohimbine hydrochloride forms a blue residue, which appears by total reflexion to have a silver rim, and is characterised by the presence of golden spots. When treated with a

drop of 25% hydrochloric acid, this residue becomes colourless, and if then dried forms a bluish-white mass which if observed at a certain angle appears as a mixture of black crystals and colourless yohimbine ferricyanide crystals. This salt, when formed by evaporation of the hydrochloride with potassium ferricyanide, is obtained in characteristic crystals, becoming yellowish-green on evaporation with 25% hydrochloric acid. With sodium nitroprusside, the hydrochloride forms a white residue with a silver-grey sheen which gradually disappears, the mass becoming bluish-white. The microscopic appearance of this residue serves to distinguish yohimbine from cocaine. G. Y.

**Detection of Magenta.** ARTURO CAROBBIO (*Boll. chim. farm.*, 1907, 46, 535—537).—The author gives the following two methods for the detection of magenta in wines, syrups, &c. (1) To 1 c.c. of the liquid are added 1—2 c.c. of paraldehyde and 4—5 drops of an aqueous solution of potassium iodide (1:1). The tube is well shaken, the formation of an emulsion being avoided. If the paraldehyde, which separates after a time, is coloured red, magenta is present. The paraldehyde may be replaced either by cineol or by ether containing a small proportion of paraldehyde or cineol. If the liquid to be tested contains sufficient alcohol to render it miscible with the paraldehyde, cineol, or ethereal reagent, it should be suitably diluted with water before applying the test. The reaction is sensitive to less than 0.000001 gram magenta. (2) One c.c. of the liquid is shaken in a test-tube with 2 c.c. of water and 2 c.c. of a saturated chloroform solution of salicylic acid. If magenta is present, the chloroform which separates subsequently will contain ros-aniline salicylate, and will hence be coloured red. T. H. P.

**Application of Benzidine in the Forensic Detection of Blood.** FRANZ UTZ (*Chem. Zeit.*, 1907, 31, 737—738).—The author recommends the benzidine test for blood as proposed by Schlesinger and Holst, provided that the reagents are made freshly. The test is carried out as follows.

Ten to twelve drops of a strong solution of benzidine in glacial acetic acid are mixed with 2 c.c. of a 3% hydrogen peroxide solution, and a few drops of the suspected solution are added. In the presence of blood, a green, bluish-green or even pure blue coloration is obtained. Traces of iron do not interfere, but pus should be absent. The test is sharper than the guaiacum reaction. L. DE K.

**Estimation of Methylarsine Di-iodide and Oxide.** J. BOUGAULT (*J. Pharm. Chim.*, 1907, [vi], 26, 193—194. Compare this vol., ii, 828).—Methylarsine di-iodide and oxide may be estimated by titrating their aqueous solutions with a potassium iodide solution of iodine, the reactions being expressed by the equations:  $\text{AsMeI}_2 + \text{I}_2 + 3\text{H}_2\text{O} = \text{AsMeO}(\text{OH})_2 + 4\text{HI}$ ;  $\text{AsMeO} + \text{I}_2 + 2\text{H}_2\text{O} = \text{AsMeO}(\text{OH})_2 + 2\text{HI}$ . The reactions take place in an acid medium, and are instantaneous. It is probable that this method of estimation is applicable to compounds containing a hydrocarbon radicle other than methyl. T. H. P.



## General and Physical Chemistry.

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**Double Refraction and Dispersion of some Double Platino-cyanides.** HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1907, 44, 23—44. Compare Abstr., 1907, ii, 689).—Determinations of the refractive indices for light of different wave-lengths were made of the following salts:  $\text{CaPtCy}_4 \cdot 5\text{H}_2\text{O}$ ;  $\text{BaPtCy}_4 \cdot 4\text{H}_2\text{O}$ ;  $\text{NaKPtCy}_4 \cdot 3\text{H}_2\text{O}$ . In this series of salts, a connexion is traced in the variation of the absorption and surface coloration, and of the double refraction, dispersion, and optic axial angles. L. J. S.

**Experiment on Colour Dispersion.** A. STROMAN (*Chem. Zentr.*, 1907, ii, 878; from *Zeitsch. phys.-chem. Unter.*, 1907, 20, 240—242).—The apparatus consists of a flask fitted with a double-bored stopper, through which pass two tubes, one bent at right angles, the other drawn out to a fine jet which passes into a tube 20 cm. long and 1 cm. wide, forming a Bunsen burner. A stream of coal-gas is passed through the flask, which contains a solution of sodium and lithium nitrates, marble, and nitric acid. The escaping gas is lit at the top of the wide tube and a platinum wire placed in the flame. On examining the flame through a carbon disulphide prism at a distance of 3 to 4 metres, four single-coloured flames produced by the sodium, lithium, and calcium are observed. W. H. G.

**Devices Facilitating the Study of Spectra.** W. NOEL HARTLEY (*Sci. Proc. Roy. Dubl. Soc.*, 1907, [ii], 11, 237—242).—In producing flame spectra at high temperatures, the author has used slips of Donegal cyanite (98% of aluminium silicate), ash-less filter papers, carborundum, quartz fibres, or asbestos fibres as support for the material which is being tested. The Mecke burner is recommended as being very suitable for spectroscopic purposes. At the high temperature of this burner, constant spectra are obtained, even if oxides or sulphates are employed. An oxide supported in the flame of a Mecke burner may be made to yield a chloride spectrum by supplying the burner with gas mixed with chloroform vapour. In the measurement of bands, the Mecke burner possesses decided advantages, since its flame is not subject to fluctuations in temperature, and is on the whole hotter than the Bunsen flame; the bands are therefore of uniform brilliancy and width, and may be photographed easily. Flame spectra of calcium, strontium and barium show that, with a constant exposure, the width of the bands increases with the quantity of substance in the flame; with a constant quantity of substance, the width and intensity of the bands increase with the exposure. J. C. P.

**Index of the Principal Lines of the Spark Spectra of the Elements.** JAMES H. POLLOK (*Sci. Proc. Roy. Dubl. Soc.*, 1907, [ii], 11, 184—216).—This index is compiled to facilitate the use of spectrum photography in chemical analysis. The author has selected from

Watts's "Index of Spectra" the principal lines of all the elements and arranged them in order of their wave-lengths. The intensity of the lines is given, and Hartley's quantitative spectra are indicated by Greek letters. The substance to be examined should be brought into solution, and the solution is then sparked between gold electrodes.

J. C. P.

**Wave-length Tables of the Spectra of the Elements and Compounds.** Sir HENRY E. ROSCOE, MARSHALL WATTS, Sir W. NORMAN LOCKYER, Sir JAMES DEWAR, GEORGE D. LIVEING, ARTHUR SCHUSTER, W. NOEL HARTLEY, WOLCOTT GIBBS, Sir WILLIAM DE W. ABNEY, and WALTER E. ADENEY (*Brit. Assoc. Report*, 1906, 76, 161—227).—Wave-length tables of the spark spectrum of chromium and of the spectrum of palladium.

G. T. M.

**Emission Spectra of Selenium.** JOSEF MESSERSCHMITT (*Chem. Zentr.*, 1907, ii, 879—880; from *Zeitsch. wiss. Photographie, Photo-physik u. Photochemie*, 1907, 5, 249—278).—The character of the lines in the vacuum tube spectra of selenium depends on the length of the spark and capacity of the tube, whereas the intensity of the lines varies with the pressure in the tube; if the self induction is high, the line spectrum changes into a band spectrum. Self induction likewise causes most of the lines in the spark spectrum to disappear; the spectrum so obtained is similar to the arc spectrum. The spark spectrum also varies with the nature of the electrodes. The same bands appear in the flame and Geissler tube spectra, although the spectrum becomes more continuous as the temperature of the flame increases.

W. H. G.

**Quantitative Spectra of Iron, Aluminium, Chromium, Silicon, Zinc, Manganese, Nickel, and Cobalt.** JAMES H. POLLOK and A. G. G. LEONARD (*Sci. Proc. Roy. Dubl. Soc.*, 1907, [ii], 11, 217—228).—These spectra have been taken, with slight modifications, by Hartley's method (see *Phil. Trans.*, 1884, 175, 49, 325; also *Abstr.*, 1885, 466). The object is to record the residuary lines, that is, the lines which are the last to disappear from the spark spectrum of a salt solution as the latter is diluted. The method of procedure adopted was to make a strong solution of the chloride of the element and dilute solutions containing one gram of the element in every 100, 1000, 10,000, or 100,000 parts of solution; these solutions were then sparked with gold electrodes

J. C. P.

**Quantitative Spectra of Barium Strontium, Calcium, Magnesium, Potassium, and Sodium.** JAMES H. POLLOK and A. G. G. LEONARD (*Sci. Proc. Roy. Dubl. Soc.*, 1907, [ii], 11, 229—236).—The degree of persistency of the lines obtained by sparking the various salt solutions has been deduced in the manner already described (see preceding abstract). Attention is drawn to the fact that the residuary lines of an element differ greatly with the method of excitation; the residuary lines tabulated in the paper therefore might not be the most persistent lines if the substances were vaporised by

anything else than the condensed spark. The flame spectra of potassium and sodium are much more brilliant than those given by the condensed spark. In the case of barium, strontium, and calcium, the most persistent lines occur in the visible part of the spectrum; in the case of magnesium, the most persistent lines occur in the ultra-violet part of the spectrum.

J. C. P.

**Spectra of Calcium and Magnesium as Observed Under Different Conditions.** W. NOEL HARTLEY (*Sci. Proc. Roy. Dubl. Soc.*, 1907, [ii], 11, 243—246).—A number of detailed observations bearing on the influence of varying pressure and of varying character of spark on the spectra of calcium and magnesium. It is noted that when a discharge passes between calcium electrodes in an exhausted tube at 5 mm. pressure, there is no direct passage of a spark. The metal points glow with a violet light; bright stationary spots of white light are seen on the negative electrode, and a great number of scintillations less bright all over the positive electrode. When sparks are passed between magnesium electrodes in a closed vessel at 5 mm. pressure, similar observations may be made of stationary bright spots and scintillations, with an occasional very brilliant green flame.

J. C. P.

**The Influence of a Strong Magnetic Field on the Spark Spectra of Lead, Tin, Antimony, Bismuth, and Gold.** JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1907, 14, 217—227. Compare Abstr., 1906, ii, 421; this vol., ii, 2, 210).—A continuation of the investigations on the Zeeman effect in the spark spectra of various metals. By using a very narrow slit attached to the spectroscope, by shorter exposures, and by introducing a calcite prism between the spark and the focussing lens in order to separate the constituents vibrating in different planes, some of the lines, previously supposed to be doublets, have been further subdivided.

The lines, which have been subdivided into three, four, or five components, are tabulated for lead, tin, antimony, bismuth, and gold. All these metals exhibit lines which belong to the same type, this being particularly noticeable amongst the quadruplets. The spectra of gold, antimony, and lead contain lines which are comparable with certain series lines of silver and copper. This indicates that these are lines of widely separated elements which belong to the same type, in that they are divided into the same number of components having similar appearances and the relative intensities, polarisations, and distances apart of which, when represented on the same scale of vibration numbers, are essentially identical.

H. M. D.

**Displacement of Absorption Spectra in Different Liquids.** ENDRE VON KAZAY (*Chem. Zentr.*, 1907, ii, 773; from *Pharm. Post.*, 1907, 40, 531—533).—Examination of the absorption spectra of magenta, potassium permanganate, alkannin, and chlorophyll in various solvents shows that an increase in the refractive index of the solvent is accompanied by a displacement of the absorption band towards the red end of the spectrum and vice versa. By employing Doppler's principle, it is possible to calculate the displacement of the

spectrum, the equation being  $\lambda_1 = \lambda(1 \pm c/v)$ , where  $\lambda$  = wave-length of line in first solvent,  $\lambda_1$  = wave-length in second solvent,  $c$  = difference of velocity of light in the two solvents, and  $v$  = velocity of light in air.  
W. H. G.

**Influence of Pressure on the Absorption Spectra of Vapours.** A. DUFOUR (*Compt. rend.*, 1907, 145, 757—758).—The study of absorption spectra in the manner described previously (*ibid.*, 173) has been extended to bromine vapour. The pressure, which was obtained by means of dry air, hydrogen, or carbon dioxide, did not exceed 15 atmospheres. Increase in pressure softens all the rays; the general absorption is greater when carbon dioxide is used than with air and hydrogen. Some rays, for example, ray  $\lambda = 5534.2$ , retain the same wave-length, whilst others increase in wave-length when the pressure is increased. Of the latter, the ray  $\lambda = 5535.4$  increases in wave-length by 0.028 (approx.) per atmosphere increase in pressure. So far, the results agree with those described previously, but the case of bromine vapour differs from the first case in that its absorption spectrum is of the classical band type, and that none of its rays exhibits the slightest Zeeman effect, whilst in the first case the rays are modified by a magnetic field.  
E. H.

**Apparatus for the Comparative Observation of Fluorescence** HEINRICH LEY and H. GORKE (*Ber.*, 1907, 40, 4473—4476).—An apparatus is described and figured by means of which the fluorescence of two solutions may be compared, or weak fluorescence observed, by comparison of a solution with the pure solvent. In this apparatus, the fluorescence of eosin can just be observed in solutions containing  $3 \times 10^{-9}$  mols. per litre.  
G. Y.

**Optical Properties of Solutions and of Dissolved Substances.** II. C. CHÉNEVEAU (*Ann. Chim. Phys.*, 1907, [viii], 12, 289—393. Compare this vol., ii, 829).—A detailed account of work already published (compare Abstr., 1904, ii, 641; 1906, ii, 509; this vol., ii, 662). A complete bibliography of the subject is appended.  
M. A. W.

**Optical Rotatory Power of Liquid Ammonia, Methylamine, and Sulphur Dioxide Solutions.** RALPH H. SHERRY (*J. Physical Chem.*, 1907, 11, 559—568).—The measurements were mostly made at room temperature ( $20$ — $23^\circ$ ) in a tube provided with a stopcock. The values obtained for  $[\alpha]_D$  in the different solvents are as follows.

*In Liquid Ammonia.*—Sucrose  $+78.0$ — $73.6^\circ$  in solutions containing 0.5—8.0 grams of solute in 16.4 c.c.; asparagine,  $-26.4^\circ$ ; amygdalin,  $-53.7^\circ$ ; coniine hydrochloride,  $+10.2^\circ$ ; raffinose,  $+102.5^\circ$ ; lactose,  $+33.0^\circ$ ; dextrose,  $+55.0^\circ$ ; galactose,  $+12.2^\circ$ ; cocaine,  $-24.0^\circ$ ; lævulose, no rotation. In mixtures of ammonia and water containing 0—100% of the latter,  $[\alpha]_D$  for sucrose diminished from  $76.1^\circ$  to  $66.5^\circ$ ; ammonium salts had no influence on the rotation in liquid ammonia, nor was mutarotation observed in any case.

*In Liquid Sulphur Dioxide.*—Strychnine,  $+69.0^\circ$ ; quinine,

- 201° to - 208° at 23°, - 208° to - 222° at 4°; coniine hydrochloride, + 5.5—7.2°; aconitine, + 16.9°; cocaine, no observable rotation.

*In Methylamine.*—Sucrose, + 75.0°; lævulose, no observable rotation.  
G. S.

**Physical Properties of Mixed Solutions of Independent Optically Active Substances.** CLERK RANKEN and WILLIAM W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1907, 27, 172—180).—With the object of investigating whether there is any difference in the influence of an optically active substance on optical isomerides when chemical combination probably does not occur, the electrical conductivity, density, and viscosity of solutions containing, as one solute, either sucrose or maltose, and, as the other, *d*-, *l*-, or racemic tartaric acid or tartar emetic, have been determined at 15° and 25°. It was found that the addition of sucrose has exactly the same effect on the *d*-, *l*-, and *r*- solutions so far as the properties in question are concerned. Maltose has also the same effect on the *d*- and *l*-, but not on the racemic, compounds, the viscosity of the latter solutions being distinctly smaller than those containing *d*- or *l*-compounds. This result is ascribed to the existence of racemic ions or molecules in the solutions.  
G. S.

**Action of Alkalis in Organic Developers.** AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Chem. Zentr.*, 1907, ii, 203—204; from *Zeitsch. wiss. Photographie, Photophysik u. Photochemie*, 1907, 5, 126—137).—The amount of reduced silver in a number of exposed plates was determined, and experiments then made to ascertain whether plates exposed to the same extent could be completely developed by using the equivalent quantity of free alkali. This was found to be impossible. To obtain equal effects with different developers, for example, quinol and catechol, varying quantities of alkali must be employed. Further, equivalent quantities of different developers in the presence of the same amount of alkali do not reduce to the same extent, but by increasing the quantity of alkali it is possible to obtain solutions which reduce to the same extent. The quantity of developer required for development is always greatly in excess of the amount equivalent to the silver reduced.  
W. H. G.

**Parent Substance of Radium.** OTTO HAHN (*Ber.*, 1907, 40, 4415—4420).—Old specimens of commercially pure thorium nitrate were found to contain relatively large quantities of radium, and the fact that a sample of this salt, nine years old, contained about 100 times more radium than a freshly prepared sample obtained from the same firm led to the conclusion that there is present in the pure commercial thorium nitrate the substance from which radium is derived directly. That this supposition is correct, follows from the fact that the quantity of radium in a solution of recently prepared pure commercial thorium nitrate increased considerably when kept for about six months. An acidified solution of the salt was treated with oxalic acid, and the quantity of radium present in the filtrate estimated; since this did not increase on keeping, it follows that the

parent substance of radium is precipitated by the oxalic acid. This is in accord with Boltwood's statement (this vol., ii, 836) that the parent substance of radium, named by this author "ionium," is an element which reacts like thorium. From a consideration of the quantities of radium present in samples of thorium nitrate of various ages, the author calculates the disintegration constant of radium to be roughly three thousand years. This is of the same order of magnitude as the value arrived at by Rutherford, and differs considerably from the value obtained by Ramsay and Cameron (Trans., 1907, 91, 1282).

W. H. G.

**Demonstration of Radium Emanation and the Radioactivity of Uranyl Molybdate.** EDGAR WEDEKIND (*Chem. Zeit.*, 1907, 31, 1108—1109).—About 1 gram of barium-radium carbonate is treated with hydrochloric acid in a suitably constructed piece of apparatus, the gas evolved transferred to a tube drawn out and sealed at one end, and then acted on by potassium hydroxide. When examined in the dark, the upper, narrow part of the tube is seen to glow, although the volume of the residual gas is exceedingly small. Should any air be present, it may be removed by adding oxygen, sparking, and treating the residue with pyrogallol or sodium hyposulphite.

The author's investigations on uranyl molybdate confirm the results obtained by Szilárd (this vol., ii, 731).

W. H. G.

**Radium Content of Uranium Preparations.** MAX LEVIN (*Physikal. Zeitsch.*, 1907, 8, 802—803).—The quantity of radium in various uranium salts prepared at different times during the last twenty-five years has been measured by determining the amount of emanation in solutions of the salts.

It is quite impossible to decide from the numbers obtained whether radium is formed from uranium or not.

Incidentally, the author has also examined the emanation from Giesel's emanation substance, and has obtained no indication of an emanation with a long period of decay.

H. M. D.

**Secondary Röntgen Radiation from Gases and Vapours.** J. A. CROWTHER (*Phil. Mag.*, 1907, [vi], 14, 653—675).—All gases and vapours when subjected to X-rays are a source of secondary radiation. The absorbability and the intensity of the secondary radiation vary with the nature of the gas. For a given primary radiation and a given gas, the intensity of the secondary radiation is proportional to the pressure of the gas. The secondary radiation from a molecule of a gas is the sum of the secondary radiations from the component atoms. For a given primary radiation, the secondary radiation from a given element in the gaseous state depends only on the mass of it present, and not on its state of chemical combination. Gases are divided into two classes, according as they merely scatter or transform the primary radiation. In the former class, containing the elements with an atomic weight less than that of sulphur, the secondary radiation per atom is proportional to the atomic weight, except in the

case of hydrogen. Elements of higher atomic weight give off secondary radiation in very much larger amounts. J. C. P.

**Secondary Cathode Rays Emitted by Substances when Exposed to the  $\gamma$ -Rays.** R. D. KLEEMAN (*Phil. Mag.*, 1907, [vi], 14, 618—644).—The rays from radium appear to consist principally of two groups. The rays of the one group are more efficient in producing secondary cathode radiation from aluminium, sulphur, iron, nickel, zinc, and tin than from lead, and are all more or less easily absorbed by each of these substances except lead. The rays of the other group are more efficient in producing secondary cathode radiation from lead than from the other substances, and are more easily absorbed by lead, mercury, and bismuth than by any of the other substances.

There is also a third weak group of rays which is most efficient in producing secondary radiation from carbon. It follows that to shield a piece of apparatus from the  $\gamma$ -rays of radium, it is better to use a combined screen of lead and one of the metals, iron, zinc, or copper, than a screen composed of only one of these metals. J. C. P.

**Radioactivity of the Max Spring at Bad Dürkheim a.d. Haardt.** ERICH EBLER (*Chem. Zentr.*, 1907, ii, 629—630; from *Verh. naturhist.-med. Ver. Heidelberg*, 1907, [ii], 9, 87—115).—An investigation to ascertain whether the water and sediment from this spring contains the, as yet unknown, first member of the radium-uranium-thorium group, a radioactive alkali metal. The sediment is far more active than the water or gas obtained from the spring; the half-life period of the emanation is 4.34 days, so that the presence of an emanation with a period of decay greater than that of radium emanation is not improbable. The induced activity produced by the emanation is, to a great extent, identical with induced radium activity; it is probable, however, that small quantities of thorium or radiothorium are present in the sediment. That the radioactivity of the mother liquor ( $D_4^{15}$  1.315) is probably due to the presence of an element of the alkali group, follows from the fact that precipitation of the alkaline earth metals leaves the liquid active, the sulphate precipitate being inactive. The investigation is being continued. W. H. G.

**Variation in the Electrical Conductivity of Stibnite under the Influence of Light-rays.** FRANS M. JAEGER (*Zeitsch. Kryst. Min.*, 1907, 44, 45—49).—Using rods cut from large crystals of Japanese stibnite for the determination of the electrical conductivity in different crystallographic directions, widely varying results were obtained until it was noticed that light had a very marked influence. For example, a 110-volt electric lamp, at a distance of 16 cm. from the preparation, caused the conductivity to increase by 210%. Maximum effects were obtained in the red and blue parts of the spectrum, and minimum in the ultra-red, green, and ultra-violet. Although the electrical conductivity varies with the direction in the crystal, there is no difference in the percentage increase due to the effect of light in the three principal crystallographic directions. Polarised light with different vibration-directions has the same effect

as ordinary light. The effect is not due to electric currents or to the heating of the crystal. Light has no effect on the conductivity when the mineral is in a powdered form or when the substance has been fused (then consisting of an aggregate of differently orientated crystals). When the source of light is removed, the conductivity returns at first quickly and then more slowly to its original value, which is reached in about twenty minutes, the lagging being much less than in selenium.

The effect cannot be due to any change in the crystalline state of the stibnite, as is the case with selenium. Japanese stibnite, according to different analyses, contains only 98%  $\text{Sb}_2\text{S}_3$ , the remainder being insoluble silicates and enclosed quartz crystals; selenium and tellurium were not detected. The phenomenon cannot therefore be attributed to any chemical cause.

L. J. S.

**Explanation of the Effect of Super-tension.** FELIX KAUFLEDER (*Zeitsch. Elektrochem.*, 1907, 13, 633—637).—Two precisely similar electrolytic cells were prepared containing platinum anodes and dilute sulphuric acid; the one cell had a platinised platinum cathode, the other a lead cathode. The difference between the potentials of the cathodes and also the rise of temperature in the cells were measured during the passage of the same current through them. The higher potential at the lead cathode was found to agree very closely with the greater rise of temperature in the cell containing it. The author holds that a cathode at which a super-tension occurs must be locally heated to a greater extent than one at which this does not occur, and that the superior reducing power of the former may be due to this higher temperature. Experiments on the reduction of benzophenone and acetophenone at thin platinum cathodes heated by the passage of electric currents show that reduction takes place in these circumstances, whilst no reduction occurs if the heating current is not used. The potential of the heated electrode is rather lower than that of the unheated one. The temperature of the heated electrode, deduced from its resistance, is about  $120^\circ$ , that of the electrolyte was kept at  $30^\circ$  to  $40^\circ$  by cooling. A heated anode gave similar results in the oxidation of *p*-nitrotoluene.

T. E.

**The Anodic and Cathodic Behaviour of Iron Mirrors and the Passivity of Iron.** WOLF J. MÜLLER and JOHANN KÖNIGSBERGER (*Zeitsch. Elektrochem.*, 1907, 13, 659—663).—The authors have measured the reflecting power of iron mirrors immersed in alkaline solutions both in their natural condition and when polarised anodically, so that rapid evolution of oxygen occurs, and when polarised cathodically, so that hydrogen is evolved. The potentials of the iron were measured, and it was proved that the metal was sometimes in the active and sometimes in the passive state. The solutions contained the ions  $\text{SO}_4^{--}$ ,  $\text{HPO}_4^{--}$ , and  $\text{CO}_3^{--}$  in addition to hydroxyl ions. In all cases, the reflecting power was the same. These experiments are regarded as a definite proof that the difference between active and passive iron is not due to a layer of oxide.

In a neutral solution of sodium phosphate, cathodic polarisation



produces no change, but anodic polarisation gives a very considerable increase in the reflecting power, which disappears when the current is interrupted, and finally passes into a diminution; the mirror is then found to be covered with a thin film, probably of oxide. This is assumed to be due to the formation of an alloy of sodium and iron, which is more readily attacked when the current is interrupted than iron itself. T. E.

**Effect of Acetone on the Transport Numbers of Sodium and Potassium Chlorides in Aqueous Solution.** HENRY F. LEWIS (*J. Physical Chem.*, 1907, 11, 569—573).—The transport numbers of sodium and potassium chlorides in mixtures of acetone and water, containing from 0—75% of the former, have been determined by means of a simple and convenient apparatus, which, however, does not admit of very accurate results. The ratio  $u/v$ , where  $u$  is the velocity of the chlorine ion,  $v$  that of the cation, diminishes with increasing proportions of acetone, and in mixtures containing 75% of the latter has only about half the value observed in water alone. G. S.

**Electrolytic Dissociation Constant of Sulphurous Acid.** WILHELM KERP and EMIL BAUR (*Chem. Zentr.*, 1907, ii, 971—972; from *Arch. Kais. Ges.-A.*, 1907, 26, 297—300).—The electrolytic dissociation constant of sulphurous acid has been determined experimentally, the value so obtained being  $K = 0.0174$  at  $25^\circ$ . This value is in close agreement with that ( $K = 0.0164$ ) obtained by Drucker by the cryoscopic method. W. H. G.

**Electrolysis of Salt Solutions in Liquefied Sulphur Dioxide at Low Temperatures.** BERTRAM D. STEELE (*Trans. Faraday Soc.*, 1907, 3, 164—165).—The author has studied the electrolysis of a nearly saturated solution of potassium iodide in liquid sulphur dioxide. When platinum or mercury electrodes are employed, the current is extremely variable. A constant and consistent current can be obtained, however, when a silver, copper, or iron cathode of large area is employed. When a platinum anode is used, iodine is liberated, and is dissolved in the surrounding solution. With a zinc anode, no iodine is liberated; the solution remains yellow, and probably contains zinc iodide. With an iron anode, no iodine is liberated, but the surrounding solution becomes blackish-green. With a mercury anode, mercurous iodide is produced, and forms a non-conducting layer on the electrode. With a platinum cathode and currents of 20 milliamperes or above, a dark-coloured, crystalline deposit is formed. This deposit, apart from small quantities of sulphur which it contains, has a composition closely corresponding with that of potassium sulphite, although in some cases it is richer in sulphur dioxide. The falling off of the current after the first few moments is due to the deposition of an insulating film of sulphur on the cathode. The deposition of sulphur is prevented by using a silver or a copper cathode.

Some preliminary measurements of ionic velocities in liquid sulphur dioxide have been made. J. C. P.

**Electrical Conductivity of Solutions in Ethylamine.**

FREDERICK L. SHINN (*J. Physical Chem.*, 1907, 11, 537—541).—The electrical conductivity of solutions of silver nitrate, and of lithium and ammonium chlorides, in liquid ethylamine, has been measured at 0°; at the latter temperature, the specific conductivity of the solvent itself was  $4 \times 10^{-7}$  reciprocal ohms. The conductivity of the solutions is less than that of the same salts in methylamine (Gibbs, *Abstr.*, 1906, i, 933), but greater than in amylamine (Kahlenberg and Ruhoff, *Abstr.*, 1903, ii, 464). The molecular conductivity of lithium chloride in ethylamine increases with dilution up to 0.8*N*, and then diminishes rapidly on further dilution, whilst the molecular conductivities of silver nitrate and ammonium chloride solutions decrease with dilution throughout, and finally appear to attain minimum values in very dilute solution.

G. S.

**Electrochemical Behaviour of Gold and its Passivity.**

ALFRED COEHN and CARL LUDWIG JACOBSEN (*Zeitsch. anorg. Chem.*, 1907, 55, 321—355. Compare Wohlwill, *Abstr.*, 1899, ii, 105).—The potentials at which chemical changes occur when gold is deposited from its solutions at the cathode have been determined by electrolysis at varying potentials, and measuring the corresponding current; the results are represented by curves in which the potentials (taking the potential of the hydrogen electrode as zero) are plotted against the current. In some cases, the nature of the changes indicated by breaks in the curves has been elucidated by electrolysis at constant potentials.

For a solution of potassium gold cyanide, there is only one break in the curve at -0.2 volt, representing the discharge of  $\text{Au}^+$  ions at the cathode. On the other hand, the curve for solutions of auric chloride shows several breaks. Above -0.905 volt, only  $\text{Au}^{+++}$  ions are discharged. In fresh solutions of auric chloride (containing no  $\text{Au}^+$  ions), a break at -1.1 volt indicates the change of  $\text{Au}^{+++}$  to  $\text{Au}^+$  ions. Between -0.985 and -0.905 volt, from solutions containing both aurous and auric chloride, both  $\text{Au}^+$  and  $\text{Au}^{+++}$  ions are discharged.

Investigation of the changes taking place at the anode during electrolysis have shown that, contrary to the general opinion, there is a limited region, between -1.2 and -1.38 volt, within which the gold electrode is dissolved in the trivalent form; above the latter potential, the anode becomes passive. On again raising the potential above -1.38 volt, the gold returns very slowly to the active condition.

The gold anode is dissolved as a univalent metal in pure potassium cyanide solution, and does not become passive even in concentrated solutions of the salt. In solutions of the commercial cyanide, however, it rapidly becomes passive, this being due to the presence of sodium salt as impurity. It is shown that the passivity in this case is due to the formation of a film of comparatively insoluble sodium gold cyanide on the anode, and it is suggested, in agreement with some previous observers (Müller and Spitzer, *Abstr.*, 1906, ii, 724), that passivity is usually brought about by the formation of an insoluble film on the electrode.

The rendering passive of the anode by sodium can be used for the detection of that metal in the presence of an excess of potassium.

G. S.

**Electrolytic Dissociation of Fused Salts.** RICHARD LORENZ (*Ber.*, 1907, 40, 4378—4380).—Polemical. A reply to Arndt (compare this vol., ii, 598, 665, 842).  
W. R.

**The Importance of Direct or Alternating Current in Heating Air or Fused Substances Electrically.** H. LEE and A. BEYER (*Zeitsch. Elektrochem.*, 1907, 13, 701—707).—Flames consuming the same amount of energy were produced by direct and by alternating currents between iron electrodes in air. The yields of nitric acid were practically the same. With platinum electrodes, the yield was better with the direct current, the reason probably being that the transition resistance at the electrode is greater in this case with alternating than with direct current, and therefore a larger fraction of the energy is lost in heating the electrode itself. The yield with platinum electrodes was lower than with iron, whilst an experiment with electrodes made of the filament of a Nernst lamp gave the highest yield of all. The experiments show that the formation of nitric oxide is purely a function of the temperature of the air, and does not depend on the nature of the current. The same result is obtained in some experiments on the formation of calcium carbide. Within the limits of error of the experiments, the quantities of carbide produced by a given expenditure of energy were the same whether the current was alternating or direct.  
T. E.

**Measurement of Pressures during Vacuum Distillations.** HERMANN J. REIFF (*Zeitsch. angew. Chem.*, 1907, 20, 1894—1897. Compare Wohl and Losanitsch, *Abstr.*, 1906, ii, 72; Ubbelohde, *Abstr.*, 1906, ii, 432).—The form of apparatus previously described (*Abstr.*, 1905, ii, 808) has been slightly modified, and is now constructed entirely of glass. A somewhat similar piece of apparatus is described by means of which it is possible to measure both the pressure of the air and of the vapour of the distillate within the distillation apparatus.  
W. H. G.

**Ebullioscopic Determinations in Phosgene, Ethyl Chloride, and Sulphur Dioxide.** ERNST BECKMANN and FRITZ JUNKER (*Zeitsch. anorg. Chem.*, 1907, 55, 371—385).—All the experiments were carried out in a slightly modified form of the ordinary Beckmann apparatus; electric heating was used, and special precautions were taken for effective condensation. The mean value of the molecular elevation constant for carbonyl chloride, determined with naphthalene, dibenzyl, and other compounds, is 29.0; the value for ethyl chloride, using the same solutes, is 19.5, and for sulphur dioxide, 14.4.

Antimony trichloride and pentachloride, arsenic and iodine trichlorides, iodine and sulphuryl chloride,  $S_2Cl_2$ , have normal molecular weights in carbonyl chloride; the same is true for iodine and sulphuryl

chloride in ethyl chloride, and for sulphuryl chloride in liquefied sulphur dioxide.

In all three solvents, sulphur dichloride gives higher values than correspond with the formula  $\text{SCl}_2$ ; the ratio of the observed to the calculated values are for phosgene 1.43, for ethyl chloride 1.26, and for sulphur dioxide 2.19.

The slight dissociating power of the three solvents in question is shown by the fact that, whereas acetic and benzoic anhydrides have normal molecular weights, acetic and benzoic acids form associated molecules in these solvents. G. S.

**New Pattern of Thermostat Designed to Supply a Rapid Stream of Water Heated to a Constant Temperature.** T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1907, 3, 119—122. Compare *Trans.*, 1905, 87, 1030).—The apparatus described and sketched in the paper makes it possible to supply a steady flow of water at constant temperature to instruments, such as a polarimeter, which cannot be immersed in a water-bath. The circulation of the water from a thermostat is effected by an eccentric rotary pump, which sucks the water out of the bath, draws it through the various jackets, and then returns it to the bath. In the author's experiments, the temperature of the flowing water did not vary by more than a few thousandths of a degree even when a maximum rate of circulation of 4 litres per minute was maintained. J. C. P.

**Constants and Variables of the Parr Calorimeter.** SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1907, 29, 1606—1622).—In a previous paper (*Abstr.*, 1900, ii, 710), a calorimeter has been described in which the coal is burned by means of sodium peroxide, the carbon dioxide and water being absorbed by the sodium oxide formed.

It is now pointed out that the sodium peroxide should not be allowed to absorb moisture from the air, or otherwise it must be standardised and a correction made. A study has been made of substances which could be used to ensure complete combustion. The most efficient accelerators were found to be (1) a mixture of potassium persulphate (2 parts) and ammonium persulphate (1 part), and (2) potassium chlorate. The corrections to be made when these substances are employed have been determined. It was stated in the earlier paper that the heat of combustion of the fuel is only 73% of the total heat developed, the remainder being due to the union of the carbon dioxide and water with the sodium oxide, and it was assumed that this 'proportion is constant even if the fuels contain varying amounts of carbon and hydrogen. It is now proved that this assumption is correct, since the heat of combustion of carbon and the heat of combustion of hydrogen each amounts to 73% of the heat of reaction of the element with sodium peroxide. The necessary corrections for the sulphur, ash, and combined water in the fuel, and for the fuse wire, are recorded. E. G.

**Heat of Formation of Lithium Oxides.** ROBERT DE FORCRAND (*Compt. rend.*, 1907, 145, 702—705. Compare this vol., ii, 615, 683).—By combining the author's value, 31.2 Cal. at 15° and 4 litres

dilution (Beketoff gives +26 Cal., Abstr., 1887, 1073), for the heat of dissolution of lithium protoxide,  $\text{Li}_2\text{O}$ , with Guntz's value (Abstr., 1897, ii, 86) +106.26 Cal. for the heat of dissolution of a gram-molecule of lithium in 28 litres of water at  $18^\circ$  (105.521 Cal. at  $15^\circ$  and 4 litres), the value +143.32 Cal. is obtained for the heat of formation of lithium protoxide. Pure lithium hydroxide can be obtained by dehydration of the hydrate,  $\text{LiOH}\cdot\text{H}_2\text{O}$ , in a current of hydrogen at  $140^\circ$ . The heat of dissolution of 2 gram-molecules of the product is +8.93 Cal. at  $15^\circ$  and 4 litres dilution. From the latter value and the heat of dissolution of  $\text{Li}_2\text{O}$ , there are obtained for the heats of combination of  $\text{Li}_2\text{O}$  with  $\text{H}_2\text{O}$  (solid) +22.27 Cal., with  $\text{H}_2\text{O}$  (liquid) +20.84 Cal., and with  $\text{H}_2\text{O}$  (gas) +31.93 Cal. The latter gives the value +791.4° for the dissociation temperature of lithium hydroxide, which is in accordance with the fact that, when heated at  $780^\circ$  in a current of inert gas, lithium hydroxide is rapidly converted into the oxide. Employment of the value 22.27 Cal. instead of the +17.04 Cal. (Abstr., 1906, ii, 727) previously given (based on Beketoff's value +26 instead of 31.2) gives the value +117.3 Cal. for the heat of formation of lithium hydroxide from its elements, instead of the 112.3 Cal. given by Berthelot. Replacement of Beketoff's value by the author's gives the values +9.33 Cal. and +152.65 Cal. for the heat of oxidation of  $\text{Li}_2\text{O}$  and the heat of formation of  $\text{Li}_2\text{O}_2$  respectively, instead of the values +7.19 Cal. and +152.64 Cal. previously obtained (Abstr., 1900, ii, 478). The increase in the heat of oxidation of  $\text{Li}_2\text{O}$  raises the calculated dissociation temperature of  $\text{Li}_2\text{O}_2$  from +2.3° to +349°. The latter value is far more than the former in accordance with the stability of the dioxide in the cold and with its superficial formation when the protoxide is heated in air. E. H.

**Calculation of Thermo-chemical Constants.** H. STANLEY REDGROVE (*Chem. News*, 1907, 96, 188—189. Compare this vol., ii, 446, 604).—The method applied previously in the calculation of the molecular heats of combustion of the hydrocarbons is used for obtaining values for the heats of formation. On account of the smaller magnitude of the heats of formation, the percentage differences between the calculated and experimental values are much larger than the corresponding differences which are met with in the case of the heats of combustion. The differences between calculated and found values are very considerable in the case of the aromatic hydrocarbons.

H. M. D.

**Heat of Volatilisation of Liquid Ammonia at its Boiling-point under Atmospheric Pressure.** EDWARD C. FRANKLIN and CHARLES A. KRAUS (*J. Physical Chem.*, 1907, 11, 553—558. Compare Abstr., 1899, ii, 284).—The experiments were made by a modification of a method first employed by Ramsay and Marshall (Abstr., 1896, ii, 349), the quantity of electrical energy required to convert a definite weight of liquid ammonia into vapour at its boiling-point,  $-33.5^\circ$ , being determined. As a mean of three experiments, the value  $\lambda = 341$  Cal. is obtained for the heat of vaporisation of 1 gram of ammonia,

which is considerably higher than the value given by Brill (321 Cal.), but is in excellent agreement with that calculated by van't Hoff's equation,  $\lambda = 0.02T^2/k$ , where  $k$  is the molecular boiling-point elevation constant, and  $T$  the boiling-point on the absolute scale. G. S.

**Thermochemistry of Electrolytes in Relation to the Hydrate Theory of Ionisation.** WILLIAM R. BOUSFIELD and T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1907, 3, 123—139. Compare Lowry, *Abstr.*, 1905, ii, 686).—The authors advocate the view that the combination of the charged radicle or ionic nucleus:  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{++}$ ,  $\text{SO}_4^{--}$ , &c., with water is a powerful exothermic process, and that the affinity of the ionic nucleus for water is the main source of the disruptive force which breaks down or ionises the molecule. The heat thus liberated is probably of the same order of magnitude as the heat absorbed by the disruption of the molecule, and the balance may be either a small positive or a small negative quantity. It is to be noted that when the two thermochemical equations:  $1/x\text{K}_x + 1/2\text{Cl}_2 = \text{KCl} +$

$105,600 \text{ cal.}$  and  $\text{KCl} + \text{aq} = \text{K}^+\text{aq} + \text{Cl}^-\text{aq} - 4400 \text{ cal.}$ , are combined, the result is  $1/x\text{K}_x + 1/2\text{Cl}_2 + \text{aq} = \text{K}^+\text{aq} + \text{Cl}^-\text{aq} + 101,200 \text{ cal.}$  So that according to the electrolytic dissociation theory, the heat of formation of a salt in dilute solution is the sum of the heats of formation of the hydrated ions. Using therefore (1) Thomsen's data for the heats of formation of salts in dilute solution, and (2) the value  $-600 \text{ cal.}$  as the heat of formation of one equivalent of hydrogen ions, deduced from the absolute potential at a calomel electrode, the authors are able to calculate the heats of formation of all the important ions, both positive and negative. The result shows that the heats of formation of the salts in dilute solution are additive quantities, so that just as there is a law of independent migration of the ions, there is also a law of independent heat of formation of the ions. It is noteworthy that no such relationship exists in reference to the heats of formation of the solid salts or in reference to their heats of dissolution. Neither is there any such relationship in reference to the heat of formation of organic compounds.

The heat of formation of an ion is complex, and is the algebraic sum of several distinct energy changes. In the case of elementary ions, such as  $\text{Na}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Cl}^-$ , these changes are: (1) the heat-change involved in the cleavage of the molecules of the element into their separate atoms; (2) the heat-change involved in electrifying these atoms; (3) the heat-change involved in the combination of the charged atoms or ionic nuclei with water. In the case of compound ions, such as  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , there is a further heat-change (4) involved in the combination of the constituent atoms of the radicle. Generally speaking, (1) and (2) will be endothermic, (3) and (4) will be exothermic, changes, and the process of forming an ion from its elements and water will be exothermic or endothermic, according as the sum of the heat-changes is positive or negative. J. C. P.

**New Method Suggested for Determining Vapour Densities.**

PHILIP BLACKMAN (*Chem. News*, 1907, 96, 223—224).—An apparatus is described which consists of a narrow glass cylinder provided at the lower end with a stopper, and at the upper end with a long capillary tube which is furnished with a stopcock. Two short threads of mercury are introduced into the capillary tube, one to close the tap and the other near the glass cylinder, the space between them acting as a pressure gauge. A small tube, containing a weighed quantity of the substance, is placed in the cylinder, and the stopper is replaced and secured with wire. The cylindrical vessel is now fitted into the neck of a flask which is connected with a condenser. On boiling a liquid of suitable b. p. in the flask, the substance is vaporised and the pressure recorded by the gauge. Some modifications of the apparatus are described, and formulæ for calculating the results are given. E. G.

**Density, Electrical Conductivity, and Viscosity of Fused Salts.** HARRY M. GOODWIN and R. D. MAILEY (*Trans. Amer. Electrochem. Soc.*, 1907, 11, 211—223).—The density, electrical conductivity, and viscosity of fused sodium, potassium, lithium, and silver nitrates, of silver chlorate, and of certain mixtures of these salts have been measured at a series of temperatures reaching to 500°.

The density measurements were made by a modified Westphal balance, in which the sinker was constructed of fused quartz. For the silver salts, a platinum ball was used as sinker. For the conductivity measurements, a cell was used formed from a cylinder of rock crystal, cut parallel to its axis through which a capillary 1.5 mm. in diameter was bored. The ends of the quartz cylinder are closed by platinum elbows, carefully ground to fit, and these form the electrodes. A modified Ostwald viscosimeter, made of platinum, was used for the viscosity determinations, the time of flow being measured by an electrical method.

In the case of all the simple salts examined, the density is a linear formation of the temperature to within 0.1%. The specific volume of mixtures of sodium and potassium nitrate is greater than that computed from the specific volumes of the components, the maximum deviation for the equimolecular mixture being 0.5%. On the other hand, with an equimolecular mixture of lithium nitrate and silver chlorate, a contraction of 20% occurs.

The specific conductivity is not strictly proportional to the temperature, but increases less and less rapidly as the temperature rises. The temperature coefficient is, in general, less than one-fifth of that found in the case of aqueous solutions. The equivalent conductivity increases very nearly linearly with the temperature. For mixtures of sodium and potassium nitrate, the equivalent conductivity is less than that computed from the equivalent conductivity of the components, and this is attributed to decrease in dissociation. In the case of an equimolecular mixture of lithium nitrate and silver chlorate, this difference is much greater, but in the same direction.

Assuming that the ionic velocities are proportional to the fluidity of the medium, the data obtained indicate that a rise of temperature tends to diminish the dissociation of the fused salts examined. The

diminution is very small in the case of potassium nitrate, 4.2% per 100° for silver nitrate, 6.4% per 100° for sodium nitrate, and 11% for 60° in the case of lithium nitrate. H. M. D.

**Cause of the Decolorisation of Coloured Liquids by means of Various Charcoals.** FRITZ GLASSNER and WILHELM SUIDA (*Annalen*, 1907, 357, 95—128. Compare Rosenthaler and Türk, this vol., ii, 12; Freundlich, *ibid.*, 155; Freundlich and Losev, *ibid.*, 534).—The authors have determined the amounts of various dyes absorbed from solution by different sorts of charcoal, alone and in presence of added salts, as also before and after treatment with alkalis and acids. It is found that the absorptive capacity of vegetable charcoals, which are free from nitrogen and contain only little ash, is extremely small, whereas nitrogenous animal charcoals have varying and, in many cases, large absorptive capacities which appear to be independent of the amount and nature of the ash and of the state of division of the charcoal, but to depend to some extent on the amounts of nitrogen and hydrogen present. It is considered that the absorptive capacity of the animal charcoals depends probably on the presence of substances containing the group  $N \cdot C \cdot N$ , which has been found of importance in the absorption of dyes by textile fibres. In support of this view, it is shown that, whilst dyes are not precipitated by potassium cyanate and only in some cases by potassium cyanide, basic dyes are precipitated completely by potassium ferrocyanide, ferricyanide, and thiocyanate, cyanuric acid, ammelide, and ammeline, but only slowly by melamine and melam, which, however, precipitate acid dyes completely. Further, it is found that inactive, nitrogenous charcoals prepared from gelatin and wool acquire a high absorptive power when heated with potassium carbonate, or to a smaller extent when heated with potassium chloride.

The absorptive capacity of lampblack, which, although free from nitrogen and ash, decolorises solutions of certain, especially basic, dyes, remains unexplained. G. Y.

**Agglutination from the Physical Standpoint. IV. The Flocculation of Aniline Colours.** OSCAR TEAGUE and BERNARD H. BUXTON (*Zeitsch. physikal. Chem.*, 1907, 60, 469—488. Compare Abstr., 1906, ii, 839—840).—In previous papers, it was shown that the flocculation of organised and non-organised suspensions only takes place when the concentration of the added electrolyte lies between certain optimal limits. Outside these limits, whether in the zone of supra-optimal concentration ("Vorzone") or in that of infra-optimal concentration ("Nachzone"), no precipitation occurs. In the present paper, it is shown that in the flocculation of aniline colours by electrolytes, supra-optimal concentrations do not occur, that is, above a certain limit of concentration precipitation always occurs. If, however, the colloidal solutions of two dyes of opposite electric charge are mixed, there is a region of optimum relative concentration in which precipitation is most complete, and in which there is a more or less definite ratio between the concentrations of the two dyes; when a larger proportion of one is present, precipitation is incomplete (supra-optimal zone with reference to that dye). In the latter case, there is



nevertheless a combination between the two dyes remaining in solution, as they are absorbed by filter paper together.

The great differences in the colloidal behaviour of dyes are not wholly accounted for by the molecular weight. An electric current causes in agar convection of acid dyes towards the anode, and of basic dyes towards the cathode. G. B.

**Agglutination from the Physical Standpoint. V. The Phenomenon of Supra-optimal Concentration.** OSCAR TEAGUE and BERNARD H. BUXTON (*Zeitsch. physikal. Chem.*, 1907, 60, 489—506. Compare preceding abstract).—Dyes which are highly colloidal (as indicated by dialysis) have a small region of optimal concentration at which they precipitate each other, that is, a slight excess of either redissolves the precipitate. With less definitely colloidal dyes, a much greater excess is required, so that the existence of a zone of supra-optimal concentration largely depends on the extent to which the dye is colloidal.

Bacteria are negatively charged, and are only agglutinated by basic dyes; the phenomena here closely resemble those of the mutual flocculation of dyes. When dialysed anti-serum is added to bacteria, there may be a region of supra-optimal concentration of the serum in which no agglutination occurs, especially if the serum has been warmed or acidified. This phenomenon (which Ehrlich attributes to pro-agglutinoids) corresponds with the prominence of the supra-optimal zone for highly colloidal dyes, since, by warming or acidifying, serum is rendered more highly colloidal. The supra-optimal zone in the precipitation of colloids by electrolytes is not readily explained; it is possibly due to decreased absorption of the electrolyte by the colloid when the solution of the former becomes concentrated. G. B.

**Collodion Membranes.** S. LAWRENCE BIGELOW and ADELAIDE GEMBERLING (*J. Amer. Chem. Soc.*, 1907, 29, 1576—1589).—A study has been made of the preparation and properties of collodion membranes, and a brief bibliography of the subject has been compiled. The membranes can be readily prepared by pouring collodion on to plate glass, or on to the surface of mercury contained in a shallow dish, and allowing it to evaporate. They can be easily fitted to the ordinary form of dialyser, and secured in position by painting the edges with collodion. A comparison of the rate of dialysis of solutions of red colloidal gold, colloidal ferric hydroxide, and colloidal aluminium hydroxide through gold-beaters' skin, collodion, and parchment paper has shown that the dialysis takes place most rapidly through gold-beaters' skin, rather less so through the collodion membrane, and much less so through parchment paper.

The effect of changes of temperature and pressure on the permeability of collodion membranes has been investigated. At constant temperature, the quantity of water passing through the membranes is nearly a linear function of the pressure. At 25°, a change of 1 mm. in the pressure causes a change in the rate at which water passes, amounting to about 0.6% of the volume of water which passes when the driving pressure is 150 mm. The results of experiments on the effect of varying the temperature while the pressure is kept constant

are irregular, but seem to indicate that the temperature coefficient is not a linear function, but increases slightly with the temperature. The quantity of water passing in unit time is approximately doubled when the temperature is increased from 20° to 30°.

The effect of increasing the thickness of the membrane is to reduce the permeability, but it is found that there are other factors concerned which have an even greater influence. Different samples of collodion have different permeabilities, but changes of temperature and pressure produce the same proportional effect in all cases. A membrane gradually becomes less permeable as its age increases, but is usually efficient for from one to three months. E. G.

**The Permeability of Artificial Lipoid Membranes for Proferments.** S. P. SWART (*Biochem. Zeitsch.*, 1907, 6, 358—365).—The membranes were prepared by impregnating silk with cholesterol or with lecithin. They permitted the diffusion of pepsin and rennet zymogens; those prepared with lecithin more readily than those made with cholesterol. G. B.

**Relation Between Osmotic Pressure and Surface Tension.** A. SELLA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 384—385).—The author indicates an inaccuracy in the theoretical deduction by Battelli and Stefanini (this vol., ii, 233) of the law stating that dilute solutions having equal surface tensions are in osmotic equilibrium. T. H. P.

**Diffusion of Colloids.** REGINALD O. HERZOG and H. KASARNOWSKI (*Chem. Zentr.*, 1907, ii, 661; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 1—2).—The coefficient of diffusion of the colloids examined is shown to be a physical constant which may be determined without difficulty. The values obtained up to the present do not vary greatly in magnitude; especially is this the case with pepsin and rennet, the values for which are almost identical. W. H. G.

**Determination of Solubility by Means of Pulfrich's Refractometer.** YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōto*, 1907, 1, 265—273).—The relation between the index of refraction of a mixture and its components may be represented with sufficient accuracy for the present purpose by the equation:  $ax + bx^2 = \delta - \delta'$ , where  $\delta$  and  $\delta'$  represent the refractometer readings for solvent and solution respectively,  $x$  represents the concentration of the solution, and  $a$  and  $b$  are constants. From the refractometer readings for the solvent and for two solutions of known concentration, the values of the constants can be obtained, and hence, when the reading for a saturated solution has been observed, its concentration can be calculated.

The method has been tested with satisfactory results for solutions of benzophenone in alcohol and potassium chloride in water, but the value obtained for the solubility of ether in water is somewhat higher than that given by former observers. G. S.

**Velocity of Dissolution of Solid Substances.** LUDWIK BRUNER and STANISLAW TOLLOCZKO (*Zeitsch. anorg. Chem.*, 1907, 56, 58—71. Compare Abstr., 1904, ii, 117; 1905, ii, 806).—In former papers, the authors have shown that the Noyes-Whitney equation (Abstr., 1897, ii, 479) holds for the rate of dissolution of slightly soluble substances, and it is now shown that, contrary to the statement of Schürr (Abstr., 1904, ii, 543), the equation also holds for the rate of solution of such a soluble salt as sodium chloride. The method employed depends on the passage of a stream of solvent over the surface of a large natural crystal of salt, and pure water and solutions of sodium chloride of various strengths were used as solvents.

The rate of dissolution of sodium chloride at a cubic, an octahedral, and a rhombododecahedral surface is the same within the limits of experimental error, in accordance with Nernst's theory connecting velocity of solution and diffusion. G. S.

**Influence of Non-electrolytes and Electrolytes on the Solubility of Gases in Water.** JAMES C. PHILIP (*Trans. Faraday Soc.*, 1907, 3, 140—145).—Supplementary to a paper already published (*Trans.*, 1907, 91, 711). The author criticises Levin's statement (Abstr., 1906, ii, 527) that non-electrolytes have no influence on the solubility of other substances. Emphasis is laid on the fact that the average molecular hydration increases with dilution, showing that the cause which is at work in lowering the solubility of gases is relatively most potent in dilute solutions. The following additional values for the average molecular hydration in normal solution at 15° have been deduced from Geffcken's work (Abstr., 1904, ii, 708):  $\text{Na}_2\text{SO}_4$ , 28.5;  $\text{Na}_2\text{CO}_3$ , 31;  $\text{K}_2\text{SO}_4$ , 37;  $\text{K}_2\text{CO}_3$ , 30;  $\text{LiCl}$ , 8;  $\text{MgSO}_4$ , 25;  $\text{H}_2\text{SO}_4$ , 11.5;  $\text{HCl}$ , 4.4;  $\text{HNO}_3$ , 2.5;  $\text{NaOH}$ , 20.5;  $\text{KOH}$ , 19.5.

J. C. P.

**Methods for Determining Degree of Hydration.** GEORGE SENTER (*Trans. Faraday Soc.*, 1907, 3, 146—152).—A discussion of the methods which have been suggested for this purpose shows that they are all affected by considerable uncertainty. On the whole, the method based on the influence which electrolytes and certain non-electrolytes exert on the solubility of gases in water seems less obviously open to objection than any of the other methods.

J. C. P.

**Solutions of Metals in Non-Metallic Solvents. I. General Properties of Solutions of Metals in Liquid Ammonia.** CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1907, 29, 1557—1571).—This investigation has been undertaken with the object of elucidating the nature of the electrical conductivity of metals, and especially with reference to the electron theory. It has been found that solutions of metals in non-metallic solvents exist, and have well-marked characteristic properties. An attempt has been made to determine the molecular condition of the metal in the more dilute solutions, to ascertain the relation between the conducting process in such solutions and that occurring in solutions

of electrolytes, and also to investigate the effect of dilution on the process.

In the present paper, an account is given of the properties of solutions of metals in liquid ammonia and other non-metallic solvents. Lithium is soluble in methylamine, less so in ethylamine, and insoluble in propylamine. Potassium dissolves slowly in ethylenediamine, but the solution is unstable. Sodium and potassium are insoluble in ethylamine, and these metals and lithium are all insoluble in secondary and tertiary amines.

When a solution of sodium chloride in liquid ammonia is submitted to electrolysis with a lead cathode and a sodium amalgam anode, a solution of the compound,  $\text{NaPb}_2$ , is formed at the cathode. This compound is also produced when lead iodide is added to a solution of sodium in liquid ammonia. Dilute solutions of the substance appear

to contain the ions  $\text{Na}^+$  and  $\text{Pb}_2^-$ ; when they are treated with a solution of a lead salt, lead is precipitated in a spongy form. Other metallic salts give precipitates containing lead and the metal of the salt employed. Tin is also soluble in a solution of sodium in liquid ammonia.

The solubility curve for sodium in liquid ammonia has been constructed partly from the data obtained by Ruff and Geisel (Abstr., 1906, ii, 228) and partly from conductivity determinations. It is shown that over a certain range of concentration, two solutions of sodium exist together, both containing less than 15% of sodium, and with a critical solution point at about  $-50^\circ$  with 10% of sodium.

The rate of the reaction:  $\text{Na} + \text{NH}_3 = \text{NaNH}_2 + \text{H}$  taking place in a sealed tube has been studied. The rate is approximately constant for some days, and then undergoes a great acceleration, probably due to the catalytic action of solid sodamide which gradually separates. The statement of Joannis (Abstr., 1891, 642) that the rate of the reaction is diminished by the presence of hydrogen was not confirmed.

E. G.

**Mutual Solubility of Solid Aromatic and the Corresponding Hexahydrogenated Compounds.** LUIGI MASCARELLI and UGO PESTALOZZA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 567—575).—Normal cryoscopic behaviour is exhibited by the following hexahydroaromatic derivatives when dissolved in the corresponding non-hydrogenated compounds: *cyclohexane* in benzene; 1:4-dimethyl*cyclohexane* in *p*-xylene; hexahydronaphthalene in naphthalene; *cyclohexanol* in phenol; methyl*cyclohexane*-2-ol in *o*-cresol; methyl*cyclohexane*-4-ol in *p*-cresol, and *cyclohexanecarboxylic acid* in benzoic acid. The same is the case when the non-hydrogenated compound is dissolved in the hexahydro-derivative, except (1) with benzene and *cyclohexane* (this vol., ii, 602), these two compounds evidently forming solid solutions; the freezing-point of mixtures of the two compounds indicates that each of these is, in the solid state, soluble to a limited extent in the other; (2) with phenol in *cyclohexanol*, the latter becoming gummy and opaque near its solidifying temperature, which is indefinite.

T. H. P.

**Electrolytic Dissociation of Partially Neutralised Weak Acids.** YUKŌ MORI (*Mem. Coll. Sci. Eng. Kyōto*, 1907, 1, 205—210).—In a recent paper, Osaka (Abstr., 1905, ii, 804), on the basis of the electrolytic dissociation theory, has made certain deductions with regard to the magnitude and variation with dilution of the hydrogen ion concentration in a solution of a weak acid, and of a mixture of two weak acids in equivalent proportions, partly neutralised by a strong base. These deductions have now been subjected to experimental proof, and it is shown that the variation with dilution is exactly in accordance with expectation, but the observed and calculated values of the dissociation constants are only in moderate agreement.

G. S.

**The Dissociation Theory in its Application to Light Absorption.** GEORGE RUDORF (*Chem. Zentr.*, 1907, ii, 202—203; from *Zeitsch. wiss. Photographie, Photophysik u. Photochemie*, 1907, 5, 24—28).—Solutions of magenta do not follow Beer's law. It is possible to calculate the degree of dissociation of this substance in very dilute solutions ( $< N/23,000$ ) from the observed change in the extinction coefficient on dilution. The values so obtained agree with those calculated by means of Ostwald's dilution law. Since electrical conductivity measurements in such dilute solutions would show seemingly complete dissociation, it follows that the measurement of the light absorption is suitable for the investigation of such dilute solutions.

W. H. G.

**Theory of Hydrolysis.** PAUL PFEIFFER (*Ber.*, 1907, 40, 4036—4042).—Werner considers that the salts of the heavy metals belong to the aquo-salt type, hence that author's theory of hydrolysis (this vol., i, 189, 238; *ibid.*, ii, 560), in the first instance a generalisation of the behaviour of the hydroxylo- and aquo-compounds studied by the present author (Abstr., 1906, i, 531; this vol., i, 1072; ii, 694) and by Werner (*loc. cit.*), must apply also to the salts of the heavy metals. Although hydrolysis may be expressed by the same mathematical formulæ, whether conceived as taking place according to Arrhenius's or to Werner's theory, the processes implied by these theories differ fundamentally. According to Arrhenius's theory, hydrolysis depends on the dissociation of water into its ions, and is limited by the competing attractions of the hydrogen and metal ions for the hydroxyl ions, whereas, according to Werner's view, the aquo-metal ion exists in equilibrium with the hydroxylo-metal and hydrogen ions, from which it follows that the extent of the hydrolysis in any case depends on the combining power of the hydrogen ions with the particular hydroxylo-metal ion. The term "constant of complex formation" is suggested for the reciprocal hydrolysis constant.

The amphoteric behaviour of certain metallic hydroxides may be explained by Werner's theory of hydrolysis. Thus, in the formation of salts by the action of acids on zinc hydroxide, it is considered that hydrogen ions are added to the hydroxyl groups forming the bivalent positive diaquo-zinc ion,  $\text{Zn}(\text{OH}_2)_2^{++}$ , whilst, in the action of alkalis on

the hydroxide, one or more hydroxyl ions are added to the zinc, forming a negative polyhydroxylo-zinc ion such as  $\text{Zn}(\text{OH})_3$ .  
G. Y.

**Hydrolysis of Salts in Aqueous Alcohol.** ALBERT VESTERBERG (*Arkiv Kem. Min. Geol.*, 1907, 2, No. 37, 1—18).—In the presence of alcohols, feeble acids can often be titrated directly, this being the case with boric acid in solutions containing a suitable proportion of glycerol or mannitol. Whether this is due to the formation of complexes or to the suppression of the hydrolysis of the salts of these acids in some other way is uncertain. The author has studied the hydrolysis of aniline acetate and hydrochloride, carbamide acetate and hydrochloride, and sodium phenoxide in alcohol of varying concentration, the conductivity of the solutions being measured at 18°.

Aniline acetate is hydrolysed to a considerably greater extent in aqueous alcohol than in pure water, the degree of hydrolysis increasing regularly with the alcohol content (compare Wislicenus and Stoeber, *Abstr.*, 1899, i, 192; 1902, i, 202). Aniline hydrochloride also undergoes hydrolysis more readily in aqueous alcohol than in water, and carbamide acetate is almost completely hydrolysed in 80% alcohol. The results obtained with carbamide hydrochloride seem to indicate that this salt is hydrolysed to a less extent by aqueous alcohol than by water.

In aqueous alcohol, acetic acid, like salicylic acid and other acids of medium strength (compare Godlewski, *Abstr.*, 1904, ii, 701), follows Ostwald's dilution law.  
T. H. P.

**Criteria of Pseudo-Acids.** HARALD LUNDÉN (*Arkiv Kem. Min. Geol.*, 1907, 2, No. 28, 1—10).—The author replies to Hantzsch's criticisms (*Abstr.*, 1906, ii, 651) on his work on amphoteric electrolytes (*Abstr.*, 1906, ii, 265). Hantzsch's view that abnormal hydrolysis is sufficient to stamp a compound as a pseudo-acid is controverted. The grounds on which he assumes a hydrolysis to be abnormal are, in many instances, as follows: (1) if a sodium salt has a neutral reaction, its hydrolysis must be less than that of sodium acetate. (2) If the hydrogen compound has a neutral reaction, its dissociation constant must be less than that of phenol, for the latter, at the same dilutions, reacts distinctly acid. The first of these criteria is shown to be inadmissible, since the magnitude of the experimental errors is sufficient to explain the absence of an alkaline reaction. As regards method (2), the author obtains for the dissociation constant of isonitrosoacetone the value  $k_a \ 3.8 \times 10^{-9}$  from the hydrolysis of ethyl acetate, and the value  $k_a \ 4.6 \times 10^{-9}$  from conductivity measurements; the agreement between these two numbers shows that the hydrolysis is not abnormal in this case. Further, the dissociation constant of isonitrosoacetone as a base,  $k_b$ , is found to be slightly less than  $1 \times 10^{-14}$ . A 0.163*N* solution of isonitrosoacetone renders litmus solution somewhat more red than a phenol solution of equivalent concentration, from which result it cannot be concluded that isonitrosoacetone is a pseudo-acid. The dissociation of isonitrosomethylpyrazolone is also found to be normal.

A trustworthy criterion for intramolecular rearrangement during salt-formation is found in the slowness of neutralisation.

T. H. P.

**Colloidal Solution.** ROBERT H. BRADBURY (*Chem. Zentr.*, 1907, ii, 771; from *J. Franklin Inst.*, 1907, 163, 383—396).—A paper dealing chiefly with the properties of colloidal and crystalloidal solutions and the differences existing between them and suspensions.

W. H. G.

**Systematic Classification of Colloids.** WOLFGANG OSTWALD (*Chem. Zentr.*, 1907, ii, 120—121; from *Zeitsch. Chem. Ind. Kolloide*, 1907, i, 291—300).—A paper dealing with the systematic classification of colloidal solutions regarded as polyphase systems.

W. H. G.

**Molecular Weight and Magnitude of the Particles of Colloids.** REGINALD O. HERZOG (*Chem. Zentr.*, 1907, ii, 661; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 2—3).—Colloidal solutions exhibit a very small or unobservable osmotic pressure, but the relationship existing between the mol. wt. and size of the particles of colloids is not yet clear.

W. H. G.

**Precipitation and Adsorption of Colloids.** HERBERT FREUNDLICH (*Chem. Zentr.*, 1907, ii, 201—202; from *Zeitsch. Chem. Ind. Kolloide*, 1907, i, 321—331).—The weight of a substance,  $x/m$ , adsorbed by unit weight of the adsorbing substance is not proportional to the concentration of the solution,  $c$ , but follows the equation  $x/m = ac^{1/p}$ , where  $a$  and  $p$  are constants; the value  $1/p$  lies between 0.1 and 0.4. When the anion is adsorbed more than the cation, as is the case with organic salts of the light metals, the concentration of the cation necessary to produce precipitation increases with the extent to which the anion is adsorbed; thus potassium formate precipitates more readily than potassium acetate, since the acetate anion is adsorbed more than the formate anion.

W. H. G.

**Liquid Crystals of Two New Compounds of Cholesterol.** PAUL GAUBERT (*Compt. rend.*, 1907, 145, 722—725. Compare Lehmann, *Abstr.*, 1906, ii, 836).—By heating cholesterol for half an hour with glycollic acid, a compound is obtained which, after repeated recrystallisation from bromoform, forms white, nacreous needles. When this is examined microscopically whilst being gradually heated, the double refraction observed at first diminishes as the temperature rises from 110°, then the crystals cease to act on parallel polarised light, but examination in a convergent beam reveals the cross of uniaxial crystals. At this instant, a slipping of the micro-cover glass shows that the substance is already liquid, and on further rise of temperature the cross disappears, the liquid becoming isotropic. The passage of the anisotropic to the isotropic liquid cannot be observed by the naked eye in the case of the pure substance, but this can be done with a product containing a slight excess of glycollic acid, or the

reverse change can be seen whilst cooling. If the substance is pure, the anisotropic liquid crystals solidify suddenly, but in the presence of a slight amount of glycollic acid they are stable at a low temperature, becoming more and more pasty.

Longer heating of cholesterol with glycerol gives a substance having similar properties. The m. p. to an isotropic liquid is  $145^{\circ}$  (approx.); the anisotropic liquid, which is rather more viscous than glycerol, solidifies at  $115^{\circ}$  (approx.), giving solid crystals in the form of spherulites. Fused malachite-green colours the liquid crystals of the two esters and renders them polychroic.

Pure fused cholesterol solidifies in two modifications, one of which forms beautiful spherulites having helical scrolls (compare Wallerant, *Abstr.*, 1906, ii, 838). E. H.

**Distribution of a Base between Two Acids.** ALFRED THIEL and HERMANN ROEMER (*Zeitsch. physikal. Chem.*, 1907, 61, 114—126).—Formulae are deduced for the equilibrium between a strong base and two monobasic acids in solution, and for the conductivity of a partly neutralised mixture of the two acids. The validity of the formulae is conditional on the assumptions (1) that the law of mass action is applicable to each electrolyte involved; (2) that the two acids are present in equivalent quantities, and (3) that the two normal salts are dissociated to an equal extent.

Experiments in which solutions containing equivalent quantities of acetic and monochloroacetic acids were neutralised to different extents with sodium hydroxide show that the conductivity of such a partly neutralised solution can be satisfactorily calculated by the authors' formulae. J. C. P.

**Conditions of Equilibrium in the Systems Zinc Sulphate—Ammonia—Water.** Mdme. N. ZUBKOWSKAIA (*J. Russ. Phys. Chem.* 1907, 39, 989—1000).—The system was investigated according to Kuriloff's method (*Abstr.*, 1906, ii, 349) for the system zinc chloride, ammonia, and water. Three stages were observed: (1) precipitate increasing; (2) precipitate decreasing; (3) reappearance of a precipitate.

In the first stage, the relation  $\text{Zn}:\text{SO}_4=4:1$  and the precipitate is most probably  $\text{ZnSO}_4\cdot 3\text{Zn}(\text{OH})_2$ . At the transition from stage (1) to (2),  $\text{Zn}:\text{NH}_3=1:1$ , and the whole solution, which is probably a pseudo-solution, coagulates at this point; at the same time the crystalline, basic salt is transformed into a colloid, and when the process is completed the colloid commences to settle, coagulation is no longer complete, and stage (2) passes into stage (3). It was observed in several cases that as the amount of precipitate diminishes, so the proportion of zinc sulphate in the precipitate increases, thus the last traces of zinc sulphate are not dissolved until the whole of the zinc hydroxide has passed into the pseudo-solution. No definite compounds are formed in stage (2), which is characterised by an increasing concentration of ammonia. It is considered that  $\text{ZnSO}_4\cdot 3\text{Zn}(\text{OH})_2$  is the only basic zinc sulphate which exists as a definite chemical compound. Z. K.



**Equilibrium between Reciprocal Salt Pairs.** YUKICHI OSAKA and JINGORO YAMASAKI (*Mem. Coll. Sci. Eng. Kyōto*, 1907, 1, 173—175. Compare Meyerhoffer, *Abstr.*, 1906, ii, 12).—Solutions of potassium carbonate and sulphate, the total concentration of which was 0.5*N*, were boiled with strontium carbonate and sulphate in a silver flask until equilibrium was attained, and it was then found that the mean value at 100° for the ratio  $K_2SO_4 : K_2CO_3$  was 95 : 1. G. S.

**Dynamic Isomerism.** HENRY E. ARMSTRONG, THOMAS M. LOWRY, SIDNEY YOUNG, JAMES J. DOBBIE, ARTHUR LAPWORTH, and MARTIN O. FORSTER (*Brit. Assoc. Report*, 1906, 76, 157—159).—The report refers to recent determinations of the proportions in which *isodynamic* compounds are in equilibrium in solution, and summarises the results of four investigations. G. T. M.

**Kinetics of the Introduction of Acids into the Diazoacetic Ester Molecule, especially with the Aid of Neutral Salts.** GEORG BREDIG and PHIL. F. RIPLEY [and, in part, W. FRAENKEL] (*Ber.*, 1907, 40, 4015—4026).—The inhibition or retardation of the decomposition of ethyl diazoacetate by dilute acids by addition of neutral salts was explained previously (Fraenkel, this vol., ii, 746) as depending on the simultaneous occurrence of another reaction resulting in the formation of a nitric ester of ethyl glycolate. This has now been confirmed in the following manner: an aqueous-alcoholic solution of ethyl diazoacetate and sodium chloride was made slightly acid to methyl-orange with hydrochloric, nitric, or sulphuric acid, when a slight evolution of nitrogen took place and the mixture became neutral; the treatment with acid was repeated until the mixture remained acid on heating. The ethereal extract of the product after evaporation and hydrolysis with alcoholic potassium hydroxide gave with silver nitrate a heavy chloride precipitate (compare Curtius, *Abstr.*, 1884, 987). The product obtained in the same manner from the reaction in presence of sodium sulphate contained sulphuric acid, presumably in consequence of the formation of the sulphate,

$$SO_2(O \cdot CH_2 \cdot CO_2Et)_2.$$

The formation of such esters must be possible in the presence of the acid only, but in this case, consequent on the greatly diminished anion concentration, can take place to only a very small extent, which may be detected in some cases by an apparent diminution of the unimolecular constant for the velocity of the evolution of the nitrogen.

From the discussion of the kinetics of the side-reaction, it is concluded that the ratio of ethyl chloroacetate formed in presence of sodium chloride to the total ethyl diazoacetate decomposed must increase with the concentration of the chlorine anions, but must be independent of the original concentrations of the ethyl diazoacetate and of the free acid, and experimental results are quoted showing that this is the case. It is found further that the extent to which the side-reaction takes place depends on the nature of the halogen anion; thus under the same conditions, but with potassium chloride, bromide, and iodide, the formation of the ethyl halogenoacetate amounts to 48.7%, 66.7%, and 84.3%, respectively of the total reaction. G. Y.

**Catalysis by Chromic Acid and its Salts. II.** EUGEN SPITALSKY (*Zeitsch. anorg. Chem.*, 1907, 56, 72—108. Compare this vol., ii, 338).—The velocity of decomposition of hydrogen peroxide by free chromic acid at 25° has been investigated by measuring the rate of evolution of oxygen, as described in the previous paper.

When the peroxide is present in considerable excess, the rate at which it is decomposed is nearly independent of its concentration, being approximately proportional to the cube root of the peroxide concentration, but when the peroxide concentration has diminished to such an extent that the ratio  $\text{H}_2\text{O}_2 : \text{CrO}_3$  is not more than 10 : 1, the velocity suddenly rises to two or three times its former value and then falls rapidly to zero, the peroxide being completely decomposed. The decomposition is relatively less rapid the greater the initial peroxide concentration for a definite concentration of chromic acid. When the peroxide is present in considerable excess, the rate of decomposition is approximately proportional to the chromic acid concentration. The reaction velocity at any instant is completely determined by the peroxide and chromic acid concentrations at that instant, for example, the sharp maximum in the velocity curve occurs at the same peroxide concentration for a definite chromic acid concentration, independent of the initial concentration of the peroxide. After the reaction, it is found that about 28% of the chromic acid has been reduced, and this proportion is independent of the initial peroxide concentration and nearly independent of the chromic acid concentration.

It is probable that the phenomena in question are best accounted for by rapid changes in the condition of the catalyst, but no definite results in this direction have yet been obtained.

It is pointed out that the course of the reaction resembles in certain important respects that of enzyme reactions. G. S.

**Catalysis by Acids and Bases of the Mutarotation of Dextrose.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1907, 29, 1571—1576).—The rate of mutarotation of dextrose is largely influenced by the presence of acids and alkalis, but is not much affected by neutral substances which do not undergo hydrolysis in solution. Experiments have been made with the object of determining the relation between the concentration of the catalysing agent and the acceleration produced.

The rate of mutarotation at 24.7° has been determined in solutions of hydrochloric acid of concentrations from 0.001 to 0.1 gram-mol. per litre, and the results show that a linear relation exists between the concentration of the hydrogen ions and the rate of mutarotation, and that in these solutions the influence of the hydroxyl ions is negligible. Osaka (*Abstr.*, 1901, i, 127) has stated that the rate of mutarotation is proportional to the square root of the concentration of the hydrogen ions, but it is found that this is only true for concentrations of hydrochloric acid between 0.01 and 0.10 gram-mol. per litre.

From the values obtained by Osaka for the rate in alkaline solution and the values now found for it in acid solution, the rate of mutarotation of dextrose at 25° in aqueous, acid, or alkaline

solution is shown to be given by the expression:  $0.0096 + 0.258(\text{H}') + 9750(\text{OH}')$ . Hydroxyl ions exert a catalytic action on the mutarotation which is nearly 40,000 times as strong as that exerted by hydrogen ions, and, for this reason, feebly acid solutions show a lower rate of mutarotation than that observed in pure water. This retardation or negative catalysis has been determined in a solution containing 0.001 gram-mol. of hydrogen chloride per litre, and has been found to be in accordance with that given by the above expression.

E. G.

**Physiological Catalysis.** GEORG BREDIG (*Centr. Bakt. Par.*, 1907, 19, 485—494. Compare this vol., i, 372).—A reply to Bokorny's criticisms (this vol., ii, 184; *Centr. Bakt. Par.*, 1907, 18, 737). The author enumerates the analogies in the action of enzymes and colloidal metals as catalytic agents, and justifies his application of the term "inorganic ferment" to colloidal platinum.

G. S.

**Variation of the Mass of the Electrons in the Interior of the Atom.** HENRI PELLAT (*Compt. rend.*, 1907, 145, 673—676).—The author considers that the enormous number of spectral rays emitted by an element can be explained without the assumption of more than a limited number of identical corpuscles in the interior of the atom. The mass of a corpuscle not only depends on its velocity, but may vary by reason of the magnetic fields which result from the motion of two or more corpuscles encroaching on one another. When such encroachment takes place, the sum of the masses of two corpuscles may be greater or less than the sum of the masses of the isolated corpuscles. Two corpuscles revolving with nearly the same velocity in the same direction may thus be influenced during a certain number of revolutions, whilst during a large number of revolutions the corpuscles will have their normal masses. The variable corpuscular masses found in connexion with the Zeeman effect and the small masses corresponding with the observed magnetic displacement of certain absorption bands are explainable on the view put forward.

H. M. D.

**Number of Electrons in an Atom.** NORMAN CAMPBELL (*Proc. Camb. Phil. Soc.*, 1907, 14, 287—291).—If the energy liberated by a radium atom in its disintegration represents the potential energy of the electrons in their orbits, the number of electrons in the radium atom can be calculated if the average energy of an electron is known. An estimate of this is obtained by assuming that the potential energy which is liberated when the orbit, in which an electron moves, becomes unstable is of the same order of magnitude as the maximum kinetic energy which the electron can possess without breaking free from that orbit. This maximum kinetic energy is identified with the least kinetic energy possessed by an electron moving outside an atom, and this, according to Thomson's measurements, is  $6.7 \times 10^{-31}$  ergs. From this, the number of electrons in the radium atom is found to be  $2.5 \times 10^5$ , which agrees closely with the older estimate based on the mass of the atom.

H. M. D.

**Valency Question.** WALTER PETERS (*Zeitsch. Elektrochem.*, 1907, 13, 657—659).—On Helmholtz's electron theory of affinity, the forces acting between the atoms of a molecule are nearly independent of the masses of the atoms. Hence if two gases have the same number of atoms, the same molecular heat, and the same ratio of specific heats at constant pressure and volume, they have the same total energy and also the same internal energy at any temperature, and therefore the total number of affinities acting between their atoms must be the same. A number of examples illustrating this conclusion are given.

T. E.

**Free Path and Number of Electrons in Metals.** L. BLOCH (*Compt. rend.*, 1907, 145, 754—757).—Drude's experimental results (*Ann. Phys. Chem.*, 1890, [iii], 39, 537; 1891, [iii], 42, 189) do not agree with the formula  $n^2\chi = \sigma_\infty T$ , where  $n$  is the index corresponding with the period  $T$ ,  $\chi$  the coefficient of absorption, and  $\sigma_\infty$  the conductivity in electrostatic units. The author has made a series of calculations to determine whether the formula  $n^2\chi = \sigma_\lambda T$ , where  $\sigma_\lambda$  has the value

$2N^1e^2\sin^2\frac{qt_2}{2}/m_1^2$  (in which  $q = 2\pi/T$  the frequency,  $t_2$  is the duration

of the mean path, and  $N^1$  the number of mean paths per unit of volume and unit of temperature), proposed by J. J. Thomson, is in accordance with Drude's values. Since  $N^1t_2 = N$  the number of free electrons per unit volume, Thomson's value may be written  $\sigma_\lambda = (Ne^2t_2/2m)\left(\sin^2\frac{qt}{2}/\left(\frac{qt_2}{2}\right)^2\right)$ , of which a particular value is  $\sigma_\lambda = Ne^2t_2/2m$ . Then assuming the truth of the expression  $n^2\chi/\sigma_\lambda T = \sin^2\frac{qt_2}{2}/\left(\frac{qt}{2}\right)^2$ , of which the left hand quantity is known from Drude's

measurements, it is required to find the value of  $t_2$ .  $N$  can be found from  $t_2$ , and the numbers found for  $N$  and  $t_2$  are compared with the values deduced from the electron theory of metals. A table is given of the results calculated for the metals studied by Drude, using the sodium D-line ( $T = 2 \times 10^{-15}$ ). These results show that all the mean paths have a duration ( $t_2$ ) of the same order, the values of  $t_2$  being greatest for the best conductors; they support Larmor's view (*Phil. Mag.*, 1907, [vi], 14, 312) that the paths are of the order of the atomic dimensions ( $10^{-8}$ ) and probably less than  $10^{-7}$ , and agree with his values for the numbers of electrons per unit volume. The values obtained for the numbers of atoms of metal per c.c. ( $N_1$ ) are greater than those obtained by Drude, over which they have the advantage of being larger for the better conductors; they contradict J. J. Thomson's hypothesis that the values of  $N/N_1$  will be equal to the atomic weights.

E. H.

**The Evolution of the Elements.** FREDERICK SODDY (*Brit. Assoc. Report*, 1906, 76, 122—131).—The report contains a brief resume of the various views held in the past with regard to the nature and origin of the chemical elements, followed by a discussion of the results obtained in the study of the radioactive elements.

G. T. M.

**New Method of Simultaneously Determining the Exact Atomic Weights of all the Elements Present in a Single Chemical Reaction.** GUSTAVE D. HINRICHS (*Compt. rend.*, 1907, 145, 715—718. Compare Abstr., 1893, ii, 317).—If  $x, y, z \dots$  are the errors in the experimental values,  $X, Y, Z \dots$  the absolute atomic weights (round-number values) giving  $X+x, Y+y, Z+z, \dots$  for the exact atomic weights, and  $\Delta X, \Delta Y, \Delta Z, \dots$  the variations produced in the atomic ratio  $R$  by an increase of one hundred-thousandth of the atomic weight, then  $x\Delta X + y\Delta Y + z\Delta Z + \dots = 10e$  represents the equation of condition where  $e$  is the analytical excess. This equation for two variables represents a line, for three, a plane. Having constructed such a graph for a given research, the perpendicular from the origin on it gives the minimum deviation of experiment from the absolute value, and the projections of this perpendicular on the axes  $X, Y, Z$  are the linear errors from which the values of  $x, y$ , and  $z$  are obtained. Applying this method, the author finds the values  $35.5 - 0.000307$  and  $108 + 0.00032$  for the exact atomic weights of chlorine and silver, and shows that the absolute atomic weights are identical with the exact atomic weights. From the work of Urbain on terbium, and of Curie on radium, the values  $H = 1 - 0.0000007$ ,  $O = 16 - 0.0000007$ ,  $Tb = 159 + 0.0000542$ , and  $Rd = 226.5$  are calculated.

E. H.

**Theory of Bases.** ALFRED WERNER (*Ber.*, 1907, 40, 4133—4145).—The author in previous researches has studied the properties of ten different series of metalammine compounds, which are characterised by having hydroxyl-groups directly attached to the metal atom. In the investigation of these hydroxyl-compounds, facts have been ascertained which allow of generalisations with respect to other types of bases, their relations towards acids, and their facts of hydrolysis and electrolytic dissociation. In this paper, the author gives a summary of his views.

A. McK.

**Constitution of Basic Salts and Analogously Constituted Complex Salts. I.** ALFRED WERNER (*Ber.*, 1907, 40, 4441—4449).—A theoretical paper dealing with the classification and constitution of basic salts.

In the last three communications on complex metal ammonias (this vol., i, 482, 1012; ii, 965), the author has shown that certain metallic dihydroxy-compounds, such as  $[(HO)_2Co(NH_3)_4]X$  and  $[(HO)_2CoEn_2]X$ , are capable of forming complex compounds with various metallic salts, the two OH groups in virtue of their residual affinities combining with the metal of the salt. This combination may be represented as

follows:  $X(A_4Co \begin{smallmatrix} \cdot OH \\ \cdot OH \end{smallmatrix} > MX_m$ , where  $M$  is the metal. Although the

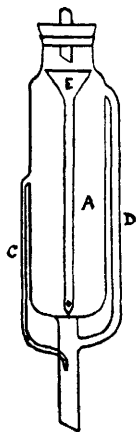
nature of the metal and of the amine in the complex,  $(A_4M < \begin{smallmatrix} OH \\ OH \end{smallmatrix})$ , will modify, to some extent, the power of the OH groups to form complex compounds, it should nevertheless be possible for metallic dihydroxides uncombined with ammonia to behave in the same

manner as those combined with ammonia. Consequently, it should be possible to obtain ammonia-free compounds corresponding with the hexol-, tetrol-, and diol-series of ammoniumcobalt compounds, and containing the complex radicles:  $\left[ M \begin{pmatrix} HO \\ HO \end{pmatrix} M \right]_3$ ,  $\left[ M \begin{pmatrix} HO \\ HO \end{pmatrix} M \right]_2$ , and  $\left[ M \begin{pmatrix} HO \\ HO \end{pmatrix} M \right]$ .

In the present paper, it is shown that a large number of basic salts which have already been prepared may be considered as belonging to the hexolseries, for example:  $\left[ Ca \begin{pmatrix} HO \\ HO \end{pmatrix} Ca \right]_3 Cl_2 \cdot 13H_2O$ ;  $\left[ Zn \begin{pmatrix} HO \\ HO \end{pmatrix} Zn \right]_3 SO_4$ ;  $\left[ Cu \begin{pmatrix} HO \\ HO \end{pmatrix} Cu \right]_3 Br_2$ .

By replacing the hydrogen atoms of the OH groups by acid radicles, compounds of the type  $\left[ M \begin{pmatrix} RO \\ RO \end{pmatrix} M \right]_3 X_2$  are obtained. Thus, when  $R = PO_3M$ ,  $AsO_3M$ , or  $VO_3M$ , the compounds are members of the apatite group, for example,  $[Ca_3(PO_4)_2]_3 CaF_2$ , apatite;  $[Pb_3(AsO_4)_2]_3 PbCl_2$ , mimetesite;  $[Pb_3(VO_4)_2]_3 PbCl_2$ , vanadinite.

W. H. G.



apparatus is  
apparatus.

**Apparatus for the Continuous Extraction of Liquids.** ORESTE PRANDI (*Chem. Zentr.*, 1907, ii, 659; from *Staz. sperim. agrar ital.*, 1906, 39, 865—866).—The cylinder *A*, closed at its lower end, is connected with a reflux condenser above. The wide tube fused on the bottom of the cylinder is connected with the flask containing the extracting solvent, and is in communication with *A* by means of the side-tubes *C* and *D*. The cylinder contains a movable funnel, *E*, at the bottom of which are a number of small holes. The

used in the same manner as the ordinary Soxhlet  
W. H. G.

## Inorganic Chemistry.

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**Ignition Temperature of Gaseous Mixtures. II.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1907, 29, 1536—1557; *Ann. Physik*, 1907, [iv], 24, 450—482).—In a previous paper (this vol., ii, 18), a method was described for determining the ignition temperature of gaseous mixtures by means of adiabatic compression, and the results obtained with mixtures of hydrogen and oxygen were recorded.

The method has now been applied to the determination of the ignition temperatures of mixtures of carbon monoxide and oxygen; hydrogen, oxygen, and nitrogen; carbon monoxide, oxygen, and

nitrogen ; and carbon monoxide, oxygen, and hydrogen. The possible sources of error are discussed, and an expression is given by means of which the ignition temperature of any mixture containing hydrogen, carbon monoxide, oxygen, and an inert gas can be calculated. The reaction between hydrogen and oxygen is bimolecular, and that between carbon monoxide and oxygen is termolecular. When the hydrogen or carbon monoxide is present in excess of the oxygen, results are obtained which indicate that in such cases the reactions do not follow the simple laws of chemical kinetics, but that the excess of the carbon monoxide or hydrogen exerts a negative catalysing effect. E. G.

**The Behaviour of Sulphur towards Water and the Vapour Pressure of Sulphur from 78—210°.** OTTO RUFF and HUGO GRAF (*Ber.*, 1907, 40, 4199—4205).—Cross and Higgin (*Trans.*, 1879, 35, 249) drew the conclusion that sulphur was capable of slightly decomposing water vapour at 90°, forming hydrogen sulphide and sulphur dioxide, as lead acetate solution was affected by the sulphur-water vapour. This result may, however, be due to lead ions and sulphur, and the problem was attacked in another way, namely, by comparing the partial pressures of sulphur in an indifferent gas, like carbon dioxide, and in water vapour ; if interaction takes place in the latter case, then the partial pressure must be greater than in the former. The partial pressure was measured dynamically by passing the gas or vapour through seven flasks of 100 c.c. capacity kept at a constant temperature in an oil-bath and weighing the sulphur deposited in a cooled vessel. The partial pressure was calculated from the expression  $p = B.D/(K + D)$ , where  $B$  is pressure in mm.,  $K$  the mol. of gas, and  $D$  the mol. of sulphur. At 115°, the partial pressures obtained in the two cases are almost identical, so that a reaction occurring to any measurable extent is excluded. In the curves obtained, there is a break at 108° and another less marked at 136°. The break at 108° ought to correspond with the transition from solid to liquid sulphur ; Smith and Holmes, however, found the m. p. of sulphur in carbon dioxide to be 114.5° (this vol., ii, 20). W. R.

**The Affinity of Sulphur for Metals.** E. SCHÜTZ (*Metallurgie*, 1907, 4, 659—667, 694—700).—The experiments were made by fusing an intimate mixture of a metal and the sulphide of another metal under a layer of carbon in graphite crucibles at a definite temperature. After cooling, the regulus and matte were analysed separately. The experiments were made in pairs, in order to reach the equilibrium from both sides, as, for instance,  $MnS + Fe$  and  $FeS + Mn$ . The series of metals, arranged in diminishing order of their affinity for sulphur, was found to be manganese, copper, nickel, iron, tin, zinc, lead.

The effect of the presence of alkaline earth sulphides and sulphates in the mixture to be melted was also examined. C. H. D.

**Combustion of Nitrogen in the Arc between Conductors of the Second Class.** EWALD RASCH (*Zeitsch. Elektrochem.*, 1907, 13, 669—675).—Priority is claimed in the use of an arc between infusible

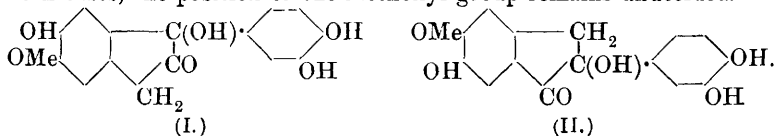


manganate in neutral solution; in presence of an alkali, there is obtained the resin formed by the action of alkalis alone.

When heated with fuming hydrochloric acid in a sealed tube at  $120^{\circ}$ , eriodictyonone yields catechol and an oil, which gives a green coloration with alcoholic ferric chloride, and is probably an impure *homocatechol*,  $C_6H_3Me(OH)_2$ .

The action of diazomethane on eriodictyonone leads to the formation of a *methyl ether*,  $C_{15}H_{10}O_4(OMe)_2$ , which crystallises in prisms, m. p.  $160^{\circ}$ , reduces ammoniacal silver solution, forms a red resin when heated with aqueous alkalis, and gives a red coloration with alcoholic ferric chloride. On further treatment with an excess of diazomethane, this ether yields the *tetramethyl ether*,  $C_{15}H_8O_2(OMe)_4$ , which crystallises in yellow needles, m. p.  $162^{\circ}$ , is insoluble in aqueous alkalis, and does not give a coloration with ferric chloride. When fused with potassium hydroxide, the tetramethyl ether forms protocatechuic acid.

In the light of these results, it is considered that the constitution of eriodictyonone must be represented by the formula I or II. In both cases, the position of the methoxyl group remains undecided.



(see also Power and Tutin, *Proc.*, 23, 243).

G. Y.

**Spectrophotometry of the Chlorophyllins and the Energetics of Chlorophyll.** M. TSVETT (*Ber. deut. bot. Ges.*, 1907, 25, 388—397. Compare this vol., i, 787).—Results obtained with an alcoholic solution of chlorophyllin show that the absorption is greater in the blue portion of the spectrum than in the red. The band  $\lambda$  460—475 can be distinguished in solutions so diluted that the band in the red portion is no longer visible.

N. H. J. M.

**Phylloxanthin.** M. TSVETT (*Biochem. Zeitsch.*, 1907, 6, 373—378).—A reply to Marchlewski's criticism (this vol., i, 867) of the conclusions drawn by the author (this vol., i, 787). The spectrum of phylloxanthin is very similar to that of  $\beta$ -chlorophyllan; neither substance can be transformed into phyllocyanin.

G. B.

**New Method of Preparing Azophenin.** WLADIMIR SCHAPOSCHNIKOFF (*Zeitsch. Farb.-Ind.*, 1907, 6, 289—291).—Details are given for preparing quinonedichlorodi-imine by the action of a solution of bleaching powder on *p*-phenylenediamine or its hydrochloride; by the method used, a pure white product is readily obtained. It is best converted into azophenin by adding aniline to its solution in benzene; other substances are also formed, but azophenin is the principal product (2.8 grams of azophenin from 3.5 grams of quinonedichlorodi-imine), and can be easily separated in a pure state.

W. A. D.

**Oxidation of Aromatic Amines by Means of Manganese Salt with Formation of Dyes.** FRITZ CRONER (*Chem. Zeit.*, 1907, 31, 948—949).—If 10 c.c. of a 0.2% aqueous solution of atoxyl

Alcohol, or excess of alkali, precipitates brown flakes, which are soluble in water, dilute acids and all soluble salts give a similar precipitate insoluble in water or alkalis. The brown, alkaline solution can be freed from alcohol by dialysis, but it is impossible to remove all the phosphorus or all the alkali. Estimations of the arsenic present in solution, by iodometry and by precipitation and distillation, agree so closely that the solution is probably a true colloidal solution of arsenic.

E. H.

**Reduction of Arsenic Tri- and Penta-sulphides to the Disulphide.** RICHARD EHRENFELD (*Ber.*, 1907, 40, 3962—3965).—The red precipitate sometimes formed on digestion of sulphides of arsenic and tin with ammonium carbonate and acidification of the solution is shown to consist of arsenic disulphide,  $As_2S_2$ , formed by reduction of the tri- or penta-sulphide by stannous chloride and hydrochloric acid. This reduction takes place quantitatively as measured by titration of the stannous chloride solution and of the hydrogen sulphide evolved. The disulphide is readily oxidised to a small extent to arsenic trioxide, whilst traces of the stannic chloride formed in the reaction are reduced by the hydrogen sulphide. Attempts to reduce arsenic trisulphide by means of arsenic, antimony, or phosphorus trichloride, or ferrous or chromous chloride, were unsuccessful.

When heated with stannous chloride in hydrochloric acid solution in a sealed tube at  $100^\circ$  for twelve hours, carbon disulphide remains almost unchanged, only a very small amount being hydrolysed, forming carbon dioxide and hydrogen sulphide.

G. Y.

**Occurrence of Helium in Natural Gas and the Composition of Natural Gas.** HAMILTON P. CADY and DAVID F. MCFARLAND (*J. Amer. Chem. Soc.*, 1907, 29, 1523—1536).—In 1903, a sample of natural gas from a well drilled at Dexter, Cowley Co. Kansas, was examined, and after sparking with oxygen yielded a residue which was evidently not nitrogen. Further examination of the gas at a later date showed that it contained 1.84% of helium.

Forty-one samples of natural gas from Kansas and other States have now been analysed, and the presence of helium has been established in all cases but one. It was observed that the amount of helium in the gas tended to increase as the amount of nitrogen increased, but that no direct relation existed between them. The different samples of gas varied widely in composition, the hydrocarbons varying from 15% to 98%, and helium from a trace up to 1.84%. Nevertheless, in spite of this variation, in the gases from Kansas a regularity was observed in the percentage of helium and total paraffin hydrocarbons along lines running across the State from north-east to south-west, which followed approximately the lines of the outcrop of the geological strata.

E. G.

**Alloys of Potassium with Aluminium, Magnesium, Zinc, Cadmium, Bismuth, Tin, and Lead.** D. P. SMITH (*Zeitsch. anorg. Chem.*, 1907, 56, 109—142).—From an investigation of these systems by Tammann's method of thermal analysis, controlled, when possible,

by microscopic observations, evidence has been obtained of the existence of the following compounds:  $\text{KZn}_{12}$  (?);  $\text{KCd}_{11}$ ,  $\text{KCd}_7$ ;  $\text{KBi}_2$ ,  $\text{K}_3\text{Bi}_7$  (?),  $\text{K}_3\text{Bi}_2$ ,  $\text{K}_3\text{Bi}$ ;  $\text{K}_2\text{Sn}$  (?),  $\text{KSn}$  (?),  $\text{KSn}_2$ ,  $\text{KSn}_4$ ;  $\text{K}_2\text{Pb}$ ,  $\text{KPb}_2$ ,  $\text{KPb}_4$ , and a fourth compound of unknown composition. Owing to the ready oxidisability of many of the alloys, microscopic observations seldom gave useful results.

Neither *magnesium* nor *aluminium* are miscible with sodium in the fused state, and no chemical compounds are formed.

*Potassium-Zinc Alloys.*—At  $600^\circ$ , potassium is insoluble in zinc, and the latter is only slightly soluble in potassium. When the temperature falls to  $585^\circ$ , the two metals react with formation of a compound, probably  $\text{KZn}_{12}$ , which separates at first in an unstable form and changes about the same temperature to a more stable form. Two other breaks in the cooling curve, at  $510^\circ$  and  $405^\circ$ , probably represent further transformations of the compound in question.

*Potassium-Cadmium Alloys.*—At  $500^\circ$ , potassium is soluble to the extent of 17 atom % in cadmium, but the latter is practically insoluble in potassium. The freezing-point curve of the alloys containing 0–17 atom % of potassium has a maximum at  $487^\circ$  and 8 atom % of potassium, corresponding with the compound  $\text{KCd}_{11}$ , and there is a break at  $473^\circ$ , indicating the existence of a second compound  $\text{KCd}_7$ , which is formed by interaction of  $\text{KCd}_{11}$  and the fused alloy in mixtures containing 8.3–13 atom % of potassium. The investigation of these alloys was rendered difficult owing to supercooling.

*Potassium-Bismuth Alloys.*—These metals are miscible in all proportions in the fused state. The freezing-point curve shows two well-defined maxima at  $540^\circ$  and 35 atom % and  $671^\circ$  and 75 atom % of potassium respectively, corresponding with the compounds  $\text{KBi}_2$  and  $\text{K}_3\text{Bi}$ , a break at  $420^\circ$ , indicating the formation of the compound  $\text{K}_3\text{Bi}_2$ , as well as two eutectic points at  $260^\circ$  and 3% and  $335^\circ$  and 50 atom % of potassium respectively. Further, the compound  $\text{K}_3\text{Bi}_2$  reacts with the fused mass when the temperature reaches  $373^\circ$ , forming a fourth compound, the formula of which has not been definitely established, but may be  $\text{K}_3\text{Bi}_7$ . At  $280^\circ$ ,  $\text{K}_3\text{Bi}$  has a transition point.

*Potassium-Tin Alloys.*—The metals are miscible in all proportions in the fused state. The great majority of the alloys melt at temperatures much higher than the melting points of their components; owing, however, to the fact that they rapidly destroy Jena glass and even steel, the investigation has not led to very conclusive results. Some evidence has been obtained of the existence of the compounds  $\text{KSn}_2$  and  $\text{KSn}_4$ , and possibly of  $\text{K}_2\text{Sn}$  and  $\text{KSn}$ ; the second compound has a transition point at  $413^\circ$ .

*Potassium-Lead Alloys.*—The investigation of these alloys was also attended with serious difficulties. The melting point of lead is lowered to  $275^\circ$  by the addition of potassium; the eutectic mixture contains about 8 atom % of the latter metal. At  $295^\circ$ , the compound  $\text{KPb}_2$  reacts with the fused mass to form the compound  $\text{KPb}_4$ ;  $\text{KPb}_2$  itself is formed by the interaction of a third compound of unknown composition and the fused mass at  $337^\circ$ . A fourth compound, probably  $\text{K}_2\text{Pb}$ , melts about  $568^\circ$ , and has a transition point at  $376^\circ$ .

In general, those metals which combine with sodium also combine

with potassium, but very few of the compounds are of corresponding composition. G. S.

**Hydrates of Sodium Sulphide.** NICOLA PARRAVANO and M. FORNAINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 464—469).—Sodium sulphide forms the following hydrates. The nonahydrate,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , is obtained by crystallisation of aqueous solutions of the sulphide at the ordinary temperature, and gives a saturated solution solidifying at  $-10^\circ$  to the cryohydrate containing 9.34% of anhydrous sulphide; at  $48.9^\circ$ , it is transformed into the hydrate,  $\text{Na}_2\text{S} \cdot 5\frac{1}{2}\text{H}_2\text{O}$ . The hexahydrate is stable between  $48^\circ$  and  $91.5^\circ$ , whilst the hydrate,  $\text{Na}_2\text{S} \cdot 5\frac{1}{2}\text{H}_2\text{O}$ , exists in a labile condition between  $48.9^\circ$  and  $91.5^\circ$ , and is stable from  $91.5^\circ$  to  $94^\circ$ . According to the solubility diagram, the nonahydrate should change into the hexahydrate at  $48^\circ$ , but this change does not take place, transformation occurring at  $48.9^\circ$  into the hydrate,  $\text{Na}_2\text{S} \cdot 5\frac{1}{2}\text{H}_2\text{O}$ ; this is one of the rare cases in which the phenomenon is observed in a transformation accompanied by absorption of heat.

T. H. P.

**Some Double and Triple Salts of Cæsium Nitrite with Nitrites of Silver, the Alkali Earths, and Lead.** GEORGE S. JAMIESON (*Amer. Chem. J.*, 1907, 38, 614—619).—The following double and triple nitrites are described. *Cæsium silver nitrite*,  $\text{CsAg}(\text{NO}_2)_2$ ; *cæsium barium nitrites*,  $\text{CsBa}_2(\text{NO}_2)_5$  and  $\text{Cs}_2\text{Ba}(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$ ; *cæsium calcium nitrite*,  $\text{Cs}_2\text{Ca}(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$ ; *cæsium strontium nitrite*,  $\text{CsSr}(\text{NO}_2)_3 \cdot \text{H}_2\text{O}$ ; *cæsium lead nitrite*,  $\text{CsPb}(\text{NO}_2)_3 \cdot \text{H}_2\text{O}$ ; *cæsium silver barium nitrite*,  $\text{Cs}_3\text{AgBa}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$ ; *cæsium silver strontium nitrite*,  $\text{Cs}_3\text{AgSr}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$ ; *cæsium silver lead nitrite*,  $\text{Cs}_3\text{AgPb}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$ , and *potassium silver lead nitrite*,  $\text{K}_3\text{AgPb}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$ .

E. G.

[**Ammonium Amalgam.**] G. McPHAIL SMITH (*Ber.*, 1907, 40, 4298—4299. Compare this vol., ii, 615).—Polemical. A reply to A. Coehn (this vol., i, 683). Ammonium amalgam is produced by leaving barium amalgam in contact with saturated ammonium chloride at the ordinary temperature. E. F. A.

**Freezing-point Diagrams of the Binary Systems: Silver Sulphide—Cuprous Sulphide and Lead Sulphide—Cuprous Sulphide.** K. FRIEDRICH (*Metallurgie*, 1907, 4, 671—673).—The freezing-point curve of mixtures of silver sulphide and cuprous sulphide has a minimum at about 70%  $\text{Ag}_2\text{S}$  and  $677^\circ$ , but there is no thermal or microscopic evidence of the formation of an eutectic, and the two sulphides appear to form an unbroken series of mixed crystals.

The freezing-point curve of mixtures of lead sulphide and cuprous sulphide has two branches, intersecting at an eutectic point at 51%  $\text{Cu}_2\text{S}$  and  $540^\circ$ . The components separate in a practically pure state, and there is no evidence of the existence of any double sulphide under the conditions of the experiment.

The examination of microscopic sections, etched with iodine in potassium iodide solution, shows the crystals to be surrounded by a well-defined eutectic.  
C. H. D.

**Reduction of Oxides, Sulphides, &c., by Metallic Calcium.** F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1907, 3, 115—117).—When fused and powdered boric anhydride is mixed with an equivalent quantity of calcium turnings, and the mixture is ignited by a fuse of metallic calcium and sodium peroxide, a very violent reaction takes place; the rapidity of the reduction, however, may be moderated by the addition of 5—10% of calcium oxide. It is advisable before carrying out such a reaction to line the crucible with a paste made from lime and strong borax solution, or from lime and strong sodium silicate solution, and to dry this paste in the steam-oven or over a flame. After this treatment, the crucible is less liable to fracture, and the product of the reaction is more easily detached. The boron produced by acting on boric anhydride (or ignited borax) cannot be obtained free from calcium; it is probable that what is produced is a mixture of boron and calcium boride. This mixture, however, may be employed for the preparation of boron trichloride.

A mixture of finely-divided sand and calcium turnings reacts vigorously. When hydrochloric acid is added to the product, a copious evolution of spontaneously inflammable gas is observed. When galena is heated with calcium turnings, metallic lead is not produced, but a grey solid which evolves hydrogen sulphide on treatment with dilute hydrochloric acid. Hämatite, pyrolusite, and chromium sesquioxide are readily reduced to the corresponding metals by metallic calcium.

The chief disadvantages in reduction by metallic calcium are the great violence of the reaction and the infusibility of the calcium oxide produced.  
J. C. P.

**Action of Soluble on Insoluble Substances.** WILLIAM OECHSNER DE CONINCK and L. ARZALIER (*Bull. Acad. roy. Belg.*, 1907, 713—715, 800).—When barium sulphate (1 mol.) is boiled during 615 hours with methylamine hydrochloride (1 mol.) dissolved in a slight excess of water, no action takes place. When litharge and ammonium chloride are pounded together in a mortar or strongly compressed, a considerable quantity of lead chloride is formed and ammonia is evolved. A mixture of cupric oxide and ammonium chloride, treated in like manner, behaves similarly, but with a mixture of litharge and potassium iodide no evidence of interaction could be obtained, perhaps because contact between the two substances was not sufficiently prolonged. On the contrary, when a mixture of litharge with (a) ammonium bromide or (b) ammonium iodide is treated in this way, lead bromide or lead iodide is formed. Under similar conditions, cupric oxide reacts with ammonium bromide to form an ammoniacal copper oxybromide, which is soluble in dilute ammonia and is unstable, gradually losing ammonia to form a green hydrated copper oxybromide mixed with a small quantity of the bromide. Green nickel oxide does not appear to react with ammonium bromide, but this reaction is being further investigated.  
T. A. H.

**Action of Carbon on Magnesia at High Temperatures.**

OLIVER P. WATTS (*Trans. Amer. Electrochem. Soc.*, 1907, 11, 279—288).—When a granular carbon resistor imbedded in magnesia is very strongly heated by an electrical current, the carbon apparently volatilises, and condenses on the interior walls of the furnace. The author has investigated the phenomenon and arrives at the conclusion that carbon and magnesium oxide react at extremely high temperatures according to the equation  $\text{MgO} + \text{C} = \text{Mg} + \text{CO}$ . The reaction is reversible, and at a lower temperature the products on the left side of the equation are again formed. The reduction of magnesium oxide is found to be effected more rapidly by certain carbides than by pure carbon. The carbides of chromium, iron, and nickel are very active, as are also siloxicon and carborundum. On the other hand, copper and tin have but slight, if any, action as carriers of carbon in the reduction of magnesium oxide.

H. M. D.

**Zinc-Cadmium Alloys.** G. HINDRICHs (*Zeitsch. anorg. Chem.*,

1907, 55, 415—418. Compare Heycock and Neville, *Trans.*, 1897, 71, 383).—The freezing-point curve of zinc-cadmium alloys consists of two branches meeting in an eutectic point at  $270^{\circ}$ ; the mixture contains 82.6% of cadmium. The metals do not enter into chemical combination and, although so closely allied, do not form mixed crystals. G. S.

**Reaction between Carbonic Acid and Lead Acetate in**

**Aqueous Solution.** JINGORO YAMASAKI (*Mem. Coll. Sci. Eng. Kyōto*, 1907, 1, 176—182, 274—275. Compare Altmann, this vol., ii, 173).—Solutions of lead acetate from  $N/50$  to  $2N$  were precipitated by excess of carbon dioxide at  $25^{\circ}$  and the filtrate analysed. The proportion of the salt precipitated (as normal carbonate) increases with decreasing concentration of the acetate up to the  $N/10$  solution, beyond which it remains constant. In solutions less than  $N/10$  with regard to the acetic radicle, the ratio of free acetic acid to lead acetate in the filtrate is the same whether solutions of the normal acetate, or solutions containing free acetic acid in addition, have been employed. When excess of sodium acetate is added previously to the lead acetate solution, the precipitation as carbonate is practically complete.

At  $15^{\circ}$ , the degree of dilution beyond which the proportion of lead precipitated is constant is the same as at  $25^{\circ}$ . G. S.

**Electrolytic Corrosion of Brasses.** AZARIAH T. LINCOLN, DAVID

KLEIN, and PAUL E. HOWE (*J. Physical Chem.*, 1907, 11, 501—536. Compare Curry, *Abstr.*, 1906, ii, 756).—A series of typical copper-zinc brasses containing 3—22.6% and 47.6—93.67% of copper (those containing 30—40% were too brittle) were annealed for some weeks at  $400^{\circ}$  to secure the attainment of equilibrium conditions, and were then subjected to electrolytic corrosion in solutions of various salts, the test piece being used as anode, a platinum wire as the cathode, and a small current passed through the solution. In the experiments, normal solutions of sodium chloride, nitrate, sulphate, acetate, carbonate, and phosphate and of ammonium nitrate, oxalate and acid oxalate, were employed. The amount and copper content of the corrosion products,

as well as the current efficiency, are given in tabular form, and in some cases the amount and copper content of the corrosion product is represented graphically as a function of the various solid solutions of which the alloys consist. Some experiments were also made with copper-zinc alloys containing a small proportion of tin.

In general, the corrosion product for alloys containing over 50% by weight of copper ( $\alpha$ ,  $\alpha + \beta$ , and  $\beta$  brasses) is of the same composition as the test piece itself, whilst for alloys of small copper content ( $\gamma + \epsilon$  and  $\epsilon + \eta$  brasses) the corrosion product is practically pure zinc. In sodium chloride, the amount of the corrosion product decreases as the proportion of copper in the brass increases; in sodium sulphate the amount of corrosion is practically constant for all the alloys, whilst in solutions of certain other salts it increases as the proportion of copper diminishes. In several instances, the current efficiency was over 100%.

The alloys containing tin gave results similar to those obtained with the zinc-copper alloys.

Some experiments on chemical corrosion were also carried out, air being bubbled for several weeks through the salt solutions in contact with the alloys, but the results were not satisfactory

G. S.

**Copper-Bismuth Alloys.** KONSTANTIN JERIOMIN (*Zeitsch. anorg. Chem.*, 1907, 55, 412—414. Compare Gautier, *L'Etude des Alliages*, 1901, 110; Hiorns, *Abstr.*, 1905, ii 461).—The freezing-point curve of these alloys falls gradually from the melting point of copper to about 700°, at which point the mixture contains 10% of copper, and then falls rapidly to the melting point of bismuth. The alloys from 0.5% to 99.5% of copper contain primarily separated copper surrounded by bismuth, so that if these metals form mixed crystals the series do not extend further than 0—0.5% and 99.5—100% of copper.

The above results differ considerably from those of Gautier; the want of agreement is ascribed to the presence of cuprous oxide in the alloys of the latter investigator.

G. S.

**Mercury Peroxide.** GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 408—412).—The author has confirmed the formation of mercury peroxide during the catalysis of hydrogen peroxide by mercury (compare Antropoff, *Zeitsch. Elektrochem.*, 1906, 12, 585), and has shown that this compound has the formula  $\text{HgO}_2$ . The peroxide is also formed by the interaction of alcoholic mercuric chloride solution and hydrogen peroxide in presence of the theoretical proportion of alcoholic potassium hydroxide solution. By this method, the peroxide is probably, as it is certainly by Antropoff's method, obtained in an anhydrous condition. Mercury peroxide is an apparently amorphous, brick-red compound, which is slowly decomposed by water, yielding hydrogen peroxide, mercuric oxide, and oxygen. Acids dissolve it, giving mercuric salts and hydrogen peroxide, whilst with hydrochloric acid it liberates chlorine. It sets free iodine from potassium iodide, and decolorises potassium permanganate solution. Its behaviour is hence that of a true peroxide. When prepared by Antropoff's

method, the dry peroxide is moderately stable, but the precipitated compound decomposes rapidly, giving mercuric oxide. The limited stability of the compound is related to the feebly positive character of mercury, and its behaviour, compared with those of the peroxides of magnesium, zinc, and cadmium, is what would be expected from the relative positions of the various metals in the periodic arrangement of the elements.

T. H. P.

**Some Mercuriodides.** ANDRÉ DUBOIN (*Compt. rend.*, 1907, 145, 713—715).—By alternately dissolving ferrous iodide and mercuric iodide in water until saturated, a liquid,  $D^{21.9}$  2.87, is obtained, which, when slowly evaporated in a vacuum, deposits beautiful deep orange-yellow, octahedral crystals,  $D^0$  4.04, of the composition  $\text{FeI}_2 \cdot 2\text{HgI}_2 \cdot 6\text{H}_2\text{O}$ . Towards solvents, it behaves similarly to the iodides of the magnesium series previously studied. Dobrosserdoff's double iodide of mercury and cobalt (*Abstr.*, 1901, ii, 510) has  $D^0$  4.17. By substituting aluminium iodide for ferrous iodide, a clear yellow liquid,  $D^{20.1}$  3.05, is obtained, which, when placed in dry air for several months, absorbs oxygen, becoming much deeper in colour, and deposits crystals of the *oxyiodide*,  $\text{HgO} \cdot 2\text{AlI}_3 \cdot 3\text{HgI}_2 \cdot 15\text{H}_2\text{O}$ , having  $D^0$  3.97. A solution of aluminium iodide dissolves silver iodide, giving a liquid,  $D^{19.8}$  2.34. This, on spontaneous evaporation, deposits yellow crystals of the composition:  $2\text{AlI}_3 \cdot 5\text{AgI} \cdot 2\text{AgO} \cdot 13\text{H}_2\text{O}$ , which alter extremely rapidly in air.

E. H.

**New Neodymium Salt.** N. A. ORLOFF (*Chem. Zeit.*, 1907, 31, 1119).—The salt,  $\text{Nd}_2(\text{U}_3\text{O}_{10})_3 \cdot 18\text{H}_2\text{O}$ , is obtained as a yellow, crystalline powder by heating neodymium hydroxide with a solution of uranyl acetate on a water-bath. Praseodymium hydroxide behaves in the same way, but aluminium hydroxide does not react with uranyl acetate.

W. H. G.

**Holmium.** ABRAHAM LANGLET (*Arkiv Kem. Min. Geol.*, 1907, 2, No. 32, 1—14).—The author has applied various fractionating methods to the further separation of fractions containing yttrium, erbium, and holmium, the spectra and the colours of the solutions being observed.

The most satisfactory method is found to be fractional crystallisation of a mixture of the chlorides from hydrochloric acid which distils unchanged in composition. This method cannot, however, be used for the complete separation of these metals, as it is ineffective in presence of a large amount of yttrium. Fractions of unaltered atomic weights were separated, but the absorption spectra of their solutions were found to vary, so that constancy of the atomic weight is not a criterion of the elementary nature of the metal present. It is doubtful whether the band occurring in the red portion of these spectra belongs to holmium, since this band is almost equally intense in all the fractions, even when the other holmium bands are not observed. There is no evidence of a decomposition of holmium into several components. The molecular conductivity may possibly serve as a means of distinguishing fractions which exhibit no differences in their atomic weights or spectra.

T. H. P.



**A New Element: Lutecium, Resulting from the Decomposition of Marignac's Ytterbium.** GEORGES URBAIN (*Compt. rend.*, 1907, 145, 759—762).—By the method of crystallisation of nitrates (Abstr., 1906, ii, 359), the author has obtained 50 grams of ytterbia free from yttria, erbia, and thulia, and agreeing with Marignac's definition (Abstr., 1879, {118}). This was submitted to prolonged fractional crystallisation from nitric acid (D 1.3). The first fractions, which exhibited slightly the absorption bands characteristic of thulia, were rejected. The atomic weight of the ytterbium contained in the others was determined by analysis of the sulphate, and the values obtained increased from 169.9 with the first to 173.8 with the last. By the action of hydrogen peroxide on the solutions of the neutral nitrates (Wyruboff and Verneuil), one-twenty-thousandth part of thoria was isolated, insufficient to affect the atomic weights. The arc spectra of the products so purified revealed no impurities. Comparison of the photographed arc spectra of the first and last fractions shows that numerous rays (in most cases intense) are present in that of the last fraction, but absent or very feeble in that of the first, and vice versa. Both spectra, however, show a large number of rays in common. Lists are given of the rays of the spark spectrum of the fractions of low atomic weight attributable to thulium, and of the rays of the spark spectrum of the fractions of high atomic weight characteristic of the new element. The rays characteristic of all the fractions and not included in these two lists belong to the "old" ytterbium, for which the author proposes the name *neo-ytterbium*, Ny. The band  $\gamma$  in the spectrum of "old" ytterbium described by Boisbaudran (Abstr., 1879, 861) is absent from the spectrum of the earths of low atomic weight (*neo-ytterbium*), but present in that of the earths of high atomic weight (rich in lutecium). Probably the bands  $\alpha$  and  $\beta$  are characteristic of *neo-ytterbium*,  $\gamma$  of lutecium. The rays 4008.2 and 3906.5, supposed by Demarçay (Abstr., 1900, ii, 656) to belong to an element  $\theta$  lying between erbium and ytterbium, were not observed.

E. H.

**Synthesis of Precious Stones of the Family of Aluminides.** FRED. BORDAS (*Compt. rend.*, 1907, 145, 710—711).—When a blue sapphire is exposed to the action of radium bromide of activity 1,800,000, the colour changes to a green, then to bright yellow, and finally to a deep yellow. Under the same conditions, a red sapphire changes through violet, blue, green to yellow. The intensity of the reaction can be varied by altering the distance of the stone from the radioactive salt, or by using radium bromide of different activity. The stones so treated are not radioactive, and do not shine in the dark under the influence of pure radium bromide. Since yellow sapphires are the most common, and blue and yellow ones are frequently met with together, it seems probable that the soil in which these precious stones are found is radioactive, and that the stones are undergoing a very slow change analogous to that observed above. It may be possible to utilise this action to detect traces of radium.

E. H.

**Absorptive Power of the Hydrates of Silicon, Aluminium, and Iron.** PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1907, 56, 46—48).—Clays and cements absorb and retain complex colouring matters, such as the aniline dyes and carmin, whilst they allow simpler compounds, such as copper sulphate, to diffuse. It is suggested that clays and cements form colloidal hydrates with water, and that these, owing to their large surface, have high absorptive power. G. S.

**Formation and Preparation of Aluminium Carbide.** CAMILLE MATIGNON (*Compt. rend.*, 1907, 145, 676—679).—Moissan prepared aluminium carbide by heating aluminium in a carbon crucible in the electric furnace (Abstr., 1894, ii, 450), but attempts to effect the combination of the two elements at a lower temperature than that afforded by the electric arc have hitherto proved unsuccessful (Mallet, this Journ., 1876, ii, 349; Franck, Abstr., 1895, ii, 167; 1899, ii, 102). The author finds, however, that when a mixture of excess of aluminium powder and lamp-black is heated in a Perrot furnace for twenty minutes, the product consists of aluminium carbide mixed with aluminium, which is readily removed by rapidly washing in the cold with hydrochloric acid or potassium hydroxide solution. Aluminium carbide can also be prepared by the following exothermic reactions: (1) by firing a mixture of carbon and a large excess of aluminium (compare Abstr., 1900, ii, 482); (2) by heating the two elements in the oxyacetylene blowpipe flame, and (3) by passing the vapours of the chlorides of carbon over heated aluminium, or by heating a mixture of aluminium and benzene hexachloride in a sealed tube at 225°.

M. A. W.

**Action of Carbonyl Chloride on Aluminium Haloid Compounds.** II. AUREL VON BARTAL (*Zeitsch. anorg. Chem.*, 1907, 56, 49—52. Compare this vol., ii, 775).—Liquid carbonyl chloride reacts very vigorously with aluminium iodide and with the latter dissolved in carbon disulphide, but no new compounds could be isolated from the products. Aluminium iodide was then heated to fusion at 195—200°, and dry carbonyl chloride passed in until the weight had increased 25%. From the solid product, iodine and unaltered iodide were removed by means of carbon disulphide; the light brown, amorphous residue had the composition  $\text{Al}_3(\text{CO})_2\text{Cl}_2\text{I}$ .

The compound in question cannot be melted even by heating in a sealed tube; it decomposes on heating at 280—300° in an open tube, aluminium chloride and iodine volatilising, and a black compound of the formula  $\text{Al}_2(\text{CO})_2$ , insoluble in water and acid, remains; the latter is converted into aluminium oxide and carbon dioxide on prolonged heating in air.

Carbonyl chloride and anhydrous aluminium fluoride do not interact even at a red heat. G. S.

**Densities and Specific Heats of some Alloys of Iron.** W. BROWN (*Sci. Trans. Roy. Dubl. Soc.*, 1907, [ii], 9, 59—84. Compare Barrett, Abstr., 1902, ii, 377; Barrett, Brown, and Hadfield, Abstr., 1905, ii, 503).—The alteration in the specific volume

(0.1269 c.c.) of pure iron caused by the addition of other elements has been determined, and the results are summarised as follows. The figures given for the alteration of specific volume refer to 1% of the added element. When carbon, up to 0.2%, is added to iron, the change in the specific volume,  $\Delta v = +0.0018$  c.c.; when the percentage of added carbon is from 0.2—1.25%,  $\Delta v = +0.0015$  c.c. When manganese, up to 2%, is added to iron,  $\Delta v = +0.00026$  c.c.; when the percentage of manganese lies between 2% and 18.5%,  $\Delta v = -0.00015$  c.c. The addition of nickel up to 20% has no effect on the specific volume, but with a percentage of nickel between 20% and 31.4%,  $\Delta v = -0.00023$  c.c. When tungsten, up to about 15%, is added to iron,  $\Delta v = -0.0009$  c.c. The addition of silicon up to 5.5% increases the specific volume, and  $\Delta v = +0.0011$  c.c. When chromium, up to 3%, is added to iron,  $\Delta v = +0.00034$  c.c., but further addition of chromium, up to 9.5%, has no effect on the specific volume of the alloy. When copper is added to iron, up to 1.5%,  $\Delta v = -0.0005$  c.c., but further addition of copper, up to about 4%, has no effect on the specific volume. The addition of cobalt, up to 7%, to iron leads to  $\Delta v = -0.0001$  c.c.; the addition of aluminium, up to 4.5%, gives  $\Delta v = +0.0025$  c.c.

The specific heat of iron is increased by about 0.0089 per 1% of added carbon, and by about 0.0006 per 1% of added manganese (up to about 18%). Nickel, added to iron up to 4%, increases the specific heat by 0.0038 for every 1% of the addition; further additions of nickel, up to 20%, have little or no effect, whilst between 20% and 31% of nickel the specific heat is increased by 0.005. Tungsten, added to iron up to 1%, increases the specific heat by 0.0028; when 3.5% of tungsten is present, the specific heat of the material is the same as that of pure iron, whilst a further addition of 12% of tungsten decreases the specific heat by 0.0093. Silicon, added to iron up to about 2%, increases the specific heat by 0.003 for every 1% of the addition; further additions of silicon have little or no effect. Chromium, cobalt, and copper, added separately to iron, have very little effect on the specific heat when a high percentage of carbon is present. Aluminium, added to iron up to 3%, has little or no effect on the specific heat.

J. C. P.

**Alloys of Iron and Chromium.** WILHELM TREITSCHKE and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, 55, 402—411. Compare next abstract).—These alloys were investigated by thermal analysis, being fused in magnesia tubes at 1700° before the cooling curve was taken. The freezing-point curve is of peculiar shape, consisting of a number of irregular bends; there is also a break in the cooling curve of the solid alloys, the temperature of which falls at first with increase in the amount of iron, and then rises to the melting point of the latter metal. Solid alloys containing 30—50% of chromium have a third break in the cooling curve at 1260°.

These abnormal results are accounted for on the hypothesis that iron and chromium unite to form a compound X, which, unlike the iron-molybdenum compound (next abstract), is completely miscible in the solid state with its components. In accordance with this view,

the observations are represented on a projected space diagram. The break on the cooling curve at  $1260^{\circ}$  represents an eutectoid in which the two series of mixed crystals and the eutectic crystallise together.

The microscopic examination bears out the above conclusions. All the alloys from 10—90% of chromium consist of two structural elements, the one which separates primarily being softer and more readily attacked by acids than the secondary.

Alloys were also prepared by reduction of the oxides with aluminium and were found to be homogeneous, consisting of polyhedral crystals. On heating these alloys at  $1700^{\circ}$  for some time, they regain the structure of those prepared at that temperature, so that equilibrium is attained fairly rapidly at high temperatures.

All the alloys up to 80% of chromium are magnetic.

G. S.

**Alloys of Iron and Molybdenum.** LAUTSCH and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1907, 55, 386—401. Compare Vigouroux, Abstr., 1906, ii, 364).—The metals were heated in tubes of magnesia for twenty to thirty minutes at  $1800$ — $1850^{\circ}$  to ensure complete fusion, and the cooling curve then determined with a thermocouple in the usual way. In this series, only alloys up to 60% by weight of molybdenum were employed.

The freezing-point curve consists of two branches meeting at about  $1360^{\circ}$ , the mixture containing 43% by weight of manganese. There are certain other breaks in the cooling curve, and the general behaviour of the alloys recalls that of a ternary system. It is therefore suggested that the metals unite to form a compound X, which is produced and decomposes very slowly. The compound does not form mixed crystals with iron, and probably not with molybdenum, but the metals themselves form two series of mixed crystals separated by a gap.

The microscopic structure of the alloys confirms these conclusions. The compound X, which is hard and resistant towards acids, does not crystallise primarily from any of the alloys prepared at  $1800$ — $1850^{\circ}$ . From 0—42.5% of molybdenum, the mixed crystals rich in iron crystallise first, and from 42.5—60% of molybdenum those rich in the latter metal.

Alloys have also been prepared at much higher temperatures (above  $2100^{\circ}$ ) by reducing the oxides with aluminium. These alloys differ from the former in that they are much richer in X; from 20—60% of molybdenum, the latter crystallises primarily from the aluminothermic alloys. When an alloy prepared by the latter method, and containing 32.7% of molybdenum, was heated for some time at  $1500^{\circ}$ , it regained to a large extent the properties of the same alloy prepared at  $1800^{\circ}$ , but the aluminothermic alloys containing 44—73% of molybdenum are scarcely affected by this treatment.

Alloys containing 0—50% of molybdenum are strongly magnetic; the aluminothermic alloys containing 70—100% of molybdenum have no action on the magnetic needle.

G. S.

**Iron-Tungsten Alloys.** HERMANN HARKORT (*Metallurgie*, 1907, 4, 617—631, 639—647, 673—682).—The alloys were prepared by

fusing pure Swedish iron with ferrotungsten in a magnesia crucible, enclosed in an outer cylinder of a specially infusible clay, and heated by a granulated carbon electric resistance furnace. The paper contains a theoretical discussion and an account of experiments bearing on the conditions necessary to obtain very high temperatures with this type of furnace. The conditions for obtaining accurate readings with the thermo-couple at temperatures up to  $1600^{\circ}$  were also thoroughly investigated. The experimental difficulties, due to absorption of gases and to the insufficient resisting power of even magnesia crucibles, made it impossible to construct a satisfactory freezing-point curve from the results. The ingots obtained also usually showed traces of imperfect mixture.

The temperature of transformation of  $\alpha$ - into  $\beta$ -iron is not influenced by the addition of tungsten. The temperature of transformation of  $\beta$ - into  $\gamma$ -iron, however, rises rapidly from  $871^{\circ}$  for pure iron to  $933^{\circ}$  for an alloy containing 10% of tungsten, the development of heat becoming progressively less.

The results of the thermal and microscopic examination indicate that mixed crystals are formed, and that a compound of iron and tungsten separates from the solid alloys rich in tungsten, being to a large extent retained in solution in alloys quenched from a high temperature.

C. H. D.

**Constitution of Roussin's Salts.** LIVIO CAMBI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 542—547. Compare Bellucci and Cecchetti, this vol., ii, 29; Bellucci and Carnevali, this vol., ii, 472).—The author discusses previous publications on the constitution of Roussin's salts, which he regards as complexes of sulphides and hyponitrites, possibly of the form  $K_2N_2O_2 \cdot 2FeS_3 \cdot 2Fe_2(N_2O_2)_3$ . The presence of hyponitrous acid is demonstrated by the action of silver nitrate, which proceeds according to the equation:  $K_2Fe_8S_6(N_2O_2)_7 + 26AgNO_3 = 2KNO_3 + 8Fe(NO_3)_3 + 7Ag_2N_2O_2 + 6Ag_2S$ . The transformation of nitrosulphides of the first series into those of the second series by the action of alkali (Bellucci and Cecchetti, *loc. cit.*) is represented by the equation:  $K_2Fe_8S_6(N_2O_2)_7 + 6KOH = K_2N_2O_2 + 3K_2Fe_2S_2(N_2O_2)_2 + Fe_2O_3 + 3H_2O$ .

T. H. P.

**Molecular Magnitude of the Ferronitrososulphides.** ITALO BELLUCCI and F. CARNEVALI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 584—590).—Determinations of the molecular weights of potassium and sodium ferronitrosulphides of the type  $Fe_4(NO)_7S_8R'$  in boiling ether gave discordant results (compare Marchlewski and Sachs, *Abstr.*, 1893, ii, 211), the numbers obtained varying from the values corresponding with the above formula to less than half of these values; similar irregularity is observed in the behaviour of the pyridine derivative,  $Fe_4(NO)_7S_8H \cdot C_5NH_5$ , in boiling ether.

It is noticed incidentally that, when ether employed for ebullioscopic measurements contains ethyl alcohol, as is often the case with the commercial rectified product, the boiling point is sometimes lowered by a solute.

The increase of  $\mu$  when the dilution of the sodium ferronitro-

sulphide is raised from  $v=32$  to  $v=1024$ , shows that the salt is one of a monobasic acid, and that it has the simple molecular formula. The constancy of the conductivities indicates the great stability of the compound.

Cryoscopic measurements of the sodium and potassium derivatives in water and acetone, and of the potassium derivative in nitrobenzene, give values for the molecular weights equal to one-half of those corresponding with the simple formulae, showing that in dilute solution complete, normal, electrolytic dissociation occurs.

That these compounds are true complex salts is shown by the various reactions in which the anion  $\text{Fe}_4(\text{NO})_7\text{S}_3'$  takes part unchanged, and by the absence of alteration in an alcoholic solution of the potassium salt when exposed to direct sunlight for several days.

T. H. P.

**Hydroxypentamminecobalt Salts.** ALFRED WERNER (*Ber.*, 1907, 40, 4098—4112).—The author has previously studied compounds of the types:  $[(\text{H}_2\text{O})(\text{HO})\text{CoEn}_2]\text{X}_2$ ,  $[(\text{H}_2\text{O})(\text{HO})\text{CoPy}_2(\text{NH}_3)_2]\text{X}_2$ ,  $[(\text{ON})(\text{HO})\text{Ru}(\text{NH}_3)_4]\text{X}_2$ ,  $[(\text{HO})_2\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2]\text{X}$ , and  $[(\text{OH})_2\text{Pt}(\text{NH}_3)_4]\text{X}_2$ . He has now prepared hydroxy-compounds, where, in addition to the hydroxy-groups, there are no other reactive groups directly attached to the metal atom.

Hydroxypentamminecobalt salts of the type:  $[(\text{OH})\text{Co}(\text{NH}_3)_5]\text{X}_2$  are prepared by the action of ammonia on the roseo-aquopentamminecobalt salts, thus:  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]\text{X}_3 + \text{NH}_3 = [(\text{OH})\text{Co}(\text{NH}_3)_5]\text{X}_2 + \text{NH}_4\text{X}$ . The roseo-salts are obtained from chloropentamminecobalt chloride (chloropurpureo-chloride),  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ . Aqueous solutions of the aquopentamminecobalt salts are acid in reaction, owing to their undergoing hydrolytic dissociation; attempts to increase this hydrolytic dissociation by means of pyridine were unsuccessful. The *nitrate*,  $[(\text{OH})\text{Co}(\text{NH}_3)_5](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , crystallises in violet-red scales; its aqueous solution is bluish-red and alkaline in reaction, although not sufficiently so as to cause the precipitation of silver oxide from silver nitrate. When added to ammonium salts, ammonia is at once liberated and aquopentamminecobalt salts are formed, thus:

$[(\text{OH})\text{Co}(\text{NH}_3)_5](\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 = [\text{Co}(\text{NH}_3)_5(\text{OH}_2)](\text{NO}_3)_3 + \text{NH}_3$ . The action of carbon dioxide on a concentrated aqueous solution of the hydroxy-salt is represented as follows:  $[(\text{OH})\text{Co}(\text{NH}_3)_5](\text{NO}_3)_2 + \text{CO}_2 = [\text{CO}_3\text{HCo}(\text{NH}_3)_5](\text{NO}_3)_2$ , bicarbonatopentammine cobalt nitrate being formed.

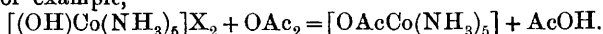
The *chloride*,  $[(\text{OH})\text{Co}(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , forms glistening scales; its aqueous solution is bluish-red and is distinctly alkaline towards litmus. The addition of ammonium chloride causes the formation of aquopentamminecobalt chloride. The *bromide*,  $[(\text{OH})\text{Co}(\text{NH}_3)_5]\text{Br}_2 \cdot \text{H}_2\text{O}$ , is a pale violet, amorphous powder; its aqueous solution is bluish-red and alkaline. The *iodide*,  $[(\text{OH})\text{Co}(\text{NH}_3)_5]\text{I}_2$ , is a violet, crystalline powder. The *dithionate*,  $[(\text{OH})\text{Co}(\text{NH}_3)_5]\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ , separates from dilute ammonia in carmine-red prisms and leaflets.

The view that the compounds described are actually hydroxy-compounds is supported by the following considerations. (1) No chemical difference can be detected between the hydrated and anhydrous salts.

(2) The hydrated salts do not exhibit in their properties any analogy with the aquopentamminecobalt salts, but resemble, for example, in the colour the chloropentammine salts. (3) The behaviour of the compounds in question towards carbon dioxide and anhydrides of aliphatic acids respectively is also in accordance with the formulæ quoted by the author.

Various bicarbonatopentammine salts are also described. Aqueous solutions of these compounds are strongly alkaline and, when heated, form hydroxylopentamminecobalt salts, thus:  $[(\text{CO}_3\text{H})\text{Co}(\text{NH}_3)_5]\text{X}_2 \rightarrow \text{CO}_2 + [(\text{OH})\text{Co}(\text{NH}_3)_5]\text{X}_2$ ; the latter behaviour favours the view that the hydroxy-group in the hydroxylopentammine salts is directly attached to the metal atom. The bicarbonato-compounds are converted by the action of ammonia into carbonatopentammine salts, thus:  $[(\text{CO}_3\text{H})\text{Co}(\text{NH}_3)_5]\text{X} + \text{NH}_3 = [\text{CO}_3\text{Co}(\text{NH}_3)_5]\text{X} + \text{NH}_4\text{X}$ .

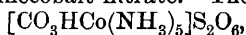
Further evidence as to the constitution of the hydroxylopentammine salts is afforded by their behaviour towards anhydrides of aliphatic acids, for example,



The resulting acetatopentamminecobalt salts are very stable.

The behaviour of the aquopentammine salts is adduced in support of the author's views on hydrolysis; the hydrolysis of the metal salts is to be ascribed to the formation from the aquo-salts of hydroxy-compounds and acids.

The *nitrate*,  $[\text{CO}_3\text{HCo}(\text{NH}_3)_5](\text{NO}_3)_2$ , is pale carmine-red; it is sparingly soluble in water, and the solution is alkaline. When potassium iodide is added to its aqueous solution, a periodide is precipitated. The *bromide*,  $[\text{O}\cdot\text{CO}_2\text{HCo}(\text{NH}_3)_5]\text{Br}_2$ , is precipitated as a violet-red powder on passing carbon dioxide into a solution of the hydroxylo-bromide. The bicarbonato-nitrate is converted by ammonia into carbonatopentamminecobalt nitrate. The *dithionate*,



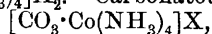
is a brick-red, crystalline powder.

*Acetatopentamminecobalt nitrate*,  $[\text{OAcCo}(\text{NH}_3)_5](\text{NO}_3)_2$ , is a carmine-red, crystalline powder. On the addition of potassium iodide, the corresponding *iodide* is precipitated as carmine-red needles. The *platinosochloride*,  $[\text{CO}_2\text{MeCo}(\text{NH}_3)_5]\text{PtCl}_4$ , forms glistening needles.

*Propionatopentamminecobalt nitrate* is a pale violet powder.

A. McK.

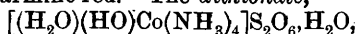
**Hydroxyloaquotetramminecobalt Salts.** ALFRED WERNER (*Ber.*, 1907, 40, 4113—4117).—In order to determine the influence exerted by the nitro-group in nitrohydroxylo-tetrammine salts,  $[(\text{NO}_2)(\text{HO})\text{Co}(\text{NH}_3)_4]\text{X}$  (compare succeeding abstract), on the hydroxy-group in these salts, the author has studied hydroxyloaquotetrammine salts,  $[(\text{H}_2\text{O})(\text{HO})\text{Co}(\text{NH}_3)_4]\text{X}_2$ . Carbonatotetrammine salts,



are readily converted into diaquotetrammine salts,  $[(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_4]\text{H}_3$ , which serve as the starting point for the preparation of the salts described.

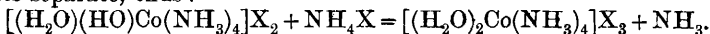
The *chloride*,  $[(\text{H}_2\text{O})(\text{HO})\text{Co}(\text{NH}_3)_4]\text{Cl}_2$ , obtained by the action of ammonia on diaquotetramminecobalt chloride, is a violet powder. The

corresponding *bromide*, obtained by the addition of potassium bromide to the chloride, is carmine-red. The *dithionate*,

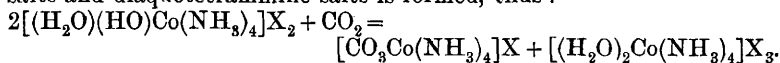


separates from water in violet leaflets. The *nitrate* is violet. The *sulphate*,  $[(\text{H}_2\text{O})(\text{HO})\text{Co}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , forms glistening, violet leaflets.

The hydroxyloaquotetrammine salts described give a distinctly alkaline reaction in aqueous solution, although they do not precipitate silver oxide from silver nitrate. With concentrated solutions of ammonium salts, ammonia is evolved and diaquotetramminecobalt salts separate, thus:

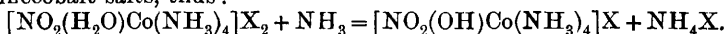


These diaquo-salts give an acid reaction in aqueous solution. By the action of carbon dioxide on the hydroxy-acids, a mixture of carbonato-salts and diaquotetrammine salts is formed, thus:



Chloro-aquotetramminecobalt chloride separates from a concentrated solution of the diaquochloride, thus:  $[(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_4]\text{Cl}_3 = [\text{H}_2\text{OClCo}(\text{NH}_3)_4]\text{Cl}_2 + \text{H}_2\text{O}$ .  
A. McK.

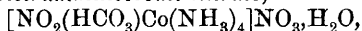
**Hydroxylonitrotetramminecobalt Salts.** ALFRED WERNER (*Ber.*, 1907, 40, 4117—4122).—The author describes hydroxylonitrotetramminecobalt salts of the type  $[\text{NO}_2(\text{OH})\text{Co}(\text{NH}_3)_4]\text{X}$ , obtained by the action of ammonia on aqueous solutions of aquonitrotetramminecobalt salts, thus:



Jörgensen has already obtained the chloride of this series by the action of dilute ammonia on solutions of chloronitrotetramminecobalt chloride, but his formulation of it as a basic chloride of the aquo-series is incorrect; all chlorides of the aquo-series are yellow, whilst the chloride in question is red.

The aqueous solutions of the salts prepared are strongly alkaline, and precipitate silver oxide at once from silver nitrate solutions. When moist, they readily absorb carbon dioxide from the atmosphere, thus:  $[\text{NO}_2(\text{HO})\text{Co}(\text{NH}_3)_4]\text{NO}_3 + \text{CO}_2 = [\text{NO}_2\text{HCO}_3\text{Co}(\text{NH}_3)_4]\text{NO}_3$ ; this behaviour is in accordance with the author's formulation. The *chloride*,  $[\text{NO}_2(\text{HO})\text{Co}(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$ , forms glistening, red crystals. The *bromide*,  $[\text{NO}_2(\text{HO})\text{Co}(\text{NH}_3)_4]\text{Br} \cdot \text{H}_2\text{O}$ , is a dark brick-red, crystalline powder. The *nitrate*,  $[(\text{NO}_2)(\text{HO})\text{Co}(\text{NH}_3)_4]\text{NO}_3$ , forms ruby-red needles.

*Bicarbonatnitrotetramminecobalt nitrate*,



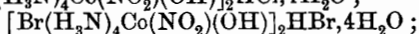
is brownish-yellow.

A. McK.

**Abnormal Inorganic Oxonium Salts.** A New Class of Basic Salts. ALFRED WERNER (*Ber.*, 1907, 40, 4122—4128).—The author describes a new type of basic salts, which he designates as abnormal oxonium salts. The action of ammonium nitrate or ammonium sulphate on hydroxylonitrotetramminecobalt salts is normal, since ammonia is liberated and normal aquo-salts are formed, thus:

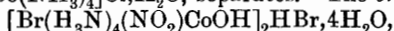


$[\text{NO}_2(\text{HO})\text{Co}(\text{NH}_3)_4]\text{NO}_3 + \text{NH}_4\text{NO}_3 = [\text{NO}_2(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4](\text{NO}_3)_2 + \text{NH}_3$ . The behaviour of ammonium chloride, bromide, or iodide is, however, different; these salts cause the separation of salts, which are, not acid, but alkaline in reaction towards litmus, and are represented as follows:  $[\text{Cl}(\text{H}_3\text{N})_4\text{Co}(\text{NO}_2)(\text{OH})_2]\text{HCl}, 4\text{H}_2\text{O}$ ;



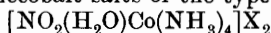
$[\text{I}(\text{H}_3\text{N})_4\text{Co}(\text{NO}_2)(\text{OH})_3]\text{HI}$ . These salts are undoubtedly uniform, and crystallise better than any other salts of the nitrotetramminecobalt series. From his study of these salts, the author finds additional evidence against the representation of oxonium salts as compounds containing a quadrivalent oxygen atom.

The *chloride*,  $[\text{Cl}(\text{H}_3\text{N})_4(\text{NO}_2)\text{CoOH}]_2\text{HCl}, 4\text{H}_2\text{O}$ , forms yellow crystals; from the mother liquors, chloronitrotetramminecobalt chloride,  $[\text{ClNO}_2\text{Co}(\text{NH}_3)_4]\text{Cl}, \text{H}_2\text{O}$ , separates. The *bromide*,



forms bronze-yellow leaflets. The *iodide*,  $[\text{I}(\text{H}_3\text{N})_4(\text{NO}_2)\text{CoOH}]_3\text{HI}$ , forms glistening bronze-yellow leaflets.

Aquonitrotetramminecobalt salts of the type



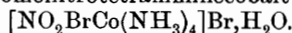
are described. The *chloride*, obtained by the action of concentrated hydrochloric acid on the abnormal chloride referred to, is a yellow, crystalline powder, which in aqueous solution gives an acid reaction. The corresponding *bromide* is a yellow, crystalline powder, is very unstable, and, when dry, is gradually transformed into a cinnabar-red salt; the transformation takes place immediately when water is added; the new salt is the esohydrate of bromonitrotetramminecobalt bromide,  $[\text{NO}_2\text{BrCo}(\text{NH}_3)_4]\text{Br}, \text{H}_2\text{O}$ , previously prepared by Jörgensen, but erroneously designated by him as aquonitrotetramminecobalt bromide.

The sulphate,  $[\text{NO}_2(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{SO}_4$ , is a yellow powder.

The nitrate forms yellowish-brown crystals.

A. MCK.

**Chloronitrotetramminecobalt Salts.** ALFRED WERNER (*Ber.*, 1907, 40, 4128—4132).—Chloronitrotetramminecobalt chloride, first prepared by Jörgensen, very readily undergoes hydrolytic dissociation, thus:  $[\text{NO}_2\text{ClCo}(\text{NH}_3)_4]\text{Cl} + \text{H}_2\text{O} = [\text{NO}_2(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{Cl}_2$ . It is now shown that the reverse change may also be effected with ease, a fact which has been overlooked by Jörgensen, who was in consequence led to a wrong formulation of compounds of the types in question. The salt described by Jörgensen as aquonitrotetramminecobalt chloride is in reality an esohydrate of chloronitrotetramminecobalt chloride,  $[\text{NO}_2\text{ClCo}(\text{NH}_3)_4], \text{H}_2\text{O}$ . Further, Jörgensen's aquo-bromide is the esomono-hydrate of bromonitrotetramminecobalt bromide,



The hydration of chloronitrotetramminecobalt chloride takes place so quickly when this salt is dissolved in water that, when nitric acid or sulphuric acid is added, only aquo-salts separate. If, however, the chloronitrochloride is covered with ice-cold water and the filtrate dropped into cold solutions of the various precipitants, it is possible to obtain chloronitrotetrammine salts.

The *chloride*,  $[\text{NO}_2\text{ClCo}(\text{NH}_3)_4]\text{Cl}, \text{H}_2\text{O}$ , obtained from chloronitro-

tetramminecobalt chloride, crystallises in red plates. The *thiocyanate*,  $[\text{NO}_2\text{ClCo}(\text{NH}_3)_4]\text{SCN}$ , is a reddish-brown, crystalline salt. The *bromide*,  $[\text{NO}_2\text{ClCo}(\text{NH}_3)_4]\text{Br}$ , and *iodide*,  $[\text{NO}_2\text{ClCo}(\text{NH}_3)_4]\text{I}$ , were also prepared. The *nitrate*,  $[\text{NO}_2\text{ClCo}(\text{NH}_3)_4]\text{NO}_3$ , is orange-red.

The theoretical significance of these compounds is discussed.

A. McK.

**Complex Metal Ammonias. V. Octamminedioldicobalt Salts.** ALFRED WERNER (*Ber.*, 1907, 40, 4434—4441. Compare this vol., i, 1012).—The compound first prepared by Gentele (*J. pr. Chem.*, 1856, [i], 3, 130) and described by Jörgensen (*Abstr.*, 1885, 726) as a basic tetramminecobalt sulphate is shown to be the sulphate of a series, termed the *octamminedioldicobalt* series, having the general formula:  $\text{X}_2 \left[ (\text{NH}_3)_4\text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co}(\text{NH}_3)_4 \right] \text{X}_2$ , in which two complex residues are assumed to be combined together through the agency of the residual affinities of the oxygen atoms of the two OH groups. The formula is in agreement with the following facts: (1) the analytical results; (2) 2 mols. of a tetrammine salt result from the decomposition of 1 mol. of an octamminedioldicobalt salt by mineral acids; (3) the acid radicle is completely ionised in aqueous solutions of the salts; (4) aqueous solutions of the salts react neutral.

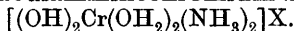
*Octamminedioldicobalt chloride*,  $[(\text{NH}_3)_4\text{CoOH}]_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ , prepared by treating the product obtained by dehydrating hydroxyloquo-tetramminecobalt sulphate (compare this vol., ii, 962) on a water-bath with ammonium chloride, forms small, dark red crystals. A solution of the salt gives with ammonium oxalate a red, crystalline precipitate, and with dipotassium hydrogen phosphate a dark orange-red precipitate. The following salts are obtained from the chloride by double decomposition: *bromide*,  $\text{XBr}_4 \cdot 4\text{H}_2\text{O}$ ,  $\{\text{X} = [(\text{NH}_3)_4\text{Co} \cdot \text{OH}]_2\}$ , a dark red, fine crystalline powder; *nitrate*,  $\text{X}(\text{NO}_3)_4$ , a bright carmine-red, crystalline powder; *thiocyanate*,  $\text{X}(\text{SCN})_4$ , a dark, violet-red, crystalline powder; *dithionate*,  $\text{X}(\text{S}_2\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$ , long, slender, light violet needles; *sulphate*,  $\text{X}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , small, violet-red needles. The compound obtained by Jörgensen (*loc. cit.*) is shown to be a complex sulphate of the octamminediol- and hexammine-series. W. H. G.

**The Reactions of the Nickel-plating Bath.** ANDRÉ BROCHET (*Compt. rend.*, 1907, 145, 627—628).—The author is studying the phenomenon of the passivity of nickel, and in this preliminary paper summarises the present state of knowledge regarding the chemistry of the process of nickel-plating. When solutions of nickel salts are electrolysed, using a nickel anode, the results are unsatisfactory; in the case of the chloride, the cathode becomes coated with the hydrated oxide of nickel; and in the case of the sulphate the bath becomes acid, owing to the accumulation of sulphuric acid caused by the passivity of the anode, and the nickel deposit, although white, is in scales containing occluded hydrogen. These difficulties are partially obviated by adding ammonium sulphate to the nickel sulphate bath (compare

Pfanhauser, Abstr., 1901, ii, 538) or boric acid to the nickel chloride bath.

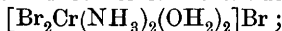
The passivity of the nickel anode depends more on the physical state of the metal than on its purity. Nickel which has been fused is more readily attacked than nickel plates, whilst the thin leaves of the metal are hardly attacked at all (compare Hittorf, Abstr., 1900, ii, 706).  
M. A. W.

### Dihydroxylodiaquodiamminechromium Salts,



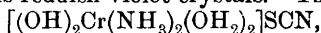
ALFRED WERNER and J. DUBSKY (*Ber.*, 1907, 40, 4085—4093).—The work of Werner and Klien (Abstr., 1902, ii, 210) has been repeated; the compounds, which were then considered to be basic salts, are now shown to be hydroxylo-compounds.

Reinecke's salt,  $[(\text{SCN})_4\text{Cr}(\text{NH}_3)_2]\text{K}$ , was oxidised by bromine to form dibromodiaquodiamminechromium bromide,



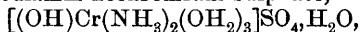
by the action of pyridine on the aqueous solution of this salt, the compound, previously described as a basic bromide, was obtained and shown to be *dihydroxylodiaquodiamminechromium bromide monohydrate*,  $[(\text{OH})_2\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2]\text{Br}, \text{H}_2\text{O}$ . The water of crystallisation is removed by careful drying of the salt at  $60^\circ$ ; on prolonged heating, more water is removed. When the hydroxylo-bromide is treated with acetic anhydride and then acted on by water and potassium thiocyanate, a precipitate of the dihydroxylothiocyanate is obtained.

The *chloride*,  $[(\text{OH})_2\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2]\text{Cl}, \text{H}_2\text{O}$ , obtained by the action of ammonia on tetra-aquodiamminechromium chloride, forms lilac-coloured crystals. The *iodide*,  $[(\text{OH})_2\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2]\text{I}$ , obtained by the addition of potassium iodide to the acetic acid solution of the bromide, forms reddish-violet crystals. The *thiocyanate*,



was also prepared. The *dithionate*,  $[(\text{OH})_2\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2]\text{S}_2\text{O}_6, \text{H}_2\text{O}$ , is a bluish-lilac, crystalline powder.

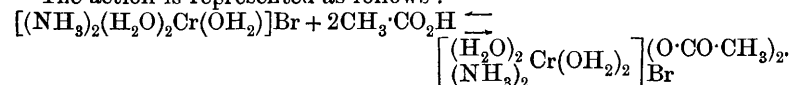
Hydroxylotriaquodiamminechromium sulphate,



obtained by Werner and Klien's method (*loc. cit.*), gave in acetic acid solution on the addition of potassium thiocyanate a precipitate of the dihydroxylothiocyanate.

The question of the basic character of the two hydroxy-groups attached to the chromium atom in the salts described is discussed. Whilst dihydroxylodiaquodiamminechromium bromide is insoluble in glacial acetic acid, it is very readily soluble in water to which a few drops of acetic acid are added. A red solution is thus obtained of the same tint as the chromium tetra-aquodiammine salts with mineral acids.

The action is represented as follows:



In spite of the presence of acetic acid, this reaction is reversible, since, when potassium bromide is added, unchanged dihydroxylodiaquodiamminechromium bromide is precipitated. If, on the other hand,

the dihydroxylo-salt is dissolved in the requisite amount of mineral acid, the addition of potassium bromide does not produce a precipitate.  
A. McK.

**Condition of Chromates and Dichromates in Aqueous Solution.** JOHN LUNDBERG (*Zeitsch. anorg. Chem.*, 1907, 55, 426—436. Compare Spitalsky, this vol., ii, 338, 695; Sand and Kaestle, this vol., ii, 178).—With the object of further elucidating the constitution of aqueous solutions of chromates and dichromates, the hydrolysis of potassium chromate in solution has been determined from its effect in accelerating the hydrolysis of ethyl acetate, and the electrical conductivity of solutions of potassium dichromate has been measured.

The hydrolysis of potassium chromate may be represented by one of the two ionic equations:  $\text{CrO}_4'' + \text{H}_2\text{O} = \text{HCrO}_4' + \text{OH}'$  or  $2\text{CrO}_4'' + \text{H}_2\text{O} = \text{Cr}_2\text{O}_7'' + 2\text{OH}'$ , to which correspond the equilibrium equations:  $[\text{HCrO}_4'] \times [\text{OH}'] / [\text{CrO}_4''] = K_1$  and  $\sqrt{[\text{Cr}_2\text{O}_7'']} \times [\text{OH}'] / [\text{CrO}_4''] = K_2$ . The values of  $K_1$  and  $K_2$ , obtained from the experiments with ethyl acetate, were both so irregular that it was not possible to decide from them whether the first or the second equation for the hydrolysis is correct, but conductivity measurements appear to show that the first one is to be preferred. From  $K_1 = 1.368 \times 10^{-7}$ , it is then calculated that in a  $N/10$  solution of potassium chromate 0.012% of the salt is hydrolysed, and that in a  $N/10$  solution of potassium dichromate, which contains chiefly  $\text{HCrO}_4'$  ions, 0.094% of the salt is ionised according to the equation:  $\text{HCrO}_4' = \text{H}^+ + \text{CrO}_4''$ .

Spitalsky (*loc. cit.*) states that dichromate solutions contain chiefly  $\text{K}^+$  and  $\text{Cr}_2\text{O}_7''$  ions, but the author considers that at least some of this observer's results are better accounted for on the view that a large proportion of  $\text{HCrO}_4'$  ions are present. G. S.

**Electrolytic Reduction of Tungstic Acid.** HEINRICH LEISER (*Zeitsch. Elektrochem.*, 1907, 13, 690—694).—No change occurs when the solution of a normal tungstate is electrolysed. If, however, a solution of metatungstic acid is electrolysed, it is reduced to a blue solution, which is very readily oxidised by exposure to the air, and from which no crystalline product could be isolated.

A solution of tungstic acid in sulphuric acid was then electrolysed in a platinum basin with a nickel gauze anode. By the use of the soluble nickel anode, anodic oxidation of the blue compound is avoided. When the reduction seemed to be complete, the solution was titrated with potassium permanganate. The results obtained at 60° to 70° in presence of a considerable excess of sulphuric acid indicate that the blue compound has the formula  $\text{W}_4\text{O}_{11}$ . With a lead cathode in place of the platinum one, the reduction appears to go further, a small quantity of a black substance always being deposited. This was analysed and found to be an oxide of the composition  $\text{WO}_2$ . T. E.

**Utilisation of Metallic Residues.** TOSIO WATANABE (*Mem. Coll. Sci. Eng. Kyōto*, 1907, 1, 183—186).—A fairly satisfactory separation

of the pure metals from mixtures of white metallic residues (turnings, clippings, &c.) rich in tin, and red residues rich in copper, can be effected by liquation. The author describes several attempts to effect the separation chemically, none of which has led to very satisfactory results. The most promising method consisted in transforming the alloy into a mixture of sulphides by fusing with lead sulphide, and dissolving out the tin sulphide with sodium sulphide solution. G. S.

**Action of Alcohol on Zirconium Sulphate.** OTTO HAUSER (*J. pr. Chem.*, 1907, [ii], 76, 363—367. Compare Abstr., 1904, ii, 568; 1905, ii, 531; this vol., ii, 626. Berzelius, *Ann. Phys. Chem.*, 1825, 4, 117; Endemann, this Journ., 1875, 1162).—The composition of the precipitate obtained on adding alcohol to an aqueous solution of zirconium sulphate varies with the temperature and concentration of the salt solution. The precipitates obtained in three experiments gave on analysis the proportions:  $\text{ZrO}_2/\text{SO}_3 = 1.227, 1.135, \text{ and } 1.108$ , and contained 17.39%—23.1% of water together with traces of alcohol. The precipitate forms a turbid solution in cold water which becomes clear when heated, and on evaporation gradually becomes viscid and solidifies to a colloidal compound of zirconium oxide hydrogel or a basic salt and sulphuric acid. When washed with water until neutral, the precipitate has  $\text{ZrO}_2/\text{SO}_3 = 1.51\text{—}1.54$ , and the composition  $3\text{ZrO}_2, 2\text{SO}_3, 8\frac{1}{2}\text{H}_2\text{O}$ .

Berzelius's compound has  $\text{ZrO}_2/\text{SO}_3 = 1.49$ . A compound of the composition given by Endemann was not obtained. G. Y.

**Antimony-Lead Alloys.** W. GONTERMANN (*Zeitsch. anorg. Chem.*, 1907, 55, 419—425. Compare Heycock and Neville, *Trans.*, 1892, 61, 888; Stead, Abstr., 1899, ii, 32; Matthiessen, *Ann. Phys. Chem.*, 1860, 110, 190).—Various investigators have found that antimony and lead do not enter into chemical combination, but, as the electrical conductivity measurements of Matthiessen indicate the possible occurrence of a compound, these alloys have been investigated again by thermal analysis.

The freezing-point curve consists of two branches meeting in a eutectic point at about  $247^\circ$  and 87% of lead. There are two breaks in the cooling curve in the neighbourhood of the eutectic temperature which differ only by  $4\text{—}6^\circ$ ; no conclusive explanation of this behaviour has been found. From 60—87% of lead, there are two well-defined layers in the solid alloy, the lower consisting of the eutectic, the upper of antimony crystals with a little eutectic.

No mixed crystals are formed, and the metals show no sign of chemical combination, even on prolonged heating at  $230\text{—}240^\circ$ .

G. S.

**Chemistry of Gold.** F. H. CAMPBELL (*Trans. Faraday Soc.*, 1907, 3, 103—113).—Experiments in which finely-divided gold was shaken with solutions of iodine in carbon tetrachloride show that unless the iodine concentration is 0.943 of what it is in the saturated solution, no formation of aurous iodide takes place. When excess of gold is

treated with iodine dissolved in potassium iodide solution, part of the gold passes into solution, and partition experiments show that this gold forms part of a complex anion  $\text{AuI}_2'$ .

In preparing aurous chloride by heating auric chloride in a current of dry air, the best temperature appears to be  $170$ — $180^\circ$ ; the change is exceedingly slow at  $140$ — $150^\circ$ . The change  $3\text{AuCl} = \text{AuCl}_3 + 2\text{Au}$  takes place at the ordinary temperature and in absence of water. Dry chlorine and aurous chloride combine readily at the ordinary temperature to form auric chloride.

Aurous bromide is readily prepared by gently heating auric bromide; it decomposes similarly to the chloride in a dry atmosphere and at the ordinary temperature:  $3\text{AuBr} = \text{AuBr}_3 + 2\text{Au}$ .

Various methods for the preparation of aurous oxide have been tested, and solutions of the nitrate have been obtained by shaking the oxide with nitric acid. Potential measurements have then been made and the normal potential  $\text{Au} | \text{Au}'$  has been calculated to be  $1.5$  volt. This is higher than the oxygen potential, which explains the difficulty of preparing the aurous compound. The solubility product for aurous oxide is estimated to be about  $0.7 \times 10^{-19}$ . J. C. P.

**A Cause of the Destruction of Platinum Vessels.** W. C. HERAEUS and W. GEIBEL (*Zeitsch. angew. Chem.*, 1907, 20, 1892—1894).—It is shown that the hydrogen present in the outer zone of the Bunsen flame diffuses through the hot platinum into the interior of a platinum crucible heated in this part of the flame. This hydrogen reduces very energetically; thus ferric oxide is partially reduced to iron, magnesium sulphate to sulphide, sodium sulphate to sulphite, &c. Consequently, a platinum crucible containing anything which on reduction would yield a substance capable of attacking platinum may be destroyed if heated in the outer zone of a Bunsen flame. In such cases, the crucible should be heated electrically.

W. H. G.

**Dihydroxylotetrammineplatinum Compounds.** ALFRED WERNER (*Ber.*, 1907, 40, 4093—4097).—It has previously been shown that in hydroxynitrosotetrammineruthenium salts,

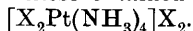


the hydroxy-group still possesses the property of adding on hydrogen ions, but the resulting nitrosoaquotetrammine salts are so unstable that they immediately undergo hydrolytic dissociation. This tendency to form aquo-salts is now shown to be scarcely perceptible with platinum compounds of similar type to the ruthenium salts referred to.

The observations of Carlgren and Cleve (*Abstr.*, 1893, ii, 127) were not sufficiently extensive to determine whether the dihydroxy-tetrammineplatinum salts, prepared by different methods, were identical or stereoisomeric. It is shown by the author that the observations, which appeared to point to isomerism, are to be ascribed to the existence of stable dimorphous forms; the dihydroxy-platinum sulphate, for example, crystallises sometimes anhydrous and sometimes with  $4\text{H}_2\text{O}$  when prepared according to one method; when prepared according to a second method, it is invariably obtained

anhydrous. In spite of repeated crystallisations, it is not possible to convert the anhydrous into the hydrated form; by the addition of a nucleus of the hydrated form to a solution of the anhydrous form, the conversion may, however, be effected. When the hydrated form is repeatedly crystallised from water, the anhydrous form is obtained.

In order to show that the hydroxy-groups of the dihydroxy-tetrammineplatinum salts prepared do not undergo electrolytic dissociation in aqueous solution, the electrical conductivity of some of the salts was determined. The salts are dissociated in the following sense:  $[(\text{OH})_2\text{Pt}(\text{NH}_3)_4]\text{X}_2 \rightarrow [(\text{OH})_2\text{Pt}(\text{NH}_3)_4]^{++}$  and  $2\text{X}^-$ , since the values obtained agree with those obtained with the type:



The salts do not show any tendency to form aquo-salts with the exception of dihydroxytetrammine platinum chloride, which forms the salt  $[(\text{H}_2\text{O})(\text{HO})\text{Pt}(\text{NH}_3)_4]\text{X}_2$ , with hydrochloric acid; the latter salt is, however, so unstable that it is converted by atmospheric moisture into the dihydroxy-chloride and hydrochloric acid.

Dihydroxytetrammineplatinum sulphate,  $[(\text{OH})_2\text{Pt}(\text{NH}_3)_4]\text{SO}_4$ , was obtained by Cleve's method, or by the action of hydrogen peroxide on tetrammineplatinum sulphate. The chloride,  $[(\text{OH})_2\text{Pt}(\text{NH}_3)_2]\text{Cl}_2$ , obtained by the addition of barium chloride to the sulphate or by the action of hydrogen peroxide on tetrammineplatinum chloride, is identical with the product described by Carlgren and Cleve. The bromide,  $[(\text{OH})_2\text{Pt}(\text{NH}_3)_4]\text{Br}_2$ , was prepared from the sulphate.

A. McK.

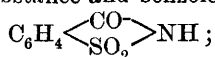
**Action of Osmium Peroxide on Soluble Metallic Iodides.** N. A. ORLOFF (*Chem. Zeit.*, 1907, 31, 1063).—Contrary to the statements in certain text-books, osmium peroxide,  $\text{OsO}_4$ , does not liberate iodine from neutral solutions of potassium iodide. From acidified solutions, however, as Alvarez (*Abstr.*, 1905, ii, 423) has shown, iodine is liberated and an emerald-green compound,  $\text{OsI}_2 \cdot 2\text{HI}$ , precipitated.

G. S.

### Mineralogical Chemistry.

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**Barlow and Pope's Theory.** FRANS M. JAEGER (*Zeitsch. Kryst. Min.*, 1907, **46**, 61—64).—Goniometric measurements are given for phthalimide,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\text{NH}$ , showing a close resemblance in crystalline form between this substance and benzoicsulphinide,



the substitution of  $\cdot\text{SO}_2\cdot$  (valency volume, 6) by  $\cdot\text{CO}\cdot$  (valency volume, 6) has no marked effect on the crystalline structure, thus confirming Barlow and Pope's theory (*Trans.*, 1906, **89**, 1675; 1907, **91**, 1150). The equivalence-parameters are calculated for these substances, and



compared with those for anthranilic acid (*o*-aminobenzoic acid) and *o* sulphobenzoic acid (Trans., 1906, 89, 1734):

	$x$	$y$	$z$
Anthranilic acid .....	2.2612	3.7945	4.8952
<i>o</i> -Sulphobenzoic acid .....	2.5708	3.8496	4.6481
Benzoic sulphinide .....	2.5183	3.6857	4.7521
Phthalimide .....	2.4623	3.3022	4.9197

L. J. S.

**Origin of Red Ochre Deposited from the Thermal Waters of the Baths of Lucca.** GIUSEPPE MAGRI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 400—408).—The red ochre deposited from these waters owes its formation to hydrolysis of the dissolved iron salts. Colloidal ferric hydroxide represents an intermediate stage in the change, and is precipitated either by micro-organisms, various electrolytes, or radioactive substances.

T. H. P.

**A New Mineral from the Ancient Lead Slags at Laurion, Greece.** ALFRED LACROIX and AUGUST B. DE SCHULTEN (*Compt. rend.*, 1907, 145, 783—785).—The new mineral was found as crystals, up to 3 mm. in length, lining the cavities of a resinous specimen of a vitreous slag containing fragments of charcoal; it is associated with the lead oxychlorides, laurionite, fiedlerite, and matlockite. The crystals are white or brownish-yellow with a vitreous lustre; they have the appearance of short, hexagonal prisms, but are really orthorhombic, with  $a:b:c=0.5770:1:0.2228$ ; hardness,  $3\frac{1}{2}$ ; D 7.1. The plane of the optic axes is parallel to (100), and the acute positive bisectrix is perpendicular to (001). Analysis gives the formula  $Pb_3(AsO_4)_2, 3PbCl_2$ :

$As_2O_5$ .	PbO.	Pb.	Cl.	Total.
12.49	38.86	36.38	12.47	100.20

The mineral differs widely from mimetite in the relative proportions of arsenic acid and chlorine, and for it the name *georgiadesite* is proposed. Arsenopyrite is known to occur with the lead ores of Laurion, and this will account for the presence of arsenic in the ancient slags, which have been acted upon by sea-water with the formation of lead oxychlorides, chloro-carbonate, and chloro-arsenate.

L. J. S.

**Powellite and Molybdenite.** WALDEMAR T. SCHALLER (*Zeitsch. Kryst. Min.*, 1907, 44, 9—13).—A mineral from Barringer Hill, Llano Co., Texas, thought to be molybdenite, was found on analysis (I) to be powellite. The loose fragments are grey, and they readily break up into small, shining scales; the scaly character being due to the pseudomorphism of the mineral after molybdenite, with which it occurs and encrusts. Similar material (anal. II), also pseudomorphous after molybdenite, occurs, with scheelite, as veins and irregular masses in a earthy, decomposed rock at Oak Springs, Nye Co., Nevada. This is a new mode of occurrence of powellite, and it is suggested

that the mineral recently described by G. Gagarine (this vol., ii, 704) as molybdate is really powellite :

	CaO.	MoO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	WO <sub>3</sub> .	SiO <sub>2</sub> .	MoS <sub>2</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.*
I.	27.46	67.90	—	nil	0.88	1.50	2.33	100.07	4.23
II.	26.44	62.43	1.17	trace	6.80	—	2.69	99.53	4.24
III.	—	46.77	15.95	—	16.51	5.50	15.87	100.60	2.99

\* Recalculated after deducting impurities.

Molybdate is recorded from Hortense, Colorado, where it occurs as small, yellow masses with molybdenite, quartz, and mica. Analysis III agrees with the formula  $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$  (this vol., ii, 480). Molybdate is soluble in 33,000 parts of water.

L. J. S.

**Rhonite, a New Aenigmatite-like Mineral in Basaltic Rocks.** J. SOELLNER (*Jahrb. Min., 1907, Beil.-Bd., 24, 475—547*).—A reddish-brown amphibole, forming a constituent of basaltic rocks from the Rhön Mountains and several other localities, was found to have microscopical characters resembling those of aenigmatite. The following analysis, by Dittrich, of material isolated from a nepheline-basanite from the Rhön Mountains shows, however, that the mineral differs considerably from aenigmatite in composition, and the name *rhonite* is therefore proposed for it. The formula is  $(\text{Ca}, \text{Na}_2, \text{K}_2)_3\text{Mg}_4\text{Fe}_2''\text{Fe}_2'''\text{Al}_4(\text{Si}, \text{Ti})_6\text{O}_{30}$ .

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.
24.42	9.46	17.25	11.69	11.39	trace	12.62	12.43	0.67	0.63	100.56

The mineral is triclinic, and the angles between the faces, as determined in thin sections under the microscope, are near to those of aenigmatite, with which rhonite is isomorphous. In habit, twinning, and cleavage, the mineral also resembles aenigmatite. It is black to brownish-black, with a metallic lustre by reflected light; in thin sections, it is reddish-brown to brownish-black, with strong pleochroism.

Petrographical descriptions are given of rocks (plagioclase-basalts, nepheline-basalts, nepheline-basanites, limburgites, &c.) from several localities (Rhön Mountains, Rhenish district, Odenwald, Bohemia, &c.), in which the mineral was identified.

L. J. S.

**Composition of the Red Clay.** FRANK W. CLARKE (*Proc. Roy. Soc. Edin., 1907, 27, 167—171*).—The paper gives the results of a complete analysis of the "red clay" characteristic of the greatest depths of the sea; imperfect analyses are already contained in the reports of the *Challenger* Expedition. Fifty-one samples from as many localities were mixed, and the average composition determined. Titanium, chromium, vanadium, molybdenum, arsenic, and certain other elements not mentioned in previous analyses have been estimated. Lithium and fluorine, as well as zirconium and other rare earths, are absent.

G. S.

## Physiological Chemistry.

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**Breathing and Metabolism.** ALBERT FRAENKEL (*Zeitsch. Biol.*, 1907, 50, 163—167).—Polemical against Voit. The thesis that lessened oxygen intake leads to increased protein decomposition is maintained.  
W. D. H.

**Behaviour of Calcium in the Blood in Experimental Poisoning by Acids.** R. A. ALLERS and SAMUEL BONDI (*Biochem. Zeitsch.*, 1907, 6, 366—372).—The blood of rabbits, killed five hours after the administration *per os* of an amount of  $N/4$  hydrochloric acid equal to 0.1 of the body weight, contained on the average 0.0159% CaO as compared with 0.069% in normal blood. There was no corresponding increase in the amount of other inorganic bases.  
G. B.

**Quantitative Methods with Hæmolytic Serum.** WILFRID H. MANWARING (*J. Biol. Chem.*, 1907, 3, 387—390. Compare Abstr., 1906, ii, 208).—Further considerations which show that it is impossible at present to devise even indirect methods of measuring hæmolysis correctly.  
W. D. H.

**Anti-inulase.** TADASU SAIKI (*J. Biol. Chem.*, 1907, 3, 395—402).—In normal rabbits' serum, inulase, and anti-inulase are absent. Serum, however, independently of its protein or alkali, inhibits inulin digestion, but not acid hydrolysis. Anti-inulase appears in rabbits' serum after the injection of inulase. The anti-serum exhibits different degrees of inhibitory action on the inulin-digesting and sucrose-inverting activities of inulase preparations. The two actions of inulase prepared from *Aspergillus* are therefore probably independent. The anti-serum has no action on intestinal sucrase.  
W. D. H.

**Hæmagglutination and Hæmolysis. I—VIII.** LEO VON LIEBERMANN, Parts III., IV., and V. in conjunction with PAUL VON LIEBERMANN, Part VII. in conjunction with B. VON FENYVESSY (*Arch. Hygiene*, 1907, 62, 227—342).—The main conclusion of this series of papers, arrived at in Part VIII., is, that in the serum of rabbits immunised against the red corpuscles of the pig, the complement resembles a soap, and the immune substance resembles oleic acid (compare von Liebermann, *Biochem. Zeit.*, 1907, 4, 25, and Noguchi, this vol., ii, 890, and following abstract).

Soap hæmolyses in very dilute solution, but is without action in the presence of some proteins (serum-albumin) and of lime salts; thus active serum is rendered inactive by the addition of calcium chloride. The immune substance, being an acid, would appear to liberate the soap from its combination with the serum-albumin, and thus enable it to exert its hæmolytic action. An artificial immune serum may be prepared from a serum-albumin solution and soap; it is activated by

the addition of minute quantities of oleic acid (in themselves insufficient to produce lysis), and can then be rendered inactive by heating to  $56^{\circ}$  (as regards lysis, but not as regards agglutination).

The acceleration of agglutination by alkalis and its retardation by acids leads to the view, that ricin is a feebly acid substance which forms an insoluble compound with the stroma, thereby setting the hæmoglobin free (Part I.). Agglutination and lysis are two stages of the same reaction, but, on the addition of alkali, lysis may occur singly through the alkali combining with the hæmoglobin, and leaving the stroma free. Guaiacum saponin (Part IV.) closely resembles ricin in combining with the stroma, although here there is no obvious agglutination. In the serum of rabbits which have been immunised against pig's corpuscles, the complement is made inactive by alkali, but regains its activity on neutralisation (Part V.). The inactivation by heating may, to a slight extent, be due to an increase of hydroxyl ions, which can be detected in a heated serum by electrical means, although not by titration (Part VI.). An attempt was made to isolate the lysin from rabbit's serum (Part VII.). It was found to be acid, thermostable, readily soluble in water, and slightly so in cold alcohol. G. B.

**Certain Chemical Complementary Substances.** HIDEYO NOGUCHI (*Biochem. Zeitsch.*, 1907, 6, 327—357. Compare this vol., ii, 890, and preceding abstract).—Two groups of experiments, hæmolytic and bactericidal, lead to similar conclusions as regards the chemical nature of the complement. The non-specific, thermostable hæmolysins, which can be extracted from serum and from various organs by alcohol, consist of soaps, and show in their action the greatest resemblance to oleates. Sodium oleate is ten times as hæmolytic as sodium stearate. Despite the differences in the behaviour of these "extract" lysins (or soaps) and complements, the two substances are not necessarily different, for comparison must be made under identical conditions. When serum is added to an oleate, the latter loses its lytic properties, but now resembles a complement, so that lysis of corpuscles, which have been sensitised previously by an amboceptor, nevertheless occurs. This artificial complement becomes inactive when it is heated to  $56^{\circ}$ , or when it is kept for a week, or when acids, or salts of the alkaline earths, are added. All these properties of the complement possibly depend on the presence of serum proteins. G. B.

**The Acid Control of the Pylorus.** WALTER B. CANNON (*Amer. J. Physiol.*, 1907, 20, 283—322).—By means of X-ray observations, it is shown that during gastric digestion peristalsis occurs continuously, but the discharge from the pylorus is occasional; this is because the pylorus is under acid control; acid in the antrum opens it, and in the duodenum closes it. The closure is intermittent because the acid in the duodenum is soon neutralised. This is supported by experimental evidence; thus moistening carbohydrates with alkali retards their normally rapid exit, and treating proteins with acid hastens their normally slow exit; the stomach empties more slowly when the alkaline bile and pancreatic juice are prevented from entering

the intestine. The effect from the duodenum is regarded as a local reflex action. W. D. H.

**Activation of Pancreatic Steapsin.** HEDWIG DONATH (*Beitr. chem. Physiol. Path.*, 1907, 10, 390—410).—Pancreatic steapsin is activated by cholic acid, but beyond a certain limit further addition of the acid causes no increase in activity. A hastening of fermentative fat-synthesis of cholic acid could not be observed with certainty. Preparations of steapsin alter, so that they become "spontaneously" activated. No activating kinase for steapsin was found in the intestinal mucous membrane. Lipase from *Ricinus* seeds is not activated by cholic acid. Pancreatic steapsin rendered inactive by heating at 60—63° is, in part, re-activated by normal horse-serum. This is due to the presence in the serum of a thermolabile agent. After the steapsin has been heated to 77—80°, re-activation by serum does not occur. Steapsin rendered inactive by the latter temperature inhibits the activity of the active ferment. W. D. H.

**The Use of Bone Ash in Metabolism Experiments on Dogs.** MATTHEW STEEL and WILLIAM J. GIES (*Amer. J. Physiol.*, 1907, 20, 343—357).—An easily assimilable diet necessary in most experiments on metabolism has the disadvantage that the faecal discharge is usually small, offensive, and fluid, and so apt to mingle with the urine. This is avoided by mixing powdered bone ash with the food. The admixture does not interfere with digestion or absorption of other substances, and the urine in contact with the faeces does not dissolve out any constituents of the ash. W. D. H.

**Metabolism of Carbohydrates.** KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1907, 10, 277—286).—The C/N ratio in the urine obtained from dogs under the following conditions: (1) meat diet; (2) fat diet; (3) carbohydrate diet, and (4) hungry, has been determined, as also the amounts of urea and ammonia in the same urines. The urea is present in largest amount after a flesh diet, and is smallest after a carbohydrate diet. The ratio non-oxidisable C/non-oxidisable N has also been calculated. The various results are:

	C/N.	Non-oxid. C/non-oxid. N.
Meat.....	0·601	2·449
Fat .....	0·719	2·268
Carbohydrate .....	0·777	2·086
Hungry .....	0·759	2·011

The results obtained for dogs differ from those obtained for other mammals which are accustomed to a mixed diet, or to a diet rich in carbohydrates.

Intravenous injection of glycine and lævulose into rabbits gives rise to pyrazine-2:5-dicarboxylic acid in the urine. J. J. S.

**Behaviour of Non-fermentable Carbohydrates in the Animal Organism.** WALTHER BRASCH (*Zeitsch. Biol.*, 1907, 50, 113—162).—A discussion of the nutritive value of different sugars; the experi-

ments recorded show both in men and animals a low assimilation limit for galactose. Experiments with pentoses on animals showed that glycogen is not formed from them, and that nitrogenous katabolism is increased.

W. D. H.

**Influence of Alcohol on Glycogen Metabolism.** WILLIAM SALANT (*J. Biol. Chem.*, 1907, 3, 403—418).—Large quantities of alcohol hasten the process by which glycogen disappears from the liver, but only after the stage of intoxication has been passed. Neglect to recognise this fact will explain the discordant results of other observers. The experiments were made on rabbits.

W. D. H.

**Fat Absorption in Isolated Loops of Intestine.** OTTO VON FURTH and JULIUS SCHÜTZ (*Beitr. chem. Physiol. Path.*, 1907, 10, 462—472).—Stearin and olein soaps are extremely badly absorbed. Oleic acid and olive oil are absorbed better. The absorption of soaps is not influenced by the addition of glycerol, and usually is unfavourably affected by the addition of bile; in one experiment, absorption was increased by the presence of bile. Bile also does not uniformly increase absorption of oleic acid or olive oil. The addition of bile and the expressed juice of the pancreas lessens absorption of oleic acid and olive oil. These conclusions are drawn from experiments on isolated intestinal loops.

W. D. H.

**Decomposition of the Active Constituents of the Rhizome of *Filicis maris* by Animal Enzymes.** MAX GONNERMANN (*Chem. Zentr.*, 1907, ii, 928; from *Apoth. Zeit.*, 1907, 22, 669—671. Compare Abstr., 1906, i, 780).—Neither aspidin nor filmarone (Kraft, Abstr., 1904, i, 1039) are decomposed into phloroglucinol and butyric acid by pepsin, pancreatin, or trypsin, consequently the decomposition of filmarone in the intestines is not necessarily due to the action of intestinal enzymes.

W. H. G.

**Oxidising Ferments in the Mature Reproductive Cells of Amphibia and their Function as Stimuli to Development.** WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1907, 6, 409—472).—Extracts from the ovaries and testes of Amphibia contain a peroxydase, which colours guaiacum tincture blue, and a catalase, which decomposes hydrogen peroxide. The latter decomposition proceeds at first at the same rate as a unimolecular reaction, but soon the constant decreases, presumably owing to the gradual decomposition of the catalase itself. By means of a graphic extrapolation method, the initial value of the velocity constant, and hence the relative concentration of the catalase, can be determined for any given extract.

In this way, it is found that spermatozoa invariably contain much more catalase than an equal weight of ova, on the average about three times as much. In the case of the peroxydase, a rough, colorimetric comparison alone is available, which, however, clearly shows that the testicular extract also contains more peroxydase than an ovarian extract. When an extract of spermatozoa is mixed, in certain proportions, with an extract of ova, there occurs, after a time, an increase or activation of the peroxydase and probably also of the catalase.

These results are discussed in connexion with a physico-chemical theory of fertilisation. The entrance of the spermatozoon into the ovum produces in the latter an increase in the oxydase concentration, leading to an autoxidation, which results in the formation of nucleins from the cell protoplasm. The nucleins are coagulated, localised, and orientated, and then constitute the astrosphere of the developing egg. G. B.

**The Formation of Glycine.** ADOLF MAGNUS-LEVY (*Biochem. Zeitsch.*, 1907, 6, 523—540).—The question whether glycine can be formed in the organism *de novo*, that is, whether it may occur in greater amount than that which is preformed in the proteins of the food, must be answered in the affirmative (for example, calculations based on the excess of glycine in a calf over that contained in the milk on which it is fed). Benzoic acid was given to cream-fed rabbits and to starving sheep; the output of glycine (as hippuric acid) was found to be much greater than the amount of glycine which could have been contained in the body proteins used up during the experiment. G. B.

**The Behaviour of Benzoylated Amino-acids in the Organism.** ADOLF MAGNUS-LEVY (*Biochem. Zeitsch.*, 1907, 6, 541—554).—The possibility that the excess of hippuric acid referred to in the preceding abstract was formed by the oxidation of higher benzoylated amino-acids, led to the subcutaneous administration of these acids to rabbits and dogs. In all cases, the benzoyl derivatives passed into the urine unchanged; no hippuric acid was formed (except in the case of an unknown amino-acid from the leucine fraction of a tryptic digestion). G. B.

**The Behaviour of Formylated Amino-acids in the Organism.** ADOLF MAGNUS-LEVY (*Biochem. Zeitsch.*, 1907, 6, 555—558).—In contradistinction to benzoylated amino-acids (compare preceding abstract), formylglycine and formyl-leucine are broken down by the organism (rabbit). G. B.

**Is the Conduction of a Nerve Impulse a Chemical or a Physical Process?** SAMUEL S. MAXWELL (*J. Biol. Chem.*, 1907, 3, 359—386).—Experiments were made on the pedal nerve of the giant slug, *Ariolimax columbianus*. The nerve is sufficiently long, and the normal rate of conduction of the impulse sufficiently slow, for purposes of measurement. Arrhenius and van't Hoff showed that a rise of 10° increases the velocity of a chemical reaction to two or three times its original rate. The present experiments show that this rise increases the velocity of nerve conduction in a corresponding manner, and the conclusion is drawn that therefore the nerve impulse is a chemical phenomenon. It is probably not an oxidation. W. D. H.

**Absorption through the Skin of Esters of Salicylic Acid.** E. IMPENS (*Plüger's Archiv*, 1907, 120, 1—18).—It is possible to administer salicylic acid through the skin by inunction. The drug is

shortly afterwards to be detected in the urine. Four preparations were investigated: (1) oil of Gaultheria (methyl salicylate), (2) amyl salicylate, (3) mesotan (methoxymethyl salicylate), and (4) spiroasal (ethylene salicylohydrin,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ ). The last-named preparation, which has only recently been introduced for therapeutic use, is by far the best; it is the most readily absorbed, especially if diluted with alcohol, and it is the least irritating to the skin.

W. D. H.

**Reducing Constituents of Cells.** ARTHUR HEFFTER (*Chem. Zentr.*, 1907, ii, 822—824; from *Med.-Naturwiss. Arch.*, 1907, 1, 81—104. Compare Heffter and Hausmann, *Abstr.*, 1904, i, 461).—It is shown that all cases of reduction not hindered by the presence of hydrogen cyanide may be carried out by means of the labile hydrogen atom of sulphhydryl compounds; thus cystein, thiolactic acid, and thioglycollic acid reduce arsenic acid to arsenious acid, tellurates and tellurites to tellurium, mercurous chloride to mercury, cacodylic acid to cacodyl, &c. In this respect, the above sulphur compounds behave like the extracts of many animal and plant cells.

Further, alkaline solutions of these SH- compounds give a purple coloration with sodium nitroprusside; compounds without a reducing action, such as thioacetic acid and thiobenzoic acid, do not give a coloration with this reagent; it is thus possible by this test to detect the presence of sulphhydryl compounds capable of acting as reducing agents. Since several animal organisms and their extracts, especially those with a reducing action, give a purple coloration with sodium nitroprusside, the author concludes there are present in them constituents containing SH- groups, and that the reducing action of animal and plant cells is not due to the action of enzymes (reductases), but to the presence of albuminous substances containing one or more SH- groups.

W. H. G.

**Salts of Muscle.** FUMIHIKO URANO (*Zeitsch. Biol.*, 1907, 50, 212—245).—Frog's muscles placed in isotonic solutions of sucrose are rendered free from sodium. The sodium salts are therefore in the lymph and interstitial fluid. This fluid amounts to one-sixth of the muscle volume. Magnesium must be distributed differently from potassium and calcium, for in the expressed juice it is present in less concentration than in the total muscle. In the preparation of the juice, there is a rise in molecular concentration which is due to injury leading water soluble materials to pass into it from the muscular stroma; this is specially true for phosphoric and lactic acids. Frog's muscle contains a not unimportant proportion of sulphates.

W. D. H.

**Action of Potassium Chloride on Muscular Contraction.** GEORGE FAHR (*Zeitsch. Biol.*, 1907, 50, 203—211).—The paralysis produced by potassium chloride is incomplete and reversible; there is a lengthening of the latent period, a decrease of conductivity, and of irritability. These three results are unequal, and vary also with the nutritive condition of the muscle.

W. D. H.



**Glycogen in Human Muscles and its Diminution after Death.**

GIUSEPPE MOSCATI (*Beitr. chem. Physiol. Path.*, 1907, 10, 337—344).—Human limb muscles contain on the average 0·4% of glycogen, the proximal more than the distal ones. At 15°, the amount slowly and continuously diminishes; when putrefaction sets in, the diminution is more rapid, and ultimately the glycogen entirely disappears. At 0°, the diminution occurs at half the rate. It is not prevented by antiseptics. W. D. H.

**Fats and Glycogen in the Liver of Selachians.**

FILIPPO BORTAZZI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 514—517).—The fats of the livers of three Selachians, *Torpedo ocellata*, *Squatina Angelus*, and *Scyllium stellare*, examined by the author have m. p. 28—29° and solidify at 24—25°. The liver of a well-nourished *Scyllium stellare* gives 51·16% of dry residue; if the animal fasts for a long time, the proportion is probably much greater than the above. The liver of the Selachians contains only relatively small proportions, 0·927—2·380%, of glycogen, and this only when the animals are well-fed. During fasting, there is a rapid disappearance of the glycogen and a simultaneous increase in the amount of fat, so that the latter must be regarded as the essential reserve material of these organisms, whilst glycogen is formed only in small quantity and is rapidly consumed or transformed into fat; the liver also contains large proportions of iron. The liver of *Thalassochelys caretta* yielded, in two cases, 4·857 and 6·554% of glycogen. T. H. P.

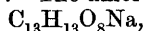
**The Elimination of Radium.**

WILLIAM SALANT and GUSTAVE M. MEYER (*Amer. J. Physiol.*, 1907, 20, 366—377).—In dogs and rabbits, radium bromide was given subcutaneously; it is eliminated by the kidney, liver, small intestine, large intestine (in a less degree), and cæcum (very slight, and in some rabbits negligible). After removal of the kidneys, elimination continues by the liver and alimentary tract as before; there is no compensatory elimination. W. D. H.

**Benzoylglycuronic Acid in Sheep's Urine after Ingestion of Benzoic Acid.**

ADOLF MAGNUS-LEVY (*Biochem. Zeitsch.*, 1907, 6, 502—522).—Benzoic acid, given in doses of 20 grams per day, is wholly excreted as hippuric acid, but after administration of 30—50 grams per day the urine contains, in addition, *benzoylglycuronic acid*,  $\text{OBz} \cdot \text{CH} \cdot [\text{CH} \cdot \text{OH}]_2 \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$ , a dextrorotatory syrup. It

was isolated as the *strychnine* salt, which crystallises in rhombic prisms and plates, m. p. 162°. The amorphous sodium salt,



has  $[\alpha]_{\text{D}}^{20} + 43 \cdot 86^\circ$ . Benzoylglycuronic acid is very easily hydrolysed, and hence reduces Fehling's solution as readily as glycuronic acid itself. Its presence in urine is further indicated by a dextrorotation (normal sheep's urine is slightly laevorotatory). The acid is analogous to the dimethylaminobenzoylglycuronic acid obtained by Jaffe (*Abstr.*, 1905, ii, 186). G. B.

**Oxyproteic Acid in Urine.** WILHELM GINSBERG (*Beitr. chem. Physiol. Path.*, 1907, 10, 411—446).—Oxyproteic acids are precipitable by mercuric acetate, and yield barium salts which are soluble in water and insoluble in alcohol. In human urine, from 3% to 5% of the total nitrogen is present in these compounds. In pathological cases, the amount comes within the same limits. In dogs, the amount averages 2%, and is remarkably constant under varying conditions of nutrition; there is thus a constant relation between protein katabolism and the excretion of oxyproteic acid. The same is true for other animals. In phosphorus poisoning, the amount excreted increases. Substances of the oxyproteic acid group yield on hydrolysis leucine and, probably, other amino-acids; they are fairly easily dialysable, and are possibly polypeptides. W. D. H.

**A Green Pigment Derived from Indole in Urine.** I. ALBERICO BENEDICENTI (*Zeitsch. physiol. Chem.*, 1907, 53, 181—191).—The action of indoline, 1-methylindoline, and 2:3:3-trimethylindoline (Plancher, *Abstr.*, 1899, i, 454) on the animal organism has been investigated. The three compounds have but little toxic action, and indoline appears to be somewhat more poisonous than its methyl derivatives. Appreciable amounts of indigotin are found in the urine of dogs or rabbits to which indoline has been given *per os* or subcutaneously, but, when the methyl derivatives are used, a red colouring matter is formed, which may be removed by extracting the urine with amyl alcohol. The red colour obtained from the trimethylindoline is stable, whereas that derived from 1-methylindoline is transformed into a green pigment when exposed to the air. The same pigment is formed when 1-methylindole is substituted for the methylindoline, although the indole is poisonous when used in large quantities. The green pigment is soluble in most organic solvents, but is most readily extracted by amyl alcohol. The pigment forms a dark green, amorphous powder, sparingly soluble in alkalis, but readily so in concentrated sulphuric acid, yielding a dark brown solution. The green alcoholic solution is decolorised when mixed with a few drops of dilute sodium hydroxide solution, but the colour reappears on the addition of acid. The solution has an absorption band between *C* and *D*. When reduced with alkali and dextrose, the pigment yields a leuco-derivative.

Methylindigotin synthesised by Heumann's method (*Abstr.*, 1891, 206, 456, 837) appears to be identical with this green pigment.

All methyl derivatives of indole in which the methyl groups are attached to carbon yield red pigments. J. J. S.

**Autolysis and Fatty Degeneration.** PAUL SAXL (*Beitr. chem. Physiol. Path.*, 1907, 10, 447—461).—Yellow phosphorus added post-mortem to organs increases the rate of autolysis. In autolysis and in phosphorus poisoning, or in organs in which autolysis is increased by the addition of phosphorus, there is no new formation of higher fatty acids. The view is held that in so-called fatty degeneration there is no actual increase in the amount of fat, but that in this condition the fat, which was previously present in the protoplasm, becomes visible in droplet form. W. D. H.

**Action of Magnesium Sulphate on the Heart.** WILLIAM DE B. MACNIDER and SAMUEL A. MATTHEWS (*Amer. J. Physiol.*, 1907, 20, 323—329).—Intravenous injection of magnesium sulphate in dogs stops the heart, and robs it of automaticity. This is believed to be due to depression of the nervous mechanism of the heart. Stimulation of the accelerator nerves causes the heart to again beat rhythmically.

W. D. H.

**The Action of Cholesterol on the Frog's Heart.** B. DANILEWSKY (*Pflüger's Archiv*, 1907, 120, 181—192).—The frog's heart was perfused with Ringer's solution, and with a solution of cholesterol in the same fluid. The concentrations of the cholesterol solutions were from 0.001% to 0.003%. Cholesterol, like lecithin, has a stimulating action on systolic activity, and acts on the muscular substance of the heart. The effect is not so pronounced as that of lecithin.

W. D. H.

**The Relations Between Adsorption and Toxicity of Salt Solutions on Fresh-Water Animals (Gammarus).** WOLFGANG OSTWALD (*Pflüger's Archiv*, 1907, 120, 19—30. Compare Abstr., 1906, ii, 112).—Curves showing the toxicity of various salts on fresh-water fish are markedly similar to those showing the extent to which they are absorbed by colloids. Further, some observers have shown that the protein matters of the organism are able to form loose compounds with salts or their ions. The present research confirms the idea drawn from such considerations that toxicity is related to this adsorption. Various formulæ expressing this relationship are given.

W. D. H.

**Toxicology of Nickel Carbonyl.** I. HENRY W. ARMIT (*J. Hygiene*, 1907, 7, 525—551).—Dissociation of nickel carbonyl takes place rapidly at body temperature in the presence of air, moisture, and carbon dioxide. This also occurs in the body, and the toxic properties do not depend on the carbon monoxide. When nickel carbonyl is inhaled, it is decomposed into carbon monoxide and a substance containing nickel (?hydrated basic nickel carbonate) before or soon after reaching the alveoli of the lungs, and the poisonous action is entirely due to the nickel which is deposited as a slightly soluble compound in a very fine state of division over the immense area of the respiratory surface.

W. D. H.

**Condition of Blood in Men Engaged in Aniline Dyeing and in the Manufacture of Nitrobenzene and its Compounds.** W. MALDEN (*J. Hygiene*, 1907, 7, 672—685).—Experiments on animals confirm observations on the blood of aniline and nitrobenzene workers. The poison gains access to the body either by inhalation (the most usual way), by cutaneous absorption, or after being swallowed; the action on the blood is the same in all cases, and consists in the early stages of a decrease in the red corpuscles, degeneration and imperfect development of these corpuscles, and loss of hæmoglobin, which varies from 5 to 50%. Later, hæmoglobin is converted into methæmoglobin, and hæmolytic occurs. Cessation from work, and inhalation of oxygen lead to recovery.

W. D. H.

**Injurious Action of Certain Inorganic and Organic Substances on Fishes.** A. SARTORY (*Chem. Zentr.*, 1907, ii, 1003—1004; from *Bull. Sci. Pharm.*, 1907, 14, 397—400).—Small fishes weighing from 15—20 grams are killed by strychnine sulphate when present to the extent of 0·003—0·004 gram per litre; with atropine sulphate, the quantity is larger, 0·2 gram per litre. They are, however, not killed by 1·9 grams of morphine hydrochloride per litre; in fact, they gradually become accustomed to this substance, so that the quantity may slowly be increased to 2·3 grams without proving fatal. W. H. G.

**Estimation of Free Diphtheria Toxin, with Reference to the Relations Between Lethal Doses, Lethal Times, and Loss of Weight in Guinea Pigs.** J. A. CRAW and GEORGE DEAN (*J. Hygiene*, 1907, 7, 512—524).—In guinea pigs, lethal doses of diphtheria toxin, multiplied by the lethal time, give approximately a constant value. Variations may be largely eliminated by taking the average of a number of experiments. The first day after a dose, the weight of the animal increases, but the larger the dose the more rapidly is this followed by a decrease. W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Disinfectant Value of the Three Isomeric Cresols.** RAPP (*Chem. Zentr.*, 1907, ii, 717; from *Apoth. Zeit.*, 1907, 22, 643—644).—It is shown that *o*-cresol, although not equal to *m*-cresol in its bactericidal action, is nevertheless as active as *p*-cresol. The isomeric chlorophenols are more active than the cresols; thus *m*-chlorophenol is five times more active than *m*-cresol.  
W. H. G.

**Losses of Ammonia from Culture Solutions.** JACOB G. LIPMAN and PERCY E. BROWN (*J. Amer. Chem. Soc.*, 1907, 29, 1358—1362).—Omeliansky's culture solution lost a considerable amount of ammonia in the process of sterilising, and further losses occurred when the sterilised solution was kept for some days. There was also a loss when unsterilised solutions were kept. When calcium carbonate was employed instead of magnesium carbonate, the loss of ammonia was less. The loss of ammonia is probably, in some cases, due to liberation of nitrogen by the interaction of ammonia and nitrous acid.  
N. H. J. M.

**Manganese and the Development of Plants. II.** GIOVANNI SALOMONE (*Chem. Zentr.*, 1907, ii, 999—1000; from *Staz. sperim. agrar. ital.*, 1907, 40, 97—117).—Experiments carried out on a large scale in open fields confirm the results obtained previously (*Abstr.*, 1906, ii, 792). Of the many compounds of manganese employed, manganous

sulphate, manganous nitrate, and manganese dioxide were found to exert the most beneficial influence on the growth of corn. A table is given, showing the proportions of the various manganese compounds which produce the best results, also the quantities sufficient to kill plants in a few days.

W. H. G.

**The Distribution of Prussic Acid in the Vegetable Kingdom.** MAURITS GRESHOFF (*Brit. Assoc. Report*, 1906, 76, 138—144).—The Report contains a complete list of plants in which hydrocyanic acid has been found, and the author discusses the rôle of this acid in phyto-synthesis.

G. T. M.

**The Chemical Aspects of Cyanogenesis in Plants.** WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Brit. Assoc. Report*, 1906, 76, 145—157).—The report contains a short description of each of the cyanogenetic glucosides and their enzymes. The physiological significance of cyanogenesis is also considered.

G. T. M. .

**Revertase in Fungi.** ENRICO PANTANELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 419—428. Compare Abstr., 1906, ii, 623).—By the action on a freshly-prepared invert sugar solution of pastes of the mycelia of *Mucor mucedo*, *Penicillium glaucum*, *Aspergillus niger*, and *Botrytis cinerea*, the presence in these organisms of intracellular revertase, as well as invertase, is demonstrated. The revertase exhibits, in general, increased activity in a slightly alkaline solution.

It is not strictly accurate to speak of the revertive action of an enzyme, since in no case does this action yield a compound capable of attack by the enzyme.

T. H. P.

**Nitrogen Content of Wheat and its Distribution to Different Parts of an Individual Plant.** R. W. THATCHER and H. R. WATKINS (*J. Amer. Chem. Soc.*, 1907, 29, 1342—1351).—The total nitrogen was determined in the different parts of the different heads of wheat grown from a single seed. Results obtained with a considerable number of varieties of wheat, grown in the same place, showed that kernels which contain a high percentage of nitrogen are light in weight and contain low amounts of total nitrogen.

The number of kernels in the spike increases with the length of the straw; there is also an increase in the weight of the kernels and of the nitrogen, whilst the percentage of nitrogen diminishes. The differences between different spikes of a plant are chiefly due to differences in nutrition and other conditions, and are not hereditary. All the heads of the same plant of average normal height are, however, fairly similar, and for the purpose of sampling for selection a single spike is sufficient.

The average weight of kernel is about the same in the upper and lower spikelets, but higher in the middle spikelets of the same head. The percentage of nitrogen increases from the top of the spike downwards. Comparing the outer and inner kernels, it is found that the former are invariably the heavier and contain the higher weights of nitrogen. The best grains, as regards weight and nitrogen content, are the outside ones from the middle of the spikelets.

N. H. J. M.

**Consumption of Nutrients by Seed Beets, Parent Beets, and Seedlings.** III. KARL ANDRLÍK, JOSEF URBAN, and VLADIMÍR STANEK (*Zeitsch. Zuckerind. Böhm.*, 1907, 32, 1—17. Compare this vol., ii, 387).—Details are given of the composition of the roots, leaves, and stems of sugar-beets at the various stages of their development during the second year of growth. The following estimations were made: average weight, dry matter, sugar, reducing substances, pentosans, total nitrogen, proteins, ash,  $K_2O$ ,  $Na_2O$ ,  $CaO$ ,  $MgO$ ,  $Fe_2O_3 + Al_2O_3$ ,  $P_2O_5$ ,  $SO_3$ , and  $Cl$ . The results are given in both tabular and curve form. T. H. P.

**Effect of Solutions of Various Salts on the Permeability of the Soil.** D. J. HISSINK (*Chem. Weekblad*, 1907, 4, 663—673).—Distilled water and solutions of sodium chloride and potassium chloride diminish the permeability of the soil. Solutions of ammonium chloride and potassium chloride increase the permeability at first, but finally diminish it. A. J. W.

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## Analytical Chemistry

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**Estimation of Chlorides or Bromides in the Presence of Thiocyanates.** M. A. ROSANOFF and ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1907, 29, 1467—1475).—A measured volume of the mixture is diluted so that the normality of the chlorine is about  $N/50$ , or in the case of bromine about  $N/100$ . After adding 1 c.c. of a saturated solution of iron ammonium alum, the liquid is heated to boiling in a large Erlenmeyer flask, and the thiocyanate is then destroyed by adding nitric acid, about three drops in the minute, until the colour has become pale orange; the whole is then boiled for a few minutes longer. When cold, one-third of the volume of nitric acid is added (for bromides one-sixth suffices), and the chlorine, or bromine, is precipitated by adding a definite volume of  $N/15$  silver nitrate. The mixture is boiled for a few minutes and filtered while still hot, the precipitate is well washed, the filtrate is made up to about three times the original bulk and when cold some more iron solution is added, and the excess of silver titrated with  $N/15$  thiocyanate solution until strongly red, when silver solution is again added until the colour just disappears.

In the case of bromides, the silver bromide need not be removed by filtration. The joint chloride, or bromide and thiocyanate, may be estimated with silver nitrate by Volhard's method (this vol., ii, 503).

L. DE K.

**Colorimetric Estimation of Iodine.** ATHERTON SEIDELL (*J. Biol. Chem.*, 1907, 3, 391—394).—Standard solutions of iodine in chloroform as used for comparison in Baumann's method fade rapidly. Various



other dyes for the making of standards were therefore tried, acid magenta gave the best results.  
W. D. H.

**Estimation of Iodates in Presence of Chlorates.** WILLIAM H. GIBSON and CRISTOPHER M. W. GRIEB (*Analyst*, 1907, 32, 381).—In acetic acid solution, potassium iodate liberates iodine from potassium iodide, whilst potassium chlorate has not the slightest action on the iodide. In order to render the reaction quantitative, a large excess of acetic acid is added to the solution containing the iodate and chlorate, and then an excess of potassium iodide. The iodine is titrated in the usual way. An excess of acetic acid is necessary, otherwise the blue colour of the starch indicator disappears prematurely.

W. P. S.

**Estimation of [Dissolved] Oxygen in Water.** WALTER CRONHEIM (*Zeitsch. angew. Chem.*, 1907, 20, 1939—1942).—The process introduced by Winkler and modified by Noll (Abstr., 1906 ii, 48) is recommended.  
L. DE K.

**The Use of Sodium Carbonate and Zinc Oxide in Sulphur and Arsenic Estimations.** W. C. EBAUGH and C. B. SPRAGUE (*J. Amer. Chem. Soc.*, 1907, 29, 1475—1476).—About 0.5 gram of the material is mixed with a sufficiency of a mixture of 1 part of dry sodium carbonate and 4 parts of zinc oxide in a porcelain crucible, some more of the soda-zinc mixture is sprinkled over the mass, and the whole is heated to redness in a muffle for fifteen or twenty minutes. The mass is extracted with water, and the sulphate and arsenate formed are estimated by the usual methods. For the arsenic estimation, the precipitation as silver arsenate and volumetric estimation of the silver contained therein by means of ammonium thiocyanate is recommended.  
L. DE K.

**Some Causes of Error in the Estimation of Phosphorus in Cast-Iron and Steel.** GABRIEL CHESNEAU (*Compt. rend.*, 1907, 145, 720—722).—In Carnot's method of double precipitation as ammonium phosphomolybdate, the customary volume of 50 c.c. of molybdate solution (75 grams of ammonium molybdate per litre) is insufficient completely to precipitate the phosphorus in 5 grams of iron, but is sufficient for 1 to 2 grams. In the case of a steel assaying 0.043% of phosphorus, at least 150 c.c. are required for 5 grams.

The necessity for this large excess of reagent is due to the large solubility of ammonium phosphomolybdate in solutions of ferric salts (0.215 gram per gram of iron as ferric sulphate in 25 c.c. of water).

Whilst pure water dissolves 0.03 gram of ammonium phosphomolybdate per litre, a 5% solution of ammonium nitrate dissolves 0.099 gram, a 10% solution 0.113 gram, a 1% solution of nitric acid 0.371 gram, a 5% solution 0.682 gram, and a 10% solution 0.901 gram. The usual procedure of washing the precipitate with dilute ammonium nitrate solution, or water feebly acidified with nitric acid, is therefore likely to have a deleterious effect.

Acid ammonium molybdate (Berlin's tetramolybdate), which the molybdate reagent deposits after prolonged heating at 60°, although soluble in water and dilute nitric acid, is reprecipitated by ammonium nitrate, the precipitation being the more complete the longer the previous heating and the higher the temperature at which it is carried out. Accordingly, prolonged heating of the phosphate solution with the molybdate will result in contamination of the phosphomolybdate with acid molybdate, and this will not be eliminated by dissolution in ammonia and reprecipitation by nitric acid. It is advisable therefore to precipitate at only a moderately high temperature. E. H.

**Simplified Elementary Analysis.** MAX DENNSTEDT (*Ber.*, 1907, 40, 4300—4301).—A criticism of Baumert's proposals (this vol., ii, 909) for the analysis of substances which are not readily burnt. The use of copper oxide and other forms of asbestos is objected to on the grounds of cost, durability, and convenience, and also because this renders the simultaneous determination of halogen and sulphur impossible. The importance of the double supply of oxygen in such cases is emphasised. E. F. A.

**Modification in the Methods of Estimation of Total Carbon and Nitrogen in Urine.** J. GAILHAT (*Bull. Soc. chim.*, 1907, [iv], 1, 1016—1025).—Instead of estimating carbon dioxide by absorption in potash, and weighing as in Desgrez's method (*Bull. Soc. Pharm.*, 1901, 345), the author absorbs the gas in standard baryta solution, and determines the excess of alkali by titration against  $N/4$  sulphuric acid. The chromic acid used by Desgrez can be replaced advantageously by hydrated manganese dioxide, since this allows the nitrogen to be determined afterwards. The chlorine in the form of chloride in the urine must be precipitated previously by the theoretical amount of silver nitrate solution. It is shown that the mixture of sulphuric acid and manganese dioxide acts exactly the same on a solution of pure urea as does sulphuric acid alone, and that to convert the whole of the nitrogen in uric acid, hippuric acid (both in 2% solution), or egg-albumin, into ammonia, the solution must contain at least 60% of sulphuric acid, and must be boiled under a reflux condenser for at least forty minutes. To estimate the total nitrogen in urine, 10 c.c., are treated with sufficient silver nitrate to precipitate the chlorides, then 5—6 grams of manganese dioxide and 5 c.c. of pure sulphuric acid are added, and the solution boiled in a reflux apparatus for twenty minutes. The excess of manganese dioxide is reduced by gradual addition of a concentrated solution of oxalic acid, the liquid diluted to 100 c.c., filtered, and 50 c.c. of the filtrate exactly neutralised with sodium hydroxide solution, treated with excess of sodium carbonate solution, diluted to 100 c.c., and filtered. Twenty c.c. of the filtrate are treated with excess of sodium hypobromite in a nitrometer, and the nitrogen evolved measured. To ensure the complete evolution of the gas, it is necessary to add 2 c.c. of a 25% solution of dextrose (compare Garnier and Michel, *Abstr.*, 1900, ii, 699) to the liquid. The above process can be applied to the residue after estimation of the carbon. E. H.

**Estimation of Carbon Disulphide in Presence of Benzene.**

EVERHART P. HARDING and JAMES DORAN (*J. Amer. Chem. Soc.*, 1907, **29**, 1476—1480).—Sixty c.c. of benzene, containing about 0.1 gram of carbon disulphide, are mixed with 1.5 c.c. of strong absolute alcoholic potassium hydroxide, and after remaining for half an hour, with frequent agitation, the solution is extracted in a separating funnel successively with 30—40 portions of water and 1 c.c. of alcoholic potassium hydroxide until the carbon disulphide has been completely extracted. The water and the alcoholic extractions are diluted to 500 c.c., and 200 c.c. are used for the titration of the potassium xanthate formed. This is effected by acidifying with acetic acid and precipitating with a definite volume of standard copper acetate. The excess of copper is then titrated iodometrically in the filtrate. From a large number of experiments, it was found that 1 part of copper oxide precipitated = 1.927 parts of carbon disulphide. L. DE K.

**Estimation of Carbon Disulphide in Illuminating Gas.**

EVERHART P. HARDING and JAMES DORAN (*J. Amer. Chem. Soc.*, 1907, **29**, 1480—1482).—About two cubic feet of the gas are passed slowly through a wash-bottle containing 50 c.c. of aqueous potassium hydroxide, D 1.27, then through a second bottle containing 30 c.c. of sulphuric acid (the column of the absorbent should be 20 cm. in height), and finally through two 8-inch test-tubes each containing 20 c.c. of a saturated solution of potassium hydroxide in absolute alcohol. The alcoholic solution is then boiled to expel absorbed gases, acidified when cold with acetic acid, and the xanthate formed titrated by means of copper acetate in the manner described in the preceding abstract.

L. DE K.

**Chemical Softening of Water.** ADAM V. RAKOWSKY (*J. Russ.*

*Phys. Chem. Soc.*, 1907, **39**, 1044—1061).—A detailed study of the methods for estimating the hardness of water leads to the conclusion that the only trustworthy ones are those of Wartha and of Gröger, the latter only for waters not exceeding 30 German degrees of hardness. All the methods ignore the reversibility of the reaction between the alkali used and the salts contained in the natural water. For a softened water to be satisfactory, it must be both of minimum hardness and minimum alkalinity. This is attained by the following new method. To 100 c.c. of the water to be investigated, various quantities of *N*/10 lime water are added, it is then filtered, and titrated. That amount of lime water which leaves only a very small quantity of free calcium oxide in solution is now added to a fresh 100 c.c. of water, and then *N*/10 sodium carbonate solution is added and the volume made up to 200 c.c., after which it is filtered and titrated; thus the amount of sodium carbonate which can be added without making the solution too alkaline can be determined, whilst the difference between the alkalinity of the resulting solution and the sodium carbonate used indicates the hardness of the water. This method can be used conveniently for very hard waters. The reaction between alkalis and the salts contained in the water proceeds at a measurable, but slow, rate, which can be increased by raising the temperature. Z. K.

**Volumetric Estimation of Magnesium in Water.** GEORGE B. FRANKFORTER and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1907, 29, 1464—1466).—Five hundred c.c. of water are freed from iron and calcium as usual, and the filtrate is acidified and evaporated until the salts begin to crystallise out. The liquid is now made up to 100 c.c., one-third of the volume of ammonia is added, and the magnesium is precipitated by addition of 25 c.c. of a 10% solution of sodium arsenate.

The precipitation is complete after two minutes' vigorous shaking. The precipitate is washed with dilute ammonia, and then redissolved in 50 c.c. of dilute sulphuric acid (1:4). The arsenic acid, which, of course, represents the magnesium, is then estimated iodometrically by means of potassium iodide and sodium thiosulphate.

The authors simply add the thiosulphate until the liquid becomes colourless. The use of starch as indicator cannot be recommended in this case. L. DE K.

**Electrolysis of the Halides of the Alkaline Earth Metals.** HIRAM S. LUKENS and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1907, 29, 1455—1460).—When employing Hildebrand's apparatus for the electrolysis of magnesium chloride, the metal forms a mass of hydroxide in the inner vessel. The same happens with calcium chloride should any magnesium be present. Barium and strontium, however, are not affected by the presence of magnesium, and behave like the alkali metals. Iron separates as hydroxide in the inner compartment, and may be separated from barium in this manner. L. DE K.

**New Results in Electro-analysis.** THOMAS P. McCUTCHEON, JUN. (*J. Amer. Chem. Soc.*, 1907, 29, 1445—1455).—A continuation of the experiments of Hildebrand (this vol., ii, 574). The silver anode cannot be replaced satisfactorily by one made of lead, cadmium, bismuth, or zinc. A number of separations have been studied, such as barium and strontium from magnesium, sodium from uranium, lithium from uranium, barium from uranium, strontium from uranium, barium from thorium, barium from cerium, barium from lanthanum, and barium from neodymium. L. DE K.

**Iodometric Estimation of Copper according to de Haën.** L. MOSER (*Zeitsch. anorg. Chem.*, 1907, 56, 143—144).—Remarks on a recent paper by Gooch and Heath (this vol., ii, 720). The author maintains the correctness of his previous statements (*Abstr.*, 1905, ii, 64, 422). G. S.

**Electrolysis of Metallic Chloride Solutions with the Use of Rotating Silver Anode and Mercury Cathode.** THOMAS P. McCUTCHEON, JUN., and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1907, 29, 1460—1465).—A series of experiments with the Hildebrand cell. The solutions contained about 0.1 gram of the metal in 50 c.c. The anode made 200 revolutions per minute, and the pressure usually equalled 8 volts. The chlorides of cerium, lanthanum, neodymium, praseodymium, zirconium, titanium, yttrium, thorium, uranium, iron,

aluminium, chromium, and tin, also zinc, nickel, and copper were tried.

With a stationary anode, cerous chloride is precipitated completely as hydroxide. With a rotating anode, it is partly dissolved as colloidal hydroxide. The same happens in the case of the chlorides of sesquioxides, whilst with those of the dioxides or protoxides no colloidal solution is formed, or if it does form, it is extremely unstable.

L. DE K.

**Sensitive Method for the Detection of Nickel in the Presence of Cobalt.** LEO TSCHUGAEFF (*Compt. rend.*, 1907, 145, 679—681).—In reply to Pozzi-Escot (this vol., ii, 818), the author asserts that the test for nickel based on the use of dimethylglyoxime described by him (Abstr., 1905, ii, 613) and extended by Kraut (Abstr., 1906, ii, 858) and Brunck (this vol., ii, 582) is far more sensitive than the ammonium molybdate test described by Pozzi-Escot. Comparative tests with the two reagents showed that a solution containing 1 part of nickel in 20,000, 1,000,000, or 2,000,000 parts of water gave a characteristic-coloured precipitate with dimethylglyoxime, but did not react with ammonium molybdate. Further, as a 5—10% solution of cobalt chloride gives a violet precipitate with ammonium molybdate, this reagent is useless for the detection of nickel in the presence of large quantities of cobalt.

M. A. W.

**Estimation of Nickel by Means of Dimethylglyoxime and its Separation from the Metals of the Ammonium Sulphide Group.** OTTO BRUNCK (*Zeitsch. angew. Chem.*, 1907, 20, 1845—1850).—Nickel may be precipitated quantitatively from ammoniacal or acetic acid solutions by means of alcoholic dimethylglyoxime. The dried precipitate contains 20.31% of nickel. In this manner, nickel may be separated from cobalt and zinc, also from manganese in acetic acid solution. Free mineral acids should be neutralised with ammonia, or else rendered harmless by addition of sodium acetate. Ferric iron should be first reduced to the ferrous state by means of excess of sulphurous acid. The separation of nickel from ferric iron, aluminium, or a chromium salt may be also carried out by adding sufficient tartaric acid to prevent the precipitation of the hydroxides by ammonia. The clear, alkaline liquid is then treated with dimethylglyoxime.

L. DE K.

**Analysis of Mixtures of Air and Inflammable Gases or Vapours.** JEAN MEUNIER (*Compt. rend.*, 1907, 145, 622—625. Compare this vol., i, 460, 579).—The use of the ordinary fixed volume eudiometer for the analysis of mixtures of air and inflammable vapours is limited to those mixtures in which the proportion of inflammable vapour is some multiple of the weight of the drop of the volatile liquid introduced by the pipette; further, it is not possible to draw the gas to be analysed into the eudiometer. A modified eudiometer tube is described by means of which a mixture of air and inflammable vapour in any proportion can be made, or into which any gas or air to be analysed can be drawn readily. The eudiometer

consists of a graduated glass tube of 300 c.c. capacity, closed at the bottom by a metal plate through which passes a long vertical screw rod carrying a leather piston, on which rests a layer of mercury, and this forms the moveable base of the eudiometer. The top of the tube is open, and can be closed by a closely-fitting glass cap, which terminates in a short capillary tube. In order to prepare a mixture of air and a vapour in any given proportion, a standard mixture is first made by introducing into the tube a definite number of drops of known weight of the volatile liquid, the glass cap is replaced, and the mercury level lowered to the desired volume. The open capillary tube is closed by the finger and the vessel shaken. The standard mixture can be diluted to any required strength by retaining a definite volume in the eudiometer by raising the mercury level and then introducing the required volume of air by lowering the same.

Any gas to be analysed can be introduced into the eudiometer by connecting the capillary tube to a tube communicating with the source of the gas and lowering the moveable base. By using a thin, flexible copper tube, 1 mm. section, it is possible to obtain samples of gas or air at a considerable distance from the apparatus. M. A. W.

**New Method for the Detection and Rapid Estimation of Methane.** NESTOR GRÉHANT (*Compt. rend.*, 1907, 145, 625—626).—In employing the special eudiometer previously described (*Abstr.*, 1906, ii, 49) for the estimation of small quantities of methane in air, the current has to be passed 400 to 600 times through the wire in order to ensure the complete combustion of the hydrocarbon; if, however, about 30—40% of electrolytic gases is added to the mixture of air and methane, the combustion is complete after a single passage of the current. By this method, the amount of fire damp in mines can be estimated in ten minutes with an accuracy of 91·5% to 103%.

M. A. W.

**Table for Determination of the Concentration of Methyl Alcohol in Per Cent. by Weight and Volume and in Weight Per Volume from the Specific Gravity at 15°/15°.** PETER KLASON and EVERT NORLIN (*Arkiv. Kem. Min. Geol.*, 1907, 2, No. 27, 1—32. Compare *Abstr.*, 1906, i, 921).—None of the existing tables connecting specific gravities and concentrations of mixtures of methyl alcohol and water are based on the sp. gr. of absolutely pure, anhydrous methyl alcohol. The table given by the authors is based on the value previously obtained (*loc. cit.*) for the sp. gr. of methyl alcohol, and shows the per cent. of the alcohol by weight and volume and the grams of alcohol per 100 c.c. for sp. gr. varying from 0·7964 to 1·0000 by increments of 0·0001. The table may also be employed, without great inaccuracy, for crude methyl alcohol, the results then giving approximately the sum of the contents of methyl alcohol and acetone. T. H. P.

**Estimation of Dextrose by the Causse-Bonnans Method.** FERNAND REPITON (*Chem. Zentr.*, 1907, ii, 1021; from *Mon. Sci.*, 1907, [iv], 21, ii, 451—453).—The author shows that better results

are obtained by taking as the end-point in the titration the golden-yellow, instead of the brownish-red, coloration. The method of working is as follows: 5 c.c. of Pasteur's copper solution (136 grams of sodium hydroxide, 80 grams of potassium hydroxide, and 105 grams of tartaric acid in 500 c.c. of water and 45—48 grams of crystallised copper sulphate in 500 c.c. of water), to which has been added 0.2 gram of potassium ferrocyanide, is heated to boiling, and the sugar solution added, drop by drop, until the golden-yellow coloration appears. The copper solution containing potassium ferrocyanide is reduced more readily than an ordinary copper solution, the ratio of dextrose required in the two cases being 82:100. W. H. G.

**The Composition of Crude Cacao Fibre.** HERMANN MATTHES and FRITZ STREITBERGER (*Ber.*, 1907, 40, 4195—4199. Compare König, *Abstr.*, 1906, ii, 905).—An examination of König's method of separating lignin, cutin, and cellulose. It is shown that there are nitrogenous substances in cacao powder, and that therefore the substance, which Fincke (this vol., ii, 416) thought to be lignin, only partly consisted of that material.

The material which König calls cellulose is altered in the treatment with the hydrogen peroxide. Pure cellulose obtained from Schleicher and Schüll's filter paper by heating with steam at four atmos. pressure was used. This cellulose always lost in weight after treatment according to König's method, and in addition becomes hygroscopic.

Different methods of isolating the crude fibre lead to very different percentages of pure cellulose, lignin, and cutin. Matthes and Müller's modification (*Zeitsch. Nahr. Genussm.*, 1906, 12, 159) gave pure cellulose 55%, and Fincke's method 37%. Separation of lignin and cellulose by König's method is not possible for cacao. W. R.

**Analysis of Mixtures of Some Volatile Fatty Acids.** A. LASSERRE (*Ann. Inst. Pasteur*, 1907, 21, 829—831).—The method is based on the fact that butyric and valeric acids are removed from their aqueous solution by repeated extraction with benzene or toluene, whilst formic and acetic acids cannot be thus extracted. A solution containing these four acids is extracted with benzene; the formic and acetic acids remaining in the aqueous portion are then estimated by means of their barium salts, or by the method of fractional distillation described by Duclaux. The benzene solution of the butyric and valeric acids is shaken with barium hydroxide solution, the alkaline solution is separated, acidified with phosphoric acid, and distilled. The fatty acids in the distillate are then estimated by conversion into their barium salts, or by fractional distillation. The process is applicable to mixtures containing isobutyric acid and normal valeric acid; propionic acid cannot, however, be thus separated, as it is equally soluble in water, benzene, and toluene. W. P. S.

**Estimation of Tartaric Acid in the Presence of Malic and Succinic Acids.** JOSEF VON FERENTZY (*Chem. Zeit.*, 1907, 31, 1118).—The solution containing the three acids is evaporated to a small volume, and alcohol is added until the solution contains 50 vol.% of it. A sufficiency of magnesium mixture is added, and then 10 c.c

of ammonia, also more alcohol up to 50%. After twelve hours, the magnesium basic tartrate is collected, washed with 50% alcohol, and then ignited. As 2 mols. of magnesium oxide = 1 mol. of tartaric acid, the weight of the magnesium oxide found should be multiplied by 1.875 to convert it into tartaric acid. L. DE K.

**Estimation of Salicylic Acid, Menthol, and Phenol in Patent Medicines.** ADOLF BEYTHIEN and P. ATENSTADT (*Zeitsch. Nahr. Genussm.*, 1907, 14, 392—402).—The following systematic process is recommended for the analysis of preparations, such as hair and mouth washes, cosmetics, &c., which contain salicylic acid, menthol, phenol, phenyl salicylate (salol), and menthyl salicylate (Abstr., 1906, i, 852), the separations being based on the fact that salicylic acid combines with sodium hydrogen carbonate, whilst phenol combines only with alkali metals or hydroxides; menthol is not acted on by either sodium hydrogen carbonate or sodium hydroxide. One hundred c.c. of an alcoholic solution of from 4—5 grams of a mixture consisting of the above-mentioned substances are well shaken with 20 c.c. of concentrated sodium hydrogen carbonate solution, then diluted with water to a volume of 200 c.c., and extracted several times with light petroleum. The aqueous portion, which now contains only the sodium salicylate and uncombined phenol, is extracted with ether to remove the phenol, and the salicylic acid is obtained by again extracting the solution with ether after acidifying. To estimate the quantity of phenol, the ethereal solution is heated with excess of  $N/2$  potassium hydroxide solution for thirty minutes under a reflux apparatus, the ether is then evaporated, and excess of  $N/2$  sulphuric acid is added, and, after the addition of a few drops of an alcoholic solution of trinitrobenzene, the solution is titrated with  $N/2$  potassium hydroxide solution until a red coloration is produced. The number of c.c. of  $N/2$  potassium hydroxide actually used (after allowing for the volume of  $N/2$  potassium hydroxide and sulphuric acid added previously) multiplied by 0.047 gives the amount of phenol present. The quantity of salicylic acid separated is estimated by one of the usual methods.

The light petroleum extract contains the menthol, phenyl salicylate, and menthyl salicylate. The solution is evaporated at the ordinary temperature and the residue, consisting of menthol, phenyl salicylate, and menthyl salicylate, is weighed. The residue is then dissolved in about 100 c.c. of alcohol, 3 grams of solid potassium hydroxide are added, and the mixture is boiled for ninety minutes under a reflux apparatus. After cooling, a large volume of water is added, and the solution is extracted with light petroleum. The extract is allowed to evaporate spontaneously, and the residue, consisting of the total menthol, is weighed. The alkaline solution, containing the phenol (from the phenyl salicylate) and the salicylic acid (from both esters), is acidified and extracted with light petroleum to remove the salicylic acid, whilst the phenol is obtained by extraction with ether. The quantities of free menthol, phenyl salicylate and menthyl salicylate present in the preparation are then calculated; 1 part of phenol corresponds with 2.276 parts of phenyl salicylate, and 1 part of salicylic acid is equivalent to 1.130 parts of



menthol or 2.00 parts of menthyl salicylate. In case cresols (free or combined) are present, the method of separating the phenol and salicylic acid is modified as follows: the solution remaining after the removal of menthol, &c. is acidified, again treated with sodium hydrogen carbonate, diluted with water, and extracted with light petroleum. This solvent removes the cresol, but not the phenol. The phenol and salicylic acid are then separated as described. The process recommended by Ditz and Cedivoda (*Abstr.*, 1900, ii, 54) may also be employed for the separation of the phenol and cresol when these are extracted together from the preparation. W. P. S.

**Estimation of Formaldehyde and its Polymerides.** LUCIEN ROBIN (*J. Pharm. Chim.*, 1907, [vi], 26, 400—402).—The author points out the necessity of adding sufficient hydrogen peroxide in the processes of determining formaldehyde which depend on the oxidation of this substance in alkaline solution to formic acid (formate).

W. P. S.

**Estimation of Acetone in Urine.** R. MONIMART (*J. Pharm. Chim.*, 1907, [vi], 26, 392—398).—The process is based on the precipitation of acetone by mercuric sulphate as described previously by Denigès (*Abstr.*, 1899, ii, 256); the acetone is then liberated from the precipitate, converted into iodoform by the addition of a known quantity of iodine, the excess of the latter is titrated, and, from the quantity of iodine used, the acetone is calculated. Fifty c.c. of the urine passed during twenty-four hours are, after filtration, mixed with 30 c.c. of Denigès' reagent, and the precipitate is collected on a filter. The clarified filtrate thus obtained is next heated on a water-bath under a reflux apparatus for fifteen minutes, and the precipitated acetone-mercury compound is then collected on a filter and washed with water. The filter and its contents are placed in a flask together with about 50 c.c. of water and 10 c.c. of concentrated sodium hydroxide solution. After a few minutes, the mixture is acidified with dilute sulphuric acid and distilled. Fifteen c.c. of distillate are collected and treated with 5 c.c. of a solution containing 8 grams of iodine and 20 grams of potassium iodide in 250 c.c. of water; after the addition of 30 c.c. of 8% sodium hydroxide solution, the mixture is placed aside for twenty minutes. Thirty c.c. of 10% sulphuric acid are then added, and the excess of iodine is titrated with *N*/10 thiosulphate solution. The difference between the quantity of iodine added and that titrated back represents the amount combined with the acetone to form iodoform.

W. P. S.

**Chronometric Method Applied to Quantitative Analysis.** GEORGES DENIGÈS (*Ann. Chim. Phys.*, 1907, [viii], 12, 394—405).—An acid solution of mercuric sulphate can be employed for the estimation of acetone, acetonedicarboxylic acid, or thiophen in solution by measuring the time that elapses between the addition of the reagent to the solution and the appearance of the precipitate, and comparing it with the tables given in the original (compare *Abstr.*, 1895, i, 411; ii, 372; 1899, ii, 256, 454).

In a similar manner, an acid solution of mercuric acetate can be used for the estimation of certain organic acids, or an aqueous solution of aniline for the estimation of aldehydes. In the original, the necessary tables are given for the estimation of malonic acid by means of mercuric acetate, and of formaldehyde by means of aniline (compare Pratesi, *Abstr.*, 1885, 782) M. A. W.

**Extraction and Estimation of Cantharidin.** PURAN SINGH (*Imp. Forest Research Inst. Reprint*, 1907, pp. 16).—Most assay methods based on the extraction of cantharidin by an organic solvent (after saponification by sodium hydroxide, acidification, and drying) are unsatisfactory. The best results were obtained by extraction with hot light petroleum and removal of the fat from the extract by cold light petroleum, in which the cantharidin is almost insoluble.

A more accurate method is founded on the solubility of sodium cantharidate in dilute alum solutions. One hundred grams of cantharides are made into a pasty mass with 2 grams of sodium hydroxide and a little water, dried, and extracted with a dilute alum solution. On evaporation, the crystalline cantharidin separates from the concentrated solution together with basic aluminium salt, which is removed by hydrochloric acid. The cantharidin may be recrystallised from chloroform, and is dried until constant in weight. Samples of Japanese cantharides were found to contain 1.6—1.9% of cantharidin. G. B.

**Estimation of Tannin by means of Iodine.** H. CORMIMBŒUF (*Ann. Chim. anal.*, 1907, 12, 395—397).—Jean (*Rev. industr.*, 1900, 36) has given an easy process for the estimation of tannin, consisting in titrating dilute solutions with standardised iodine, using starch-paper as indicator. The author has used the method, and has also tried Boudet's modification of it (*Abstr.*, 1906, ii, 911); he considers that the process is utterly untrustworthy. L. DE K.

**Stanek's Method for the Estimation of Choline.** A. KIESEL (*Zeitsch. physiol. Chem.*, 1907, 53, 215—239).—Staněk's method (*Abstr.*, 1906, ii, 60, 314, 700) for the estimation of choline yields good results when applied to pure choline, but as other bases, such as phenylethylamine, lupanine, and the bases present in the impure histidine fractions, also yield precipitates with potassium tri-iodide, the method appears to be of but little use when applied to complex mixtures of bases such as are present in plant extracts.

Stanek's method of extracting plant tissues with 95% alcohol is not to be recommended, as all the choline is not removed. Extraction with warm or cold water is preferable. J. J. S.

**Some New Ureometers.** ALBERT GARCIA (*Ann. Chim. anal.* 1907, 12, 390—393).—A reply to Pozzi-Escot (this vol., ii, 414).—The author considers that the ureometer recommended is but an inferior modification of his own instrument. L. DE K.

**The *p*-Dimethylaminobenzaldehyde Test for Indole.** W. E. MARSHALL (*J. Hygiene*, 1907, 7, 581—588).—The high estimate of the value of this test (which was introduced by Ehrlich) formed by Böhme is fully confirmed. Other substances, such as scatolecarboxylic acid, which formerly were difficult to distinguish from indole, do not give the indole reaction with this reagent. The method lends itself to colorimetric estimations.

W. D. H.

**A New Reaction for Antipyrine.** F. A. STEENSMAN (*Pharm. Weekblad*, 1907, 44, 1066—1067).—The reagent is prepared by diluting a solution of 1 gram of *p*-dimethylaminobenzaldehyde in 5 c.c. of 25% hydrochloric acid to 100 c.c. with absolute alcohol. When a small portion of this reagent in presence of a trace of antipyrine is evaporated to dryness in a porcelain dish on the water-bath, a light red stain is left. With minute traces of antipyrine, the reagent should be diluted with its own volume of absolute alcohol, and a very small amount employed. The test serves for the detection of 0.001 mg. of antipyrine. Aqueous solutions should be extracted with chloroform, the solvent evaporated, and the residue dissolved in the reagent.

To detect antipyrine in pyramidone, 100 mg. of pyramidone are dissolved in the reagent, and the solution evaporated as before. It is possible to detect 0.005 mg. of antipyrine in 100 mg. of pyramidone.

A. J. W.

**Detection and Estimation of Morphine in Organs.** WILLEM VAN RYN (*Pharm. Weekblad*, 1907, 44, 1353—1356).—One hundred mg. of morphine hydrochloride were administered to a rabbit. After forty-five minutes, 15 c.c. of urine were passed, but this did not contain morphine. After two and a-half hours, another 100 mg. were injected subcutaneously, and, after six hours in all had passed, the animal, which was recovering, was killed, and the various organs, also the blood and the urine, were submitted to the usual analysis (extraction with alcohol and tartaric acid, purification by ether, extraction with amyl alcohol in alkaline solution). The amyl alcohol was then again shaken with dilute sulphuric acid, and this after being partially neutralised with sodium carbonate was rendered alkaline with ammonia and shaken repeatedly with chloroform. The chloroform was then evaporated to a small bulk in a weighed beaker, and the alkaloid precipitated by adding fifty times the bulk of light petroleum. The clear liquid was then poured off, and the beaker and contents dried at 95° and weighed.

From the stomach and contents were recovered 31.5 mg. of morphine from the intestine 14.6 mg., from the liver 8 mg., from the kidneys 1 mg., from the brain distinct traces, from the urine 70.3 mg., and from the blood 2 mg.; total 127.4 mg. (=167.8 hydrochloride), or 83.9% of the total amount administered. The result shows that the greater portion of the alkaloid accumulates in the urine.

L. DE K.

**Detection of Albumin [in Urine].** CHARLES TANRET (*Bull. Soc. Chim.*, 1907, [iv], 1, 974—975).—The preliminary precipitation of uric acid from urines containing a large proportion of urates before

testing for albumin by Tanret's or Millon's reagent, as suggested by Repiton (*ibid*, 751), is superfluous. As the author pointed out in his original communication (*J. des Connaiss. méd.*, 1871), it is only necessary, either to heat the solution and so re-dissolve the precipitated uric acid, or to use a sufficiently diluted urine, in which case the acid is not precipitated. Concerning the presence of mucinoids in urine, see Grimbert and Dufau (*Abstr.*, 1906, ii, 912). The author has never observed the precipitation from urine of benzonaphthol, administered as a medicine, by the addition of Tanret's reagent (Repton, *loc. cit.*).  
T. H. P.

**Detection and Estimation of Albumin in Urine.** OTTO MAYER (*Chem. Zentr.*, 1907, ii, 853; from *Schweiz. Woch. Chem. Pharm.*, 1907, 45, 446—449).—Several tests must be made with urine which has been filtered clear; should filtration alone be insufficient, the urine is first shaken with kieselgur or magnesia. 1. Ten c.c. of urine are boiled with 5 c.c. of a solution of salt (1:3) acidified with acetic acid; the formation of a precipitate denotes the presence of albumin. Any resinous acids precipitated by this treatment may be redissolved by shaking with alcohol. 2. The urine is mixed with an equal volume of 6% acetic acid; a turbidity points to the presence of mucin. 3. A solution is prepared by adding to 100 c.c. of water, 2 grams each of mercuric chloride and common salt, 4 grams of citric acid and 25 c.c. of 30% acetic acid. A mixture of equal parts of this solution and urine becomes turbid, even with only 0.001% of albumin; mucin is precipitated at the same time, so a comparison must be made with the preceding test. 4. Five drops of a 20% solution of sulphosalicylic acid are added to 5 c.c. of urine slightly acidified with acetic acid; in the presence of very small quantities of albumin (0.0015%), the mixture becomes opalescent; a precipitate is obtained with larger quantities of albumin. Should the urine be poor in albumin and rich in mucin, about 20 c.c. of it must be shaken with 10—20 drops of dilute acetic acid, filtered, and the test carried out with the filtrate.

A rapid method for the approximate estimation of albumin is given: 5—10 c.c. of a solution of 5 grams of mercuric chloride, 5 grams of citric acid, and 40 grams of sodium chloride in 500 c.c. of water is carefully covered by means of a fine pipette with 5 c.c. of urine; when albumin is present to the extent of 0.001%, a well-defined, white ring forms, in about one and a-half minutes, on the boundary of the two liquids. Should it appear before this, the urine is diluted with water until the ring appears in the stated time. The percentage of albumin present is obtained from the degree to which the urine has been diluted.  
W. H. G.

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